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Methyl Complexes of the Transition Metals

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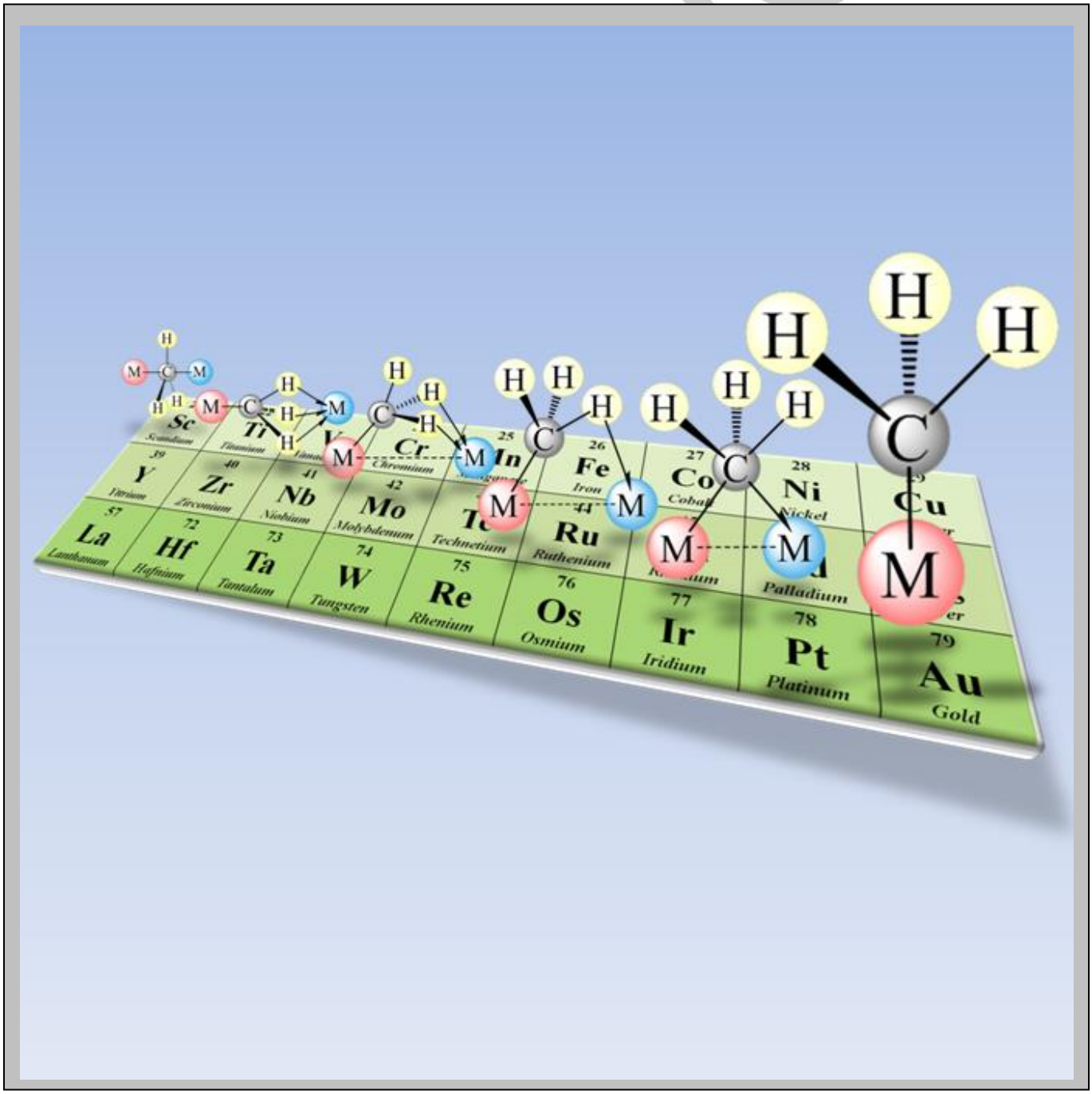
Dedicated to Prof. Pierre Braunstein in recognition of his contributions to inorganic and organometallic chemistry



Abstract: Organometallic chemistry can be considered as a wide area of knowledge that combines concepts of classic organic chemistry, *i.e.* based essentially on carbon, with molecular inorganic chemistry, especially with coordination compounds. Transition metal methyl complexes probably represent the simplest and most fundamental way to view how these two major areas of chemistry combine and merge into novel species with intriguing features in terms of reactivity, structure, and bonding. Citing more than 500 bibliographic references, this review aims to offer a concise view of recent advances in the field of transition metal complexes containing M—CH_3 fragments. Taking into account the impressive amount of data that are continuously provided by organometallic chemists in this area, this review is mainly focused on results of the last 5 years. After a panoramic overview on M—CH_3 compounds of groups 3 to 11 which includes the most recent landmark findings in this area, two further sections are dedicated to methyl-bridged complexes and reactivity.

1. Introduction

Transition metal methyl complexes are a unique class of metal organic compounds, as they bear the simplest alkyl function.[1-7] The methyl ligand shares with other alkyls the distinctive reactivity of the σ-M—C bond and takes part in elementary reactions that are the base of fundamental academic and industrial transformations. In addition, its small size and the unfeasibility of β-hydrogen elimination allows reactions that are difficult with other alkyl groups. Moreover, methyl complexes feature interesting electronic and molecular structures, including the first hexamethyl transition metal compound, WMe_6, prepared by Wilkinson *et al.* in 1973,[8a] which headed a series of hexamethyl complexes of *d*-block elements described along the 1970's and 1980's decades.[8b-h] Relevant theoretical and structural aspects have also been highlighted within severalhomobimetallic species with bridging methyl ligands synthesized recently.[9,10] Aside from main group methyl compounds, including LiMe, Mg(Me)X, $ZnMe_2$, or $AlMe_3$, of great fundamental and practical relevance,[1-6] methyl complexes of transition metals can be arguably considered the most important family of compounds with σ-M-C bonds.[7] They have led to major breakthroughs in organometallic chemistry, from the isolation of the first methylidene complex[11] to the low temperature characterization of the first σ-CH_4 complex.[12] This review offers an overview of transition metal methyl complexes (TM-CH_3), focusing in the last 5 years. It begins with a brief description of synthetic methods, followed by a selection of recently reported complexes with terminal and bridging methyl ligands from the groups 3 to 11 of the periodic table. A specific section is dedicated to methyl-bridged species with three-centre two-electron bonds. The review concludes highlighting relevant reactivity of the methyl group in this class of compounds.

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Ernesto Carmona (PhD degree, University of Seville, 1974, with Professor F. Gonzalez-García) did postdoctoral work at Imperial College London with (the late) Professor Sir Geoffrey Wilkinson (1974-1977). He then returned to Sevilla, to become full Professor of Inorganic Chemistry in 1983. Over the years, his research interests have concentrated in the activation of small, unsaturated molecules, like N_2, CO, CO_2, C_2H_4, etc. by compounds of several transition elements. His research group has also studied the structural characteristics of metallocenes of some actinide and main group elements, as well as the activation of C-X bonds (X= H, C, O, etc.) by rhodium, iridium, and platinum compounds stabilized by cyclopentadienyl, hydrotris(pyrazolyl)borate, and bulky phosphine ligands. More recently, efforts have been directed toward the study of zinc-zinc bonded compounds and in the last years to the study of complexes that contain molybdenum-molybdenum multiple bonds.

Jesús Campos was born in Sevilla, Spain, where he studied Chemistry receiving the First National Award in 2007. After a year at University of Manchester he returned to University of Sevilla to join the group of Prof. Ernesto Carmona, where he received his PhD in 2012 after a visiting stay in the laboratories of Prof. Maurice Brookhart at University of North Carolina. He returned to the US for two years as a postdoctoral researcher in the group of Prof. Robert H. Crabtree at Yale University to work in green catalysis and energy-related transformations. He was recently awarded with a Talentia/Marie Curie Fellowship to work in the group of Prof. Simon Aldridge at University of Oxford. His interests include all aspects of inorganic and organometallic chemistry, with particular emphasis in novel catalytic applications.

Joaquín López-Serrano studied chemistry at the University of Murcia, Spain, where he completed his PhD thesis with Dr. A. Abad and Prof J. Vicente in 2004. Then he joined the group of Prof. S. B. Duckett at the University of York (UK), with a postdoctoral position, where he used NMR techniques to study the mechanism of inorganic reactions. In 2008 he returned to Spain where he obtained a Ramón y Cajal research contract. Currently he works at the Instituto de

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Investigaciones Químicas of the Spanish Council for Scientific Research (CSIC) and the University of Sevilla. He is interested in the study of inorganic and organometallic reaction mechanisms by experimental, mainly NMR, and computational methods.

Riccardo Peloso was born in Mantova, Italy, in 1979. He obtained the degree in Industrial Chemistry in 2003 at the University of Parma with Prof. M. Catellani and G. P. Chiusoli. He completed his PhD studies on copper(I) organometallic chemistry at the University of Pisa under the supervision of Prof. Guido Pampaloni. After a six-months stay with Prof. Walter Baratta, he joined the group of Prof. Pierre Braunstein in Strasbourg in 2007. Since 2009 he has been a member of the group of organometallic chemistry and homogenous catalysis of the University of Sevilla. In 2011 he obtained a Juan de la Cierva research contract from the Spanish Ministry of Science and Innovation. His current interests are mainly focused on synthetic aspects of organometallic and coordination chemistry.

2. Synthesis and Structures: a systematic overview on *d*-block elements

By the time this review was being written, a survey of methyl complexes of transition metals in the Cambridge Structural Database (CSD)[13] returned 5349 entries with an average of more than 200 new complexes being reported each year for the past two decades (Figures 1 and 2a). By 1975, when Lappert *et al*.[14] and Schrock and Parshall[15] published some of the first reviews on metal σ-hydrocarbyls, 155 such complexes had been structurally characterized, roughly half of which were methyl complexes. Since 2010, more than one thousand new methyl complexes of transition metals have been crystallographically characterized (Figure 2b). With such wealth of structures, this section does not intend to be comprehensive. It will instead focus on selected examples of terminal and bridging methyl complexes of transition metals reported in the last five years or so. Dinuclear complexes with bridging methyl ligands (*i.e.* excluding higher nuclearity) will receive special attention, including the role of the bridging methyl in the formation of three-centre two electron bonds.[9]

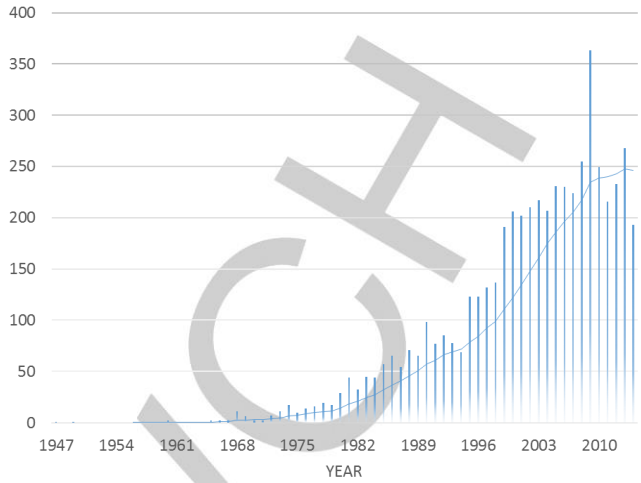
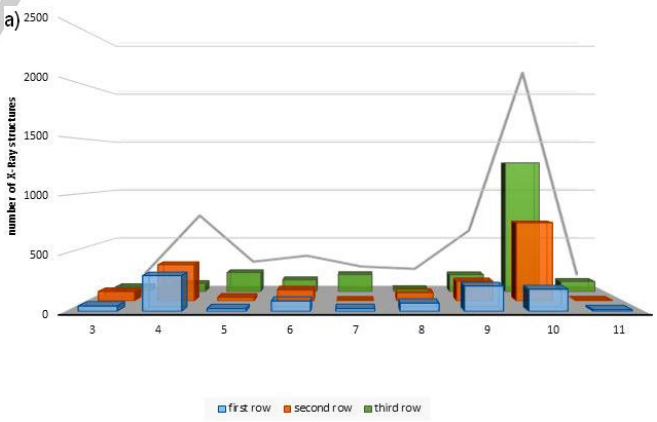


Figure 1. Transition metal methyl complexes structurally characterised per year until 2014 (bars) and ten years moving average (line).

There are structurally characterized σ-bonded methyl complexes of all transition metals, from a mere four examples of technetium methyls and, perhaps more surprisingly, only one silver complex, to more than one thousand platinum methyls. By group, the most abundant are methyl complexes of group ten elements (2/5 of the total) followed by group four metal complexes (1/7). By row, third row metal methyl complexes constitute nearly one-half of all examples, mainly due to the contribution of platinum species. This trend is reverted in some groups, such as in group four where there is approximately the same amount of titanium and zirconium methyls and both families are almost four times more abundant than the hafnium methyl family.



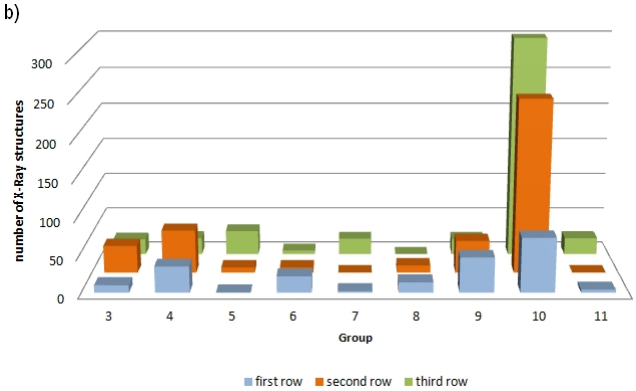
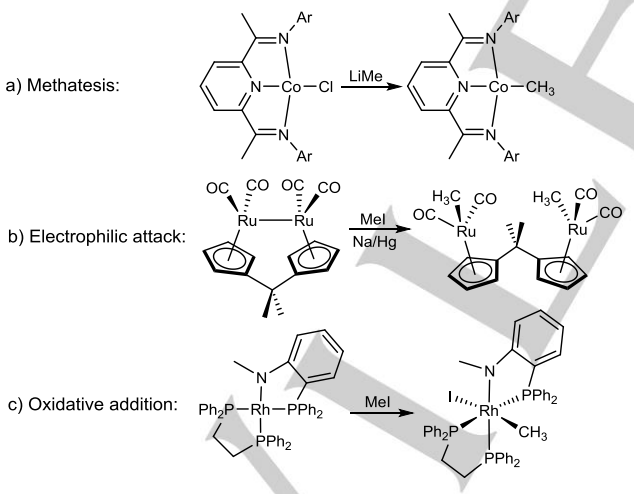


Figure 2. a) Structurally characterized transition metal-methyl complexes by group and row. The grey line represents the totals by group. b) Structurally characterized transition metal-methyl complexes by group and row since 2010.

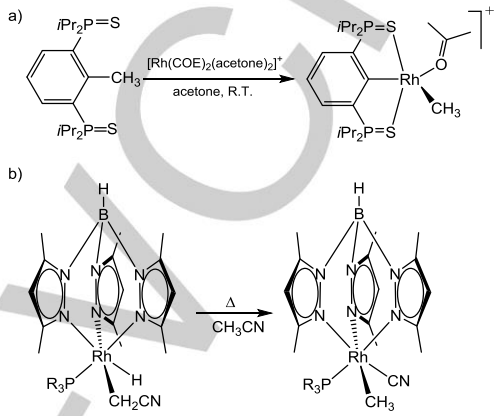
2.1. General methods for the generation of TM—CH_3 bonds in transition metal complexes.

Synthetic procedures for the preparation of transition metal methyl complexes involve in almost all cases one of the following reactions:[2] a) *metathesis* from metal halides using a nucleophilic main-group organometallic reagent such as LiMe, Mg(Me)X, $MgMe_2$, $ZnMe_2$, $HgMe_2$, $SnMe_4$; etc.; b) *electrophilic attack* on an electron-rich metal complex using a $Me^{\delta+}$-X reagent; c) *oxidative addition* of a Me-X reagent (X = halide or pseudo-halide). Selected recent examples of each method are shown below (Scheme 1):[16-18]



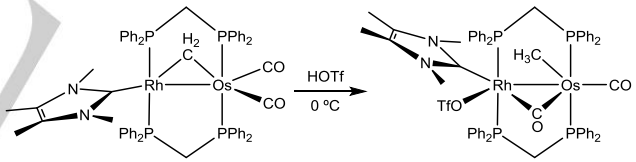
Scheme 1. General methods for the synthesis of metal methyls. Examples from refs. 16 (a), 17 (b), and 18 (c).

Beyond these methodologies, it is worth mentioning the possibility of creating a methyl-metal unit *via* activation of more inert bonds in combination with specifically designed organometallic environments. For instance, Milstein and Jones reported on the formation of Rh—CH_3 bonds by activation of C—C bonds. Thus, a C_{aryl}—CH_3 bond of a bidentate S,S ligand adds oxidatively to a cationic Rh(I) precursor giving rise to an octahedral Rh(III) complex (Scheme 2a),[19] whereas acetonitrile is activated by an *in situ* generated Rh(I) unsaturated species which cleaves the C—CN bond and affords a methyl cyanide Rh(III) complex. (Scheme 2b).[20]



Scheme 2. Examples of generation of M—CH_3 bonds by C—C activation from refs. 19 (a) and 20 (b).

As further examples for the generation of M—CH_3 bonds, hydrogenation of Ir=CH_2 fragments[21] and protonation of bridging CH_2 in dinuclear Os-Ru complexes[22] (Scheme 3) were recently reported to afford the corresponding methyl complexes.

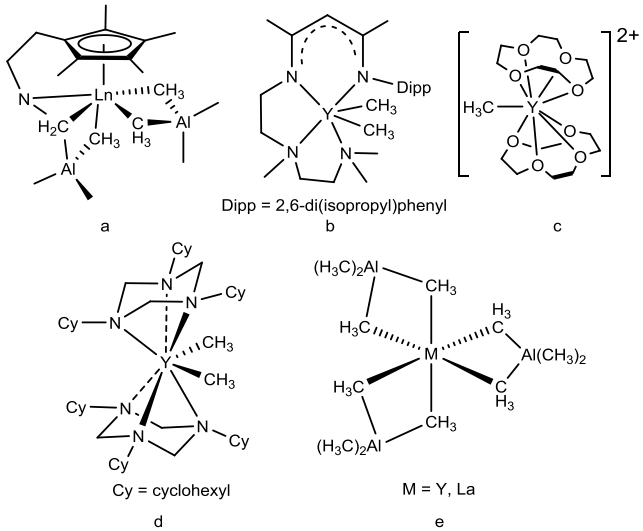


Scheme 3. Generation of a terminal methyl-metal bond by protonation of a bridging methylene group (ref. 22).

2.2. Compounds of groups 3-11 with TM—CH_3 bonds

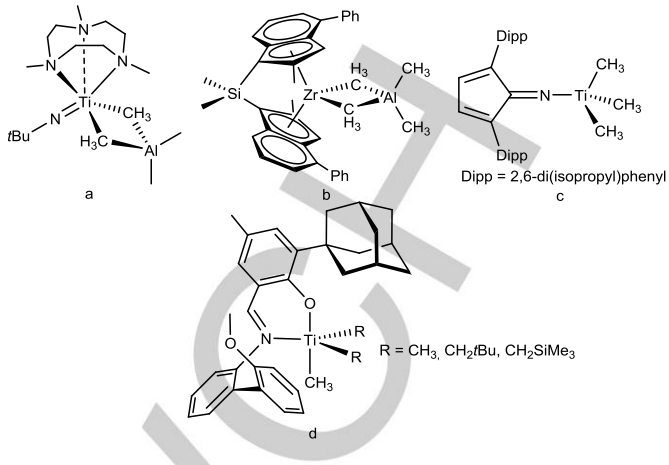
Group 3. Alkyl complexes of group 3 metals and the lanthanides have shown to be active catalysts in Ziegler-type polymerization. A large number of studies have been performed on neutral and anionic species,[23,24] but cationic species[25] have also shown to be relevant intermediates in the context of α-olefin polymerization catalysis and are related to the chemistry of group 4 elements.[26] Common ancillary ligands of Group 3 metal methyls include cyclopentadienyl derivatives,[27] amidinates,[28] and β-diketiminates.[29] Cationic methyl complexes usually feature crown ethers as stabilising ligands,[30] but cyclic polynitrogen bases have also been successfully used (Scheme 4).[31] Many group 3 methyl complexes feature Ln-CH_3-Al (Ln = Sc, Y, lanthanides) bridges (some can be described as $AlMe_4^-$ adducts), since homoleptic [Ln($AlMe_4$)$_3$] are good starting materials and

many polymerization reactions catalysed by group 3 (and group 4) metals require Lewis acidic $AlMe_3$. Interestingly homoleptic $[Sc(AlMe_4)_3]$ has not been structurally characterized yet.[32] $[Li_3Ln(Me)_6)(THF)_n]$ have been prepared as synthetic equivalents to elusive $LnMe_3$.[25]



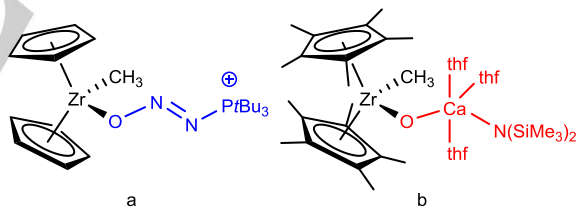
Scheme 4. Methyl metal complexes of group 3 elements from refs. 27 (a), 29 (b), 30 (c), 31 (d), and 32 (e).

Group 4 metal methyl complexes constitute the second most abundant group of TM-CH_3 after those of group 10 metals. Many of these species, particularly metallocenes, have a role in olefin polymerization (Ziegler-Natta type) catalysis, usually in the presence of MAO (MAO = methylalumoxane) or stabilized by related Lewis bases.[33] Electron-deficient methyl (or alkyl) metal cations of the type Cp'_2M^+-R have been shown to be the initiating or active species in many cases.[34-36] In this context the first $AlMe_3$ adduct of a TM-alkyl cation, a heterobimetallic species containing a titanium imido methyl cation, has been structurally characterized by Mountford *et al.* This species is a model for the proposed resting state during MAO activated catalytic olefin polymerization (Scheme 5).[37] A unique structurally characterized $AlMe_3$ adduct of an *ansa*-zirconocene-Me cation has been also reported.[38] Recent examples of non-metallocene catalysts for ethylene polymerization are the neutral methyl complexes of titanium stabilized with bulky iminato ligands (L)$TiMe_2X$ (L = imidazolin-2-imide; X = Cl or Me). These complexes have shown to require low amounts of MAO co-catalyst.[39] Labinger and Bercaw have structurally characterized mono- and trimethyl neutral titanium complexes stabilized with phenoxy-imine ligands and demonstrated their catalytic activity in olefin trimerization following activation (methyl abstraction) with $B(C_6F_5)_3$.[40,41]



Scheme 5. Recent examples of group 4 methyl complexes (refs. 37, a; 38, b; 39, c; 40, d; 41-42, e).

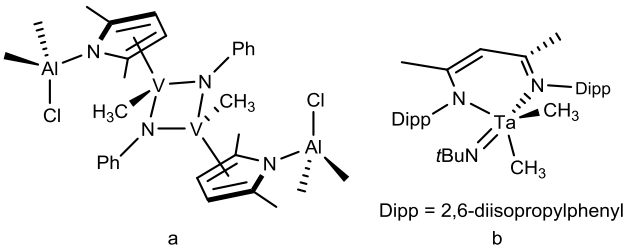
The Lewis acidic character of the $[Cp_2M\text{-}CH_3]^+$ (M = Ti, Zr) moiety has been employed by Stephan *et al.* to replace the borane fragment, $B(p\text{-}F\text{-}C_6H_4)_3$, of a frustrated Lewis pair-nitrous complex, $tBu_3P(N_2O)BAr_3$.[42] The resulting $[tBu_3P(N_2O)ZrCp_2(CH_3)]^+$ cation has been structurally characterized (Scheme 6). The $[Cp^*_2Zr\text{-}CH_3]^+$ (Cp^* = C_5Me_5) fragment has been tethered to a calcium moiety through an oxygen link, and the resulting heterobimetallic compound has been shown to catalyse intramolecular hydroamination reactions.[43]



Scheme 6. Zirconium complexes including the $[ZrCp_2Me]^+$ fragment from refs 42 (a) and 43 (b).

Group 5. There is a relatively small amount of structurally characterized σ-alkyl V, Nb, and Ta complexes.[44] In a recent example, a dinuclear low-valent vanadium methyl complex stabilized by π-bonded pyrrolyl and μ-imido ligands that catalyses the synthesis of ultrahigh molecular weight polyethylene, has been structurally characterized by Gambarotta and Duchateau.[45] Similarly, like other d^0 early-metal alkyls, d^0 Group 5 metal methyl complexes have been tested as olefin polymerization catalysts.[46a] At variance with group 4 metallocenes, systems based on group 5 metallocenes/MAO like Cp_2MCl_2 (M = Nb, Ta) have no catalytic activity, although the isoelectronic $[CpM(1,3\text{-diene})(CH_3)]^+$ fragments are catalysts for the living polymerization of ethylene.[46b] Thus, Arnold and Bergman have reported examples of well defined, structurally

characterized cationic Nb(V) and Ta(V) methyl complexes with β-diketiminate and imido ligands (Scheme 7) and have studied their reactivity and catalytic activity.[47]



Scheme 7. Vanadium and tantalum methyl compounds from refs. 45 (a) and 47 (b).

In line with the above the simple $TaMe_3Cl_2$ was reported in 1964, yet its solid state structure, featuring a trigonal bipyramidal geometry, was only reported in this decade.[48] This species has been recently used by Copéret, Basset, and collaborators to synthesize a well-defined silica-supported Ta(V) surface complex characterized by solid state NMR, that serves as precatalyst for ethylene trimerization (Figure 3).[49] Parkin *et al.* have also used $TaMe_3Cl_2$ to synthesize a series of complexes featuring a planar terphenyl C,C,C pincer ligand.[50] The same precursor has been employed by Schafer *et al.* to obtain phosphoramidate $Ta(Me)_3$ complexes that are active in room temperature hydroalkylation catalysis.[51]

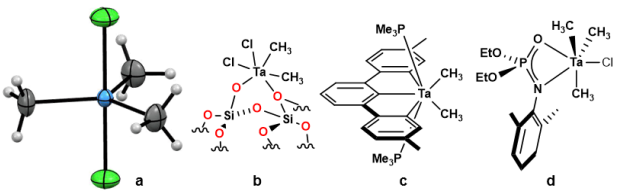
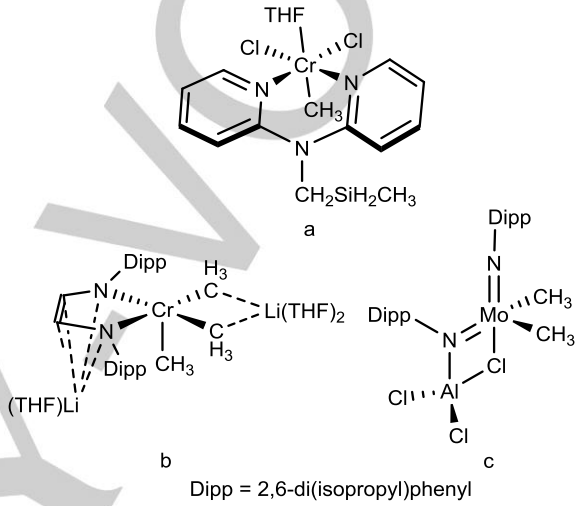


Figure 3. ORTEP plot of the molecular structure of the $TaMe_3Cl_2$ (ref. 48) and three recent examples of tantalum methyl compounds (refs. 49, a; 50, b; 51, c).

Group 6. One early example of methyl complex of group 6 metals is homoleptic WMe_6, which was synthesized by Wilkinson in 1973,[8] however its distorted trigonal prismatic (C_{3v} symmetry) solid state structure had to wait over 30 years to be revealed by Seppelt *et al*.[52] The same group has contributed with many examples of homoleptic methyl complexes of groups 5 to 7.[53-55] Most methyl complexes of group 6 metals reported recently are chromium complexes. Mono Cp-Cr species have been used as commercial ethylene polymerization catalysts.[56] Related olefin oligomerization mediated by chromacycles is also an area of considerable industrial interest. In this context, while ethylene trimerization is better understood,[57-59] selective tetramerization to produce 1-octene remains a challenge. Duchateau, Gambarotta, *et al.* have structurally characterized a Cr(III) monomethyl complex with a N-alkylated 2,2,'-dipyridylamine ligand that, in the presence of MAO, produces 1-octene as the only α-olefin (along with low molecular weight polyethylene wax; Scheme 8).[60] In an attempt to study the catalytic activity of related Cr(II)-monoalkyls with diimine ligands in olefin polymerization, Theopold and coworkers have prepared a series of mono- and bimetallic methylchromium complexes and studied the redox non-innocent behaviour of the diimine ligand.[61] Further examples include dimethyl-molybdenum and dimethyl-tungsten imido complexes as catalysts for olefin dimerization.[62,63]



Scheme 8. Chromium and molybdenum methyl bonded compounds from refs. 57 (a), 58 (b), and 59 (c).

Dichromium, dimolybdenum, and ditungsten complexes with multiple metal-metal bond deserve separate comment. These type of compounds have received much attention recently, particularly since the publication by Power *et al.* of the first stable compound with a quintuple metal-metal bond.[64,65] Different researchers, including some of us, have recently reported several examples of this type of complexes bearing methyl ligands. Those include a dichromium complex obtained by reductive alkylation and oxidative addition of MeI to a Cr—Cr quintuple bond[66] and a trimethyl dimolybdenum(II) *ate* complex featuring a Mo-Mo quadruple bond, two terminal and one bridging methyl ligands.[10] Mulvey *et al.* have recently synthesized the sodium methylchromate dimer $Me_8Cr_2[Na(OEt_2)]_4$. The $(Me_8Cr_2)^{4-}$ core of the molecule has D_{4h} symmetry with each Cr atom being coordinated to four Me functionalities in an approximate square planar environment. Each Na^+ cation is coordinated to four Me and one O atom of one Et_2O. This species is paramagnetic and has a Cr···Cr distance of 3.263(2) Å (Figure 4),[67] which is significantly longer than that of the diamagnetic lithium THF-solvated $Me_8Cr_2[Li(THF)]_4$ (THF = tetrahydrofuran)[68] [1.968(2) Å][69]. The latter molecule was described as having quadruple Cr—Cr bond. Because of the above differences the authors question that these species should be seen as contact ion pairs with $(Me_8Cr_2)^{4-}$ and alkali metals. A role for Li···Me agostic

interactions in enforcing short Cr···Cr bonds had already been proposed by Gambarotta.[69] More recent examples of structurally characterized complexes of group 6 metals with metal-metal bonds include dichromium complexes with $[Cr_2(\mu\text{-}Me)_2]$ core that have a role as catalysts in olefin trimerization,[58] or a series of heterobimetallic complexes containing Mo≡Mo triple bonds bridged by methyl and methylene groups. The synthesis of these species from $Mo_2(OR)_6$ (R = neopentyl, cyclohexyl) and $ZnMe_2$, implies C—H activation by the Mo≡Mo moiety.[70]

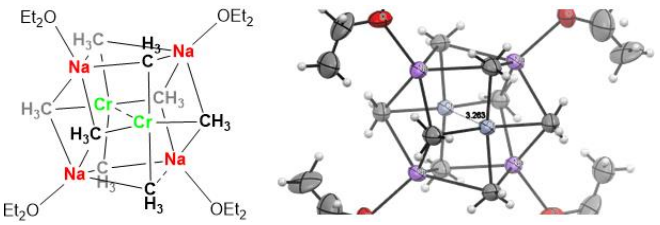
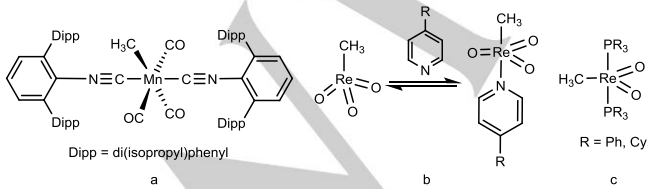


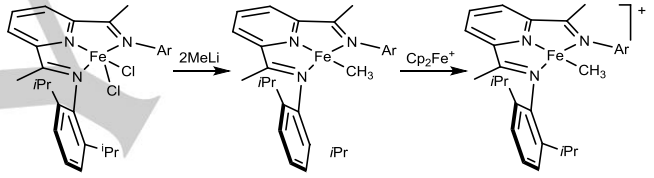
Figure 4. Molecular structure representation and Ortep plot of a Heteropolymetallic Cr-Na complex featuring bridging methyls (ref. 67).

Group 7. Organometallic chemistry of Mn is dominated by complexes with CO ligands,[71] and there are relatively few examples of Mn methyl (or alkyl) complexes. In a recent report, $[MnMe(CO)_3(CNAr'')_2]$ was obtained *via* electrophilic substitution from anionic $[Mn(CO)_3(CNAr'')_2]^-$ (Ar'' = terphenyl fragment) and CH_3I (Scheme 9).[72] Regarding Tc, the first example of structurally characterized Tc-Me compound appeared in 1990,[73] since then only three other examples have been reported. More abundant are the complexes with Re—CH_3 bonds.[54,55] Many recent examples are structurally derived from Re(VIII) oxides. One relevant example is methyltrioxorhenium (MTO), which is a versatile catalyst in oxidation and hydrogen transfer reactions including olefin epoxidation.[74] A series of Lewis adducts of MTO have recently been obtained by reaction of the parent compound with pyridine derivatives and their photochemical properties and performance in epoxidation of 1-octene have been studied.[75] In the same context, Abu-Omar has prepared and structurally characterized phosphine adducts of methyldioxorhenium(V) (MDO) and has used them to support his proposal that MDO is the active catalyst in the dehydrogenation of vicinal diols with MTO.[76]



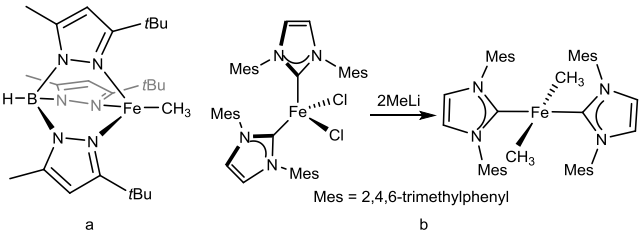
Scheme 9. Manganese and rhenium methyl compounds of refs. 72 (a), 75 (b), and 76(c).

Group 8. Most prominent group 8 TM-CH_3 complexes contain iron and only examples of this class will be cited here. A structurally characterized trigonal bipyramidal iron methyl complex with the tridentate $Si(o\text{-}C_6H_4PPh_2)_3$ ligand has been reported by the group of Peters in a study of stepwise N_2 reduction.[77] The group of Chirik has studied a series of cationic, neutral, and anionic bis(imino)pyridine (PDI) iron alkyl complexes by a combination of techniques including X-Ray diffraction, Mössbauer spectroscopy, and DFT in order to gain insight into the redox activity of single-component (without MAO or other cocatalyst) ethylene polymerization catalysts.[78] The cationic complex $[(^{iPr}PDI)FeMe][BPh_4]$, which may be related to the active species obtained from $(^{iPr}PDI)FeCl_2$ and MAO, was obtained by oxidation of neutral $[(^{iPr}PDI)FeMe]$ with a ferrocenium salt. Square planar $[(^{iPr}PDI)FeMe]$ was prepared in turn by reductive alkylation of $(^{iPr}PDI)FeCl_2$ (Scheme 10). The reaction was shown to proceed through a $(^{iPr}PDI)Fe(R)Cl$ intermediate the reactivity of which dictated the outcome of the alkylation. Thus, the small LiMe yielded exclusively the monomethyl complex of Scheme 10, whereas the bulkier $LiCH_2SiMe_3$ could either afford a monoalkyl analogue or alkylate further to form $[(^{iPr}PDI)Fe(CH_2SiMe_3)_2]$.[79]



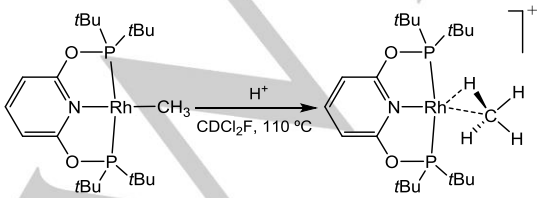
Scheme 10. Preparation of Fe(II) and Fe(III) methyl complexes supported by an anionic PDI ligand (refs. 78 and 79).

The previous complexes are examples of low-electron-count iron compounds. Bulky tris(pyrazolyl)borate ligands (Tp) have also been used to stabilise 14-electron tetracoordinated complexes, including $TpFeCH_3$ (Scheme 11).[80,81] Another example of low electron count Fe(II)-methyl complex is square planar $(IMes)_2FeMe_2$ that was prepared by Glorius and collaborators by reacting $Fe(N(SiMe_3)_2)_2$ with IMesCl (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and treating the resulting $(IMes)_2FeCl_2$ with LiMe. The geometric change from the dichloride to the dimethyl complex was attributed by the authors to both the steric properties of the IMes ligands and the strong ligand field created by the σ-donor character of the carbene and the methyl ligands. The NHC-stabilized (NHC = N-Heterocyclic Carbene) dimethyl and the parent dichloride complexes catalyse hydrosilylation and transfer hydrogenation reactions.[82]



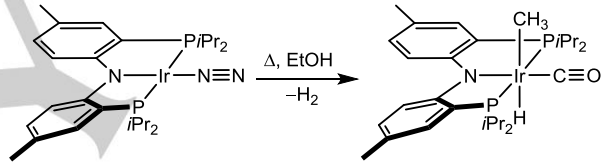
Scheme 11. Iron methyl complexes stabilized by a) a bulky Tp ligand (refs. -80 and 81); b) a mesityl substituted NHC ligand (ref. 82).

Group 9. Structural chemistry of Co(II) has similarities with that of Fe(II). An example is $(IMes)_2CoMe_2$, which has square planar coordination around the metal, as shown by X-Ray diffraction[83] and is analogous to the above mentioned Fe(II) complexes of Glorius.[82] Another series of recent examples of cobalt complexes structurally analogous to their iron counterparts are a number of neutral[84] and cationic cobalt methyl complexes with bis(imino)pyridine ligands, the latter studied by Chirik *et al.*[16] as catalysts in ethylene polymerization reactions. Enantiopure versions of these type of complexes have been structurally characterised and shown to be active catalysts for asymmetric alkene hydrogenation.[85] The same type of complexes have been used for alkene hydroboration with pinacolborane (HBPin).[86] The bis(imidazolidene)pyridine methyl complex, $[(CNC)Co(II)Me]^+$, structurally related to the above (bis)iminopyridine, was also obtained by oxidation of [(CNC)CoMe] with ferrocenium.[87] Cobalt(I) methyl complexes with (bis)phophinopyridine PNP pincer ligands, which undergo H radical loss, have been characterized by the group of Milstein.[88] A number of Rh(I) and Rh(III) methyl complexes – more than forty – have been structurally characterized in the last five years, being most of them supported by chelating bidentate[18,89] or tridentate[19,20,90] ligands. Two relevant examples of C—C activation reactions that generate a Rh—CH_3 bond were cited above.[19,20] Square-planar Rh(I) carbonyl methyl complexes stabilized by (diisopropylphosphino)ethane or (diisopropylphosphino)methane have been recently reported to react with $HSi(OEt)_3$ affording the corresponding silyl complex with liberation of CH_4.[89f] The characterization of the first methane complex[12] in 2009 by Brookhart, Goldberg, and co-workers represents, without any doubt, a landmark discovery in transition metal chemistry and was made possible thanks to a Rh(I) methyl complex supported by a bulky PNP ligand (Scheme 12, see more in the reactivity section).



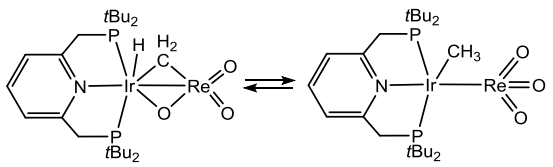
Scheme 12. Formation of the first σ-methane complex characterized in solution (ref. 12).

The chemistry of mononuclear methyl derivatives of iridium is largely dominated by the presence of tridentate P,C,P,[91] P,N,P,[92] N,N,P,[93] and O,P,O[94] ligands, although interesting examples of complexes containing carbene,[95] diphoshine,[96] and N-donating[97] polydentate ligands also appeared recently. Only two cluster-type molecules exhibiting Ir—CH_3 bonds have been structurally characterized in the last 5 years by Adams' group.[98] Research in the field of Ir alkyls is often devoted to the stoichiometric and, in some cases, catalytic activation of C—H,[94,95a,96c] C—C, and C—O[91b] inert bonds. A bulky porphyrin Ir(III) methyl complex has been employed for the catalytic insertion of organic carbenes into C—H and Si—H bonds.[97d] Homobimetallic and heterobimetallic complexes of Ir and Rh exhibiting a terminal ligated CH_3 group have been characterized by Cowie and coworkers (see Section 3 for further discussion).[96b,c] A peculiar square-pyramidal Ir(III) methyl complex stabilized by the anionic ligands $GaMe_2^-$ and $GaMe_3Cl^-$ has recently been reported.[99] The well-known ability of [Ir(PNP)] fragments to activate inert bonds can be nicely exemplified by a recent report of Nocera's group,[92c] which describes the selective decarbonylation of ethanol to CO, CH_4, and H_2 leading to an octahedral methyl hydride Ir(III) complex (Scheme 13).



Scheme 13. Ethanol is cleaved by an Ir(I) complex and generate an Ir(III) methyl derivative (ref. 92c)

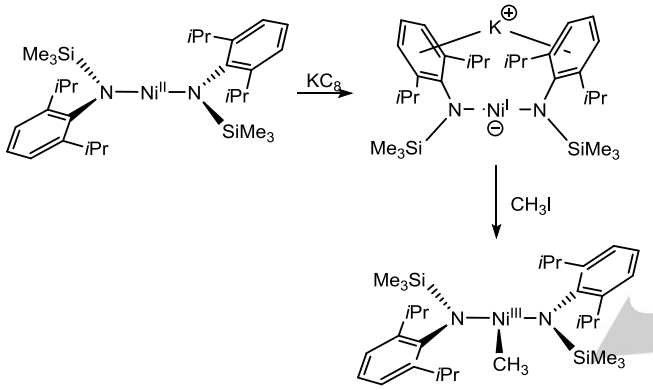
The existence of a dynamic interconversion between a terminal methyl and μ-CH_2/hydride complex has been demonstrated for Re-Ir dinuclear complexes supported by bulky PNP pincer ligands (Scheme 14):[92d]



Scheme 14. Reversible conversion of a μ-CH_2/hydride Ir-Re bimetallic complex into the corresponding terminal methyl species (ref. 92d).

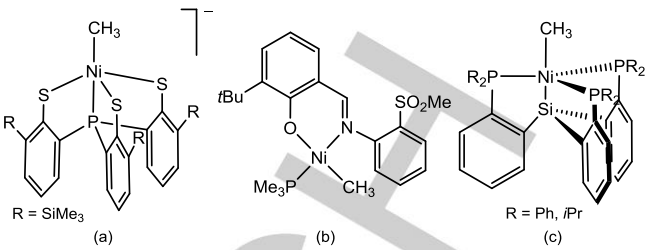
Group 10. Group ten metals provide the largest family of methyl metal complexes within transition elements (see Figure 2). Since 2010, almost 700 structures of these metals with a M—CH_3 unit have been deposited in the CCDC database, most of them containing the two heaviest elements of the group. In this section we will present the most recent discoveries in the chemistry of methyl nickel complexes and select only a few examples for Pt and Pd, encouraging other authors to

specifically review this topic. In the latest years much attention has been focused on nickel organometallics both for catalytic applications and academic purposes, *e. g.* unusual oxidation states, low coordination numbers, stoichiometric activation of small molecules, bioinorganic model systems. Mononuclear square-planar Ni(II) complexes stabilized by bi- or tridentate ligands[100] are the most represented class within the over 70 crystallographically characterized structures of the Ni—CH_3 unit since 2010. Nevertheless, Tilley *et al.* reported recently on a tri-coordinate Ni(III) methyl complex stabilized by bulky amido ligands[101a] (Scheme 15) and on its catalytic activity in cross-coupling reactions.[101b] Similarly, Y. Lee and collaborators have observed the formation of a Ni(III)—CH_3 bond by oxidative addition of iodomethane to a Ni(I) carbonyl complex.[102]



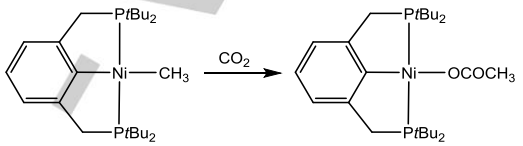
Scheme 15. Synthesis of the tricoordinate Ni(III) methyl complex reported by Tilley and collaborators (ref. 101a).

A tetradentate trianionic ligand has been used by G.-H. Lee and collaborators in order to build up a model for the Methyl CoM-reductase, which displays an unusual pentacoordinate environment for the metal in the +3 oxidation state (Scheme 16a).[103] The relevance of Ni(III) carbyl species supported by amido-pyridine N,N,N,N ligands in cross coupling reactions has also been established.[104] Great efforts have been made in developing Ni catalysts for alkene polymerization, particularly for the production of highly branched polyolefin structures. Leading publications by Marks,[105] Mecking,[106] Brookhart,[107] and Agapie[108] often present mixed phenolato-imine hemilabile ligands in conjunction with the Ni(II)—CH_3 fragment (Scheme 16b). Dinuclear complexes of this type are also described.[105c,108] A Ni(II) methyl derivative stabilized by a monoanionic tris(phosphino)silyl ligand (Scheme 16c) has been chosen by Peters and Tsay to generate thermally stable nickel adducts of dinitrogen and dihydrogen after protonolysis of the Ni—CH_3 bond.[109]



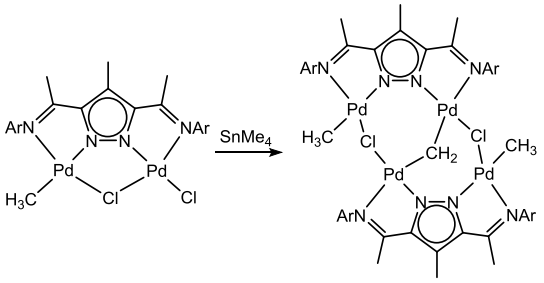
Scheme 16. Nickel methyl complexes of refs. 103 (a), 105a (b), and 109 (c).

Reactivity with CO_2[110] (Scheme 17) and hydrogenolysis of the nickel-methyl bonds[111] have been explored for pincer type PCP and PBP ligands, respectively.



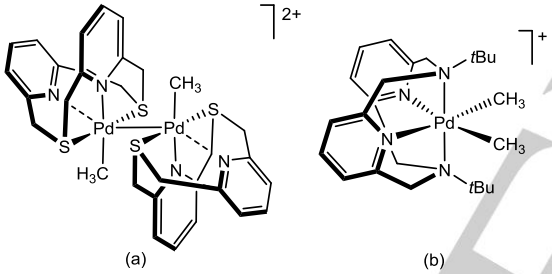
Scheme 17. CO_2 insertion into a Ni(II)—CH_3 bond (ref. 110).

The importance of palladium catalysts in many organic transformations is reflected in the high number of recent studies concerning palladium methyl derivatives, most of them stabilized by P,O donating ligands. Polymerization, copolymerization, and oligomerization of olefins have deeply been investigated in the last years. Mecking's group has described a number of Pd methyl derivatives containing phosphine-sulfoxide and -sulfonate bidentate ligands and studied their activity as homogenous catalysts for alkene copolymerization,[112a-c] Mizoroki-Heck reactions,[112d] and also for the preparation of heterogeneous catalysts.[112c] Related systems have been described by Nozaky and collaborators who employ bisphosphine monoxides as ancillary hemilabile ligands.[113] Phosphine-sulfonate and carbene-sulfonate ligands have also been used by Jordan.[114] N,N,N-phenanthroline-oxazoline palladium methyl complexes have been reported to catalyze CO/styrene copolymerization.[115] Moving to structural and stoichiometric reactivity studies, Braunstein and Danopoulos described last year an unusual group interchange involving the rupture of Pd–CH_3 and P–Ph bonds in palladium(II) complexes bearing non-symmetric diphosphines.[116] A unique transformation of a dinuclear palladium complex into a tetranuclear methylene bridged one was observed by Meyer and coworkers taking advantage of compartmental nitrogen ligands (Scheme 18):[117]



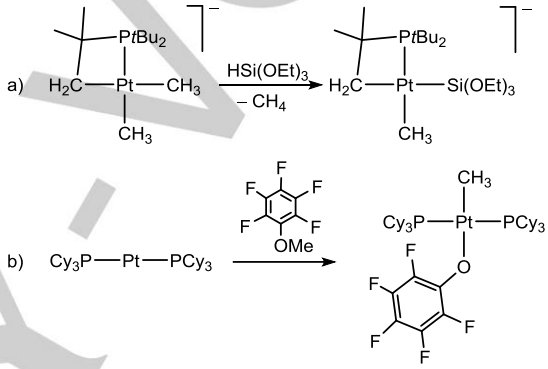
Scheme 18. Dimerization of a bimetallic Pd complex to form a tetranuclear methylene-bridged species (ref. 117).

Homo and heterobimetallic complexes of Pd and Pt exhibiting metal-methyl bonds have been generated by rational design of bridging structures,[118] while unsupported Pd(II)—Pd(II) interactions have been observed in square planar methyl-palladium complexes with tetradentate pyridine-thioether ligands (Scheme 19a).[119] Related pyridine-amino systems proved to be effective in the stabilization of several Pd(III) species, as reported by Mirica and coworkers in recent years (Scheme 19b).[120]



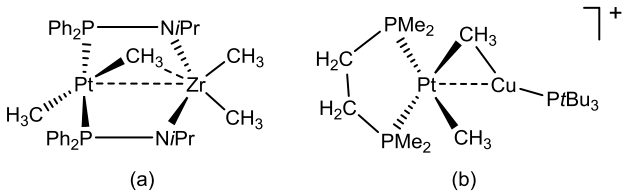
Scheme 19. a) Pd-Pd interactions in mixed S,N in Pd(II) methyl complexes with a S,N-donor ligands (ref. 119); b) a diamino-dipyridine ligand stabilizes a dimethyl Pd(III) complex (ref. 120a).

Platinum methyl derivatives in both +2 and +4 oxidation states constitute a very ample family of organometallic compounds, mainly due to the availability of stable, easy-to-handle metal precursors such as $PtMe_2(DMSO)_2$, $[PtMe_2(dimethylsulfide)]_2$, $[PtMe_3I]_4$, etc. Aiming to offer a general and concise view on recent advances in this field, we will briefly mention some catalytic applications and focus the discussion on structural and synthetic aspects. Recently, Periana and coworkers investigated the mechanism of methane oxidation performed by the "Periana Catalytica" $(bpym)PtCl_2$ catalyst (bpym = 2,2'-bipyrimidine) in concentrated sulfuric acid, which converts CH_4 into a mixture of methanol, $CH_3OH_2^+$, and CH_3OSO_3H and SO_2. In accordance with theoretical and kinetic studies which also involve the synthesis of mono- and dimethylated Pt(II) complexes bearing 2,2′-bipyrimidine as the ancillary ligand, a relevant role of Pt(IV) species for reaction with methane is discarded, being C-H activation performed by Pt(II) to generate Pt(II)-CH_3 intemediates.[121] In 2014, a challenging 1,2-selective catalytic hydrosilylation of conjugated dienes was accomplished by means of an anionic cyclometallated Pt(II) monomethyl compound resulting from the reaction of the corresponding dimethyl derivative with $HSi(OEt)_3$ (Scheme 20a).[122] A series of square-planar Pt(II) methyl complexes have been prepared by Perutz *et al.* by oxidative addition of O—CH_3 bonds of highly fluorinated arylethers at a linear platinum(0) centre (Scheme 20b).[123] Noteworthy activation processes have also been documented by Puddephatt's group, that reported on the cleavage of C_{aryl}-S bonds by $[PtMe_2(dimethylsulfide)]_2$ leading to polymethylated SMe^- bridged bimetallic compounds.[124a] Carbon-silicon bond activation under oxidative conditions has also been described.[124b]



Scheme 20. a) A dimethyl cyclometallated Pt(II) anion is converted in a methyl-silyl complex by reaction with $HSi(OEt)_3$ (ref. 122); b) oxidative addition of a CH_3—O at a Pt(0) diphosphine complex (ref. 123)

A number of heterobimetallic complexes including a Pt—CH_3 unit appeared recently.[118,125] In a series of Pt-Zr dinuclear species, the influence of the electron-donating ability of the metalloligand $RR'Zr(iPrNPPh_2)_2$ on the Pt···Zr bond separation was discussed by Thomas and collaborators, who also reported on an unusual anagostic Zr···CH_3—Pt interaction (Scheme 21a).[125a] Chen *et al.* were successful in isolating a rather elusive intermediate in transmetalation reactions performed with copper reagents and described a unique heterobimetallic Cu-Pt complex held together by a labile d^8–d^{10} bond supported by a bridging methyl group (Scheme 21b).[125b]



Scheme 21. Examples of heterobimetallic complexes including Pt—CH_3 units from refs. 125a (a) and 125b (b).

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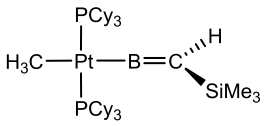
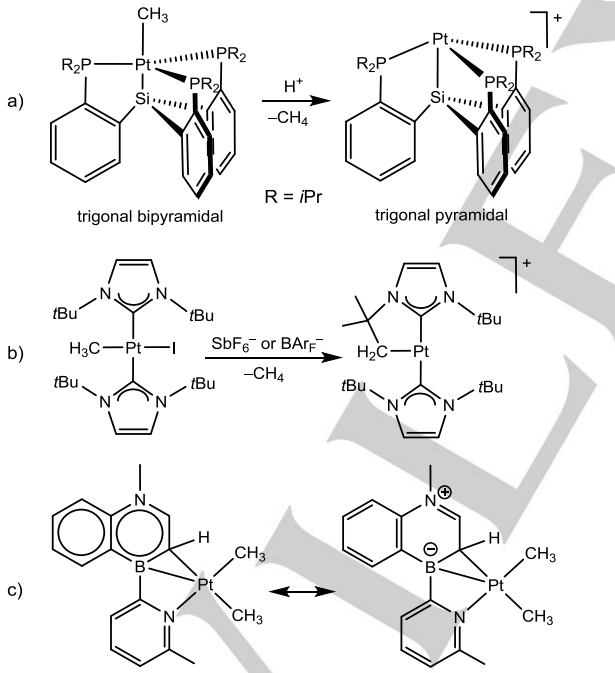
Platinum chemistry in conjunction with boron-based ligands has experienced a remarkable growth in recent years.[126] Leading research in this field has been carried out by Braunschweig's group, culminating in the full characterization of an alkylideneboryl Pt(II) methyl complex in 2014 (Scheme 22).[126b] Efficient oxidative C–H bond cleavage and C–C coupling has recently been documented within the coordination environment of dimethyl- and diphenylplatinum(II) fragments stabilized by pyridylborato ligands.[126d]



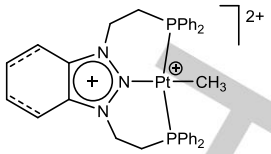
Scheme 22. The unprecedented alkylideneboryl Pt(II) methyl complex described by Braunschweig and collaborators (ref. 126b)

Methyl derivatives of Pt(II) play also a prominent role in the generation of unusual coordination modes,[126c] unsaturated species,[127] and in the investigation of unexpected geometries[128] and reactivity[129] of organometallic compounds. Some examples are shown in Scheme 23.



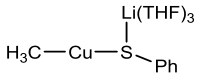
Scheme 23. Representative examples of unusual coordination geometries and coordination modes in Pt(II) methyl species or obtained from them (a, ref. 122; b, ref. 121a; c, ref. 126c)

A nitrenium methyl Pt(II) complex reported recently by Gandelman and collaborators constitutes an extremely rare example of cationic ligand bonded to a cationic metal centre (Scheme 24).[130]



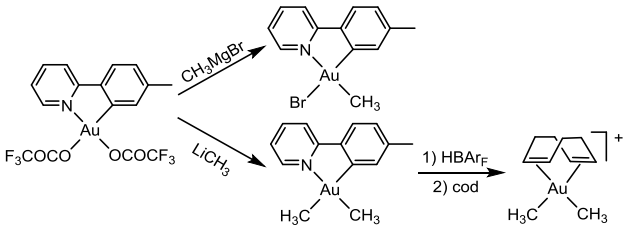
Scheme 24. The nitrenium Pt(II) methyl complex prepared by Gandelman *et al.* in 2014 (ref. 130).

Group 11. Methyl complexes of coinage metals are largely limited to gold species. In spite of the great importance of transmetallation reactions involving groups 11 elements, to the best of our knowledge, only one silver(I) coordination compound exhibiting a covalent Ag—CH_3 has been described to date,[131] while in recent years only a handful of copper(I) species containing Cu-methyl fragments have been crystallographically characterized. As mentioned before (see group 10), a bimetallic species showing a Pt—Cu interaction supported by a bridging CH_3 group has been described by Chen *et al.*[125b] Two further complexes of this class, which have been provided recently by Bertz and Ogle, consist in cuprate anions supported by an alkene ligand in one case (*vide infra*, Reactivity Section), and by a phenyltiolate in the other one (Scheme 25).[132] A rare example of photoluminescent copper cluster with bridging methyl groups was reported in 2010 by Cavell and coworkers.[133]



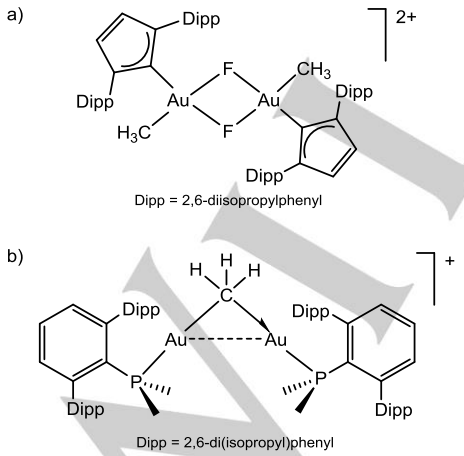
Scheme 25. One of the few examples of structurally characterized methyl complexes of copper(I) (ref. 132).

In comparison with copper and silver analogues, gold chemistry in this field is much richer, which is witnessed by the considerable number of Au(I) and Au(III) derivatives described crystallografically in the last five years. Both structural and reactivity approaches are well represented in the corresponding bibliography. Mainly focusing on cyclometallated systems based on bipyridine ligands, Tilset and collaborators have obtained a series of Au(III) methyl complexes of particular synthetic interest taking advantage of the presence of labile ligands, such as triflate[134aa] and trifluoroacetate[134b] anions, directly bound to the metal centre (Scheme 26). An analogous strategy in conjunction with the selective protonation of the cyclometallated carbon atom has been employed to synthesize the first Au(III) alkene complex exhibiting only gold-carbon bonds at the metal (Scheme 26).[134c]



Scheme 26. Representative examples of Tilset's Au(III) methyl complexes and their synthesis (refs. 134a, 134c)

In 2011 a combined theoretical and experimental contribution by Toste's group suggested the formation of Au(II)—Au(II) intermediates in the mechanism for oxidative heteroarylation of alkenes.[135a] Among several chloride derivatives, the electrochemical behavior of a bimetallic gold methyl complex supported by a dicarbene ligand was analysed. The same research group prepared a rare example of molecular gold-fluoride complex stabilized by bulky carbenes (Scheme 27a) and provided the first experimental evidence for C-C coupling at a Au—CH_3 gold center in the presence of arylboronic acids.[135b] N-heterocyclic carbenes complexes of gold(I) were also used by Wend and Ahlquist in order to investigate their reactivity with organic electrophiles, and in particular in C-C coupling reactions involving the Au-bonded methyl group.[136] In a somehow related article, Bercaw and Labinger studied the reductive elimination of MeI from gold(III) methyl complexes.[137] Macrocyclic diphosphines and[138] bidentate N,N,[139] N,O,[140] and O,O[140,141] donating ligands has also been recently employed for the preparation of coordination compounds of the Au(III)—CH_3 unit. As a final remark, it is worth mentioning here a very recent contribution by some of us which describes an unprecedented methyl bridged digold(I) complex stabilized by a sterically demanding terphenyl phosphine (Scheme 27b).[142]

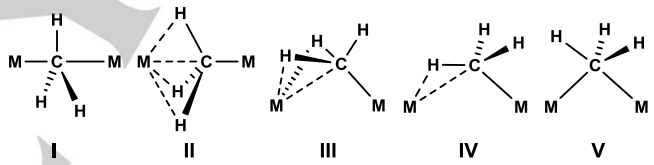


Scheme 27. a) Homobimetallic Au(III) methyl fluoride complex prepared by Toste and co-workers (ref. 135b); b) novel methyl bridged Au(I) dinuclear complex reported by our group (ref. 142).

2.2. Bridging methyl complexes of transition metal. Three-center two-electron bonds.

The previous section focused on structurally characterized complexes with terminal methyl ligands, although some complexes with bridging methyls were mentioned. This section will deal with homo- and some hetero-dimetallic complexes of transition metals with bridging methyl ligands. Some excellent reviews and book chapters have focused on this topic,[143] some considering the metal-metal bonding of the bridging methyl compounds and the nature of the bridging ligands as three-centre two-electron bonds.[9,144]

A search in the Cambridge Structural Database for bimetallic transition metal complexes with bridging methyl ligands produced only 75 results, a very small number compared to the more than five thousand entries retrieved for metal methyl (TM—CH_3) compounds. Most compounds feature early transition metals, for example, there are at least 19 di-yttrium species, 7 compound containing scandium and with 11 zirconium, whereas there are no examples with silver and only one example with gold which has already been described.[142] The relative abundance of examples of early transition metals may be related to their role in olefin polymerization.[36,145]



Scheme 28. Bridging modes for a methyl ligand in bimetallic complexes (ref. 143)

Bridging modes for a methyl ligand in bimetallic complexes are represented in Scheme 28 (modified from reference 143).

Mode I is common among di-zirconium species (Figure 5). In these, the Zr-Me-Zr bridge is not symmetric, with the shorter bond slightly above 2.40 Å and the longer below 2.56 Å, both bonds being longer than the average Zr—Me bond of 2.29 Å (CSD). These complexes are cationic and have been described as Lewis pairs with the [Zr]—CH_3 fragment acting as the base and the $[Zr]^+$ fragment as the acid.[146,147]

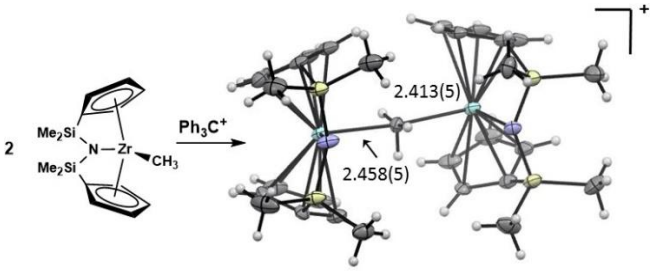
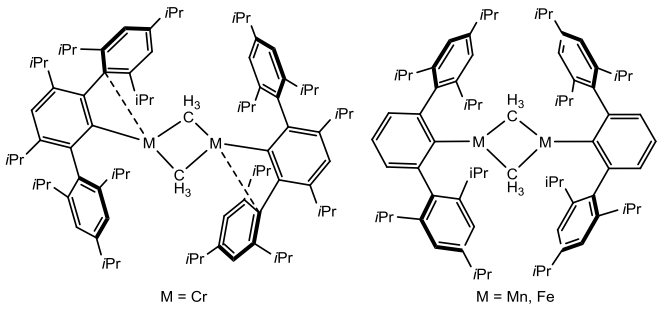


Figure 5. Recent example of type I coordination mode of a bridging methyl ligand (ref. 146).

Complexes of middle and late transition metals exhibit bridging modes IV (featuring agostic bonds) and V.

There are few examples of symmetrical type V methyl bridges,[10,148] a recent example being the dimanganese and diiron complexes stabilized by bulky terphenyl ligands shown in Scheme 29.[149] Interestingly the dichromium analogue features unsymmetrical Me bridges and long range interactions between the C_{ipso} of the flanking aryls and the Cr atoms.[149]



Scheme 29 Examples of methyl bridged homobimetallic complexes stabilized by bulky terphenyl ligands (ref. 149).

During the study of a Cr(II) ethylene polymerization catalyst Gambarotta, Duchateau *et al.* obtained a paramagnetic dichromium complex, which was active in alkene trimerization[58] and structurally similar to $[(\eta^5\text{-}C_5Me_5)Cr(\mu\text{-}Me)]_2$.[150] Related examples by the same authors include dichromium(III) complexes with two and three bridging methyls and non-innocent diimine ligands already mentioned in the previous section.[61] Also, recent examples of heterobimetallic transition metal complexes with bridging methyl ligands include a Cu(I)-CH_3-Pt(II) species relevant to transmetallation processes,[125b] or an early/late Zr-CH_3-Pt complex in which a methyl exchange process takes place.[125a]

In many occasions the methyl bridge features an agostic interaction with one of the metals (*i. e.* type IV bridging mode), however the energy difference between this situation and the symmetric bridge (type V) may be small.[151] Agostic interactions in metal alkyl complexes are a case of 3-centre-2-electron bonds, and are related to important chemical transformations including insertion reactions related to polymerization catalysis or C—H activation.[152] Computational studies of agostic interactions in early and late transition metal complexes have been reported in the last years.[153-154] Characterization of such interactions may in some cases, particularly with α-agostic interactions, require NMR and theoretical analysis, in addition to X-ray diffraction data, since the latter technique may not be precise enough to reveal the activation of the bridging C—H bond.[148] As an example, a series of heterobimetallic complexes of rhodium and osmium with bridging methyls have been characterized by X-ray diffraction and NMR.[155] The agostic nature of the interaction of the bridging methyl was determined partly based on analysis of its J_{CH} coupling constant, which, at *ca.* 125 Hz, according to the authors, was deemed significantly lower, than that found for other methyl fragments (135-140 Hz). This was attributed to thermal averaging of the *normal* C-H coupling of ca. 140 Hz with the ca. 90 Hz coupling expected for the bridging proton according to directly measured values.[156] An additional support for the agostic interaction was that the ^{1}H chemical shift δ of the bridging methyl increased in samples with monodeuterated bridges, as a result of the isotopic perturbation resonance (IPR) effect.[153]

The effect of the bridging ligand on the nature of the metal-metal bond and the bond order has been studied in detail by Baik, Frieser and Parkin[144,157] using dimolybdenum complexes.[158] According to their analysis, the resulting effect of a bridging methyl (or H) ligand can be seen as the protonation of one of the metal-metal bonds. The metal-metal bond order is reduced by one unit, as one of the metal-metal π interactions becomes part of the 3-center-2-electron bond with the bridge. These findings support the elegant *half-arrow* electron counting method that provides a simple description of the bonding in inorganic compounds with 3-centre-2-electron interactions (Figure 6).[9]

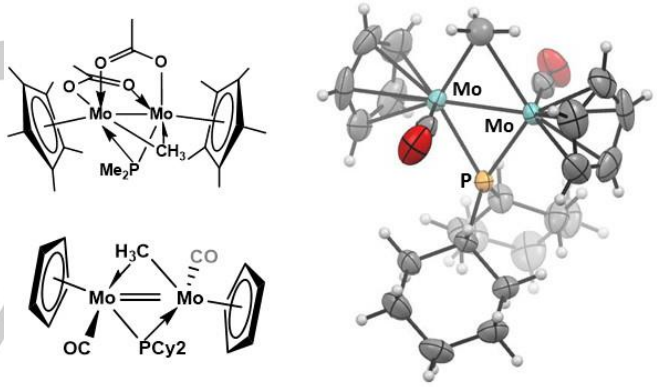


Figure 6. The *half arrow* counting method predicts 18-electrons count for the molybdenum atoms of the two dimolybdenum complexes shown above (refs. 9,144,157). It also predicts single and double Mo—Mo bonds. This method distinguishes bridging ligands and accounts for 3c-2e bridging methyls.

3. Reactivity

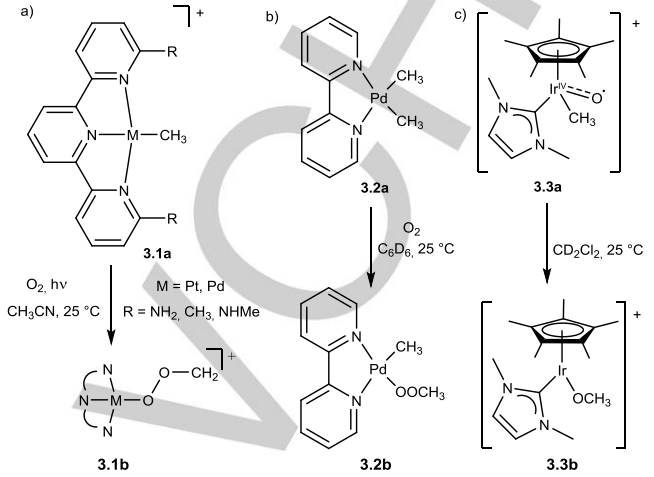
Despite the apparent simplicity of the methyl ligand it exhibits rather rich reactivity. The slim sterics of the CH_3 group facilitate certain reactions that are challenging or forbidden for more hindered hydrocarbyl ligands. It offers the possibility of sharing the coordination sphere of the metal with bulky ancillary ligands, and gives easier access to bridging methyl species. TM-CH_3 compounds serve as ideal models in reactivity studies of more elaborated alkyl ligands. Additional benefit arises from the fact that, in contrast to other σ-alkyl complexes, β-hydrogen elimination is not possible. In most cases the reactivity of TM—CH_3 involves cleavage of the metal-carbon σ-bond, although there are examples in which the less reactive C—H bonds are activated. Similar to other sections of this article, in this section

attention will focus on reactivity studies on TM-Me compounds reported from 2010, although previous work will be briefly discussed when appropriate. A general discussion of most common elementary reactions at the TM—CH_3 fragment will be firstly presented. This will be followed by recent reports on the role of the title compounds as reactive intermediates in synthetic and catalytic applications. At the end we will centre our attention in μ-bridging methyl complexes, where the close proximity of two or more metal centres broadens the reactivity routes of the methyl group.

3.1 Elementary Reactions involving the TM—CH_3 fragment

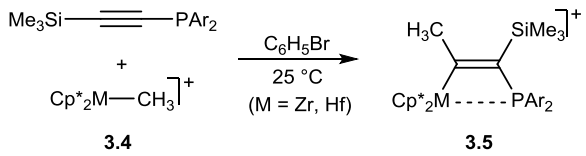
Migratory insertion. Migratory insertion is arguably the most common reaction found in TM—CH_3 fragments. Insertion of a wide variety of metal-ligated groups into M—CH_3 bonds has been reported over the years, including alkenes,[78,108c,112e,117,159] alkynes,[160] allenes,[161] isocyanides,[162] as well as small molecules such as CO,[163] CO_2,[100j,164] or SO_2.[165] In fact, several of these insertion reactions constitute the basis of some of the most prevalent industrial chemical processes, such as olefin polymerization and carbonylation. Owing to the vast amount of literature reports concerning these reactions, especially olefin and CO insertion, we will mainly highlight recent results in other less common but highly relevant insertion processes.

An attractive chemistry arises from the insertion of oxygen into TM—CH_3 bonds, a pivotal step in the selective catalytic oxidation of alkanes (methane in particular), which is still one of the great challenges in catalysis research.[166] In a general methane oxidation scheme, oxidative addition of methane over a transition metal would lead to a TM-methyl complex which could later be (oxy)functionalized, ideally by an environmental oxidant such as O_2. Late transition metals are especially interesting owing to their ability to activate C—H bonds. In recent years, the groups of Goldberg[167] and Britovsek[168] have demonstrated that molecular oxygen can be inserted into Pt(II)- and Pd(II)-methyl bonds to generate methylperoxo ligands (Scheme 30). In all cases radical chain pathways were proposed. More recently, Ison and Cundari accomplished the insertion of an oxo ligand into an Ir—CH_3 bond to form a proposed Ir-OCH_3 intermediate (**3.3b** in Scheme 30) that subsequently released a molecule of methanol, with the overall process following a radical mechanism.[169] Dimethyl ether has also been produced from a Pt(IV)-methyl intermediate in methanolic solutions.[170] A non-radical pathway was suggested for the insertion of an oxo group into an Fe—CH_3 bond in the calculated intermediate [Cp*Fe(P(OCH_2)$_3$CEt)(O)CH_3] derived from the oxidation of [Cp*Fe(P(OCH_2)$_3$CEt)$_2$$CH_3$] using O_2.[171] In a general approach, the insertion of oxygen into group 9 and 10 M—CH_3 bonds has been studied by computational methods, pointing out to the benefits of using hemilabile ligands,[172a] *i.e.* chelating ligands with ine substitutionally labile group that can be displaced from the metal centre while remaining available for recoordination.[172b-d] Remarkably, the insertion of an oxygen atom into a Re—CH_3 bond has been shown to be catalyzed by flavins, with rate enhancements up to 600-fold.[173] Although group 12 elements are not included in this review, it is worth mentioning here the controlled insertion of O_2 into a Cd—CH_3 bond, which allowed for isolation of the first structurally authenticated cadmium organoperoxide.[174]



Scheme 30. Selected examples of oxygen insertion into TM-CH_3 bonds (refs. 167, a; 168, b; 169, c).

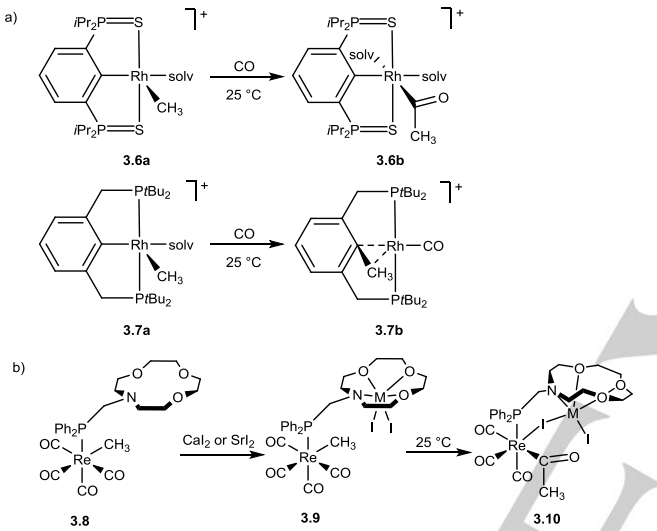
Cationic [^{R}Cp$_2$ZrCH$_3$]$^+$ zirconocenes have been frequently employed as catalysts in olefin polymerization.[175] As in late-transition metals, the olefin is first inserted into the Zr—CH_3 bond and subsequent chain-growth by consecutive olefin insertions takes place. The same has been shown to occur with acetylenes.[176] However, the group of Erker has recently disclosed a prevailing alternative reactivity that consists in the 1,1-carbozirconation (and carbohafnation) of diarylphosphino(trimethylsilyl)acetylene, formally the insertion of the alkyne into the M—CH_3 (M = Zr, Hf) bond, accompanied by 1,2-migration of the silyl group (Scheme 31).[177] This unique reactivity resembles that of the Wrackmeyer 1,1-carboration[178,90e] and has led to the formation of organometallic Frustrated Lewis pairs alike **3.5** with remarkable facility for the activation of small molecules.



Scheme 31. Organometallic FLP formation by 1,1-carbometalation (ref. 177).

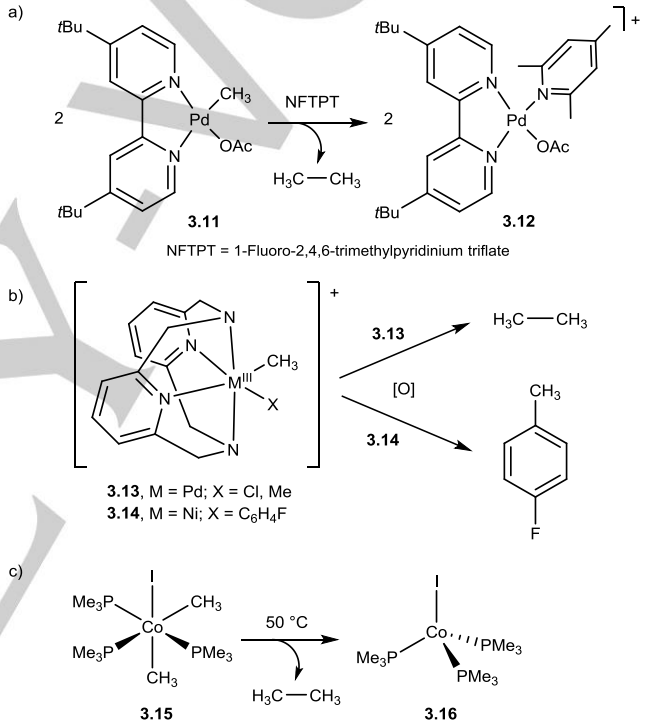
In an interesting study, Milstein and co-workers investigated the divergent behavior of rhodium complexes bearing sulfur (**3.6a**) or phosphorus (**3.7a**) based pincer ligands towards migratory insertion into a Rh—CH_3 bond (Scheme 32a). The higher electrophilicity of the sulfur atoms resulted in preferred migration to carbon monoxide (**3.6b**), while in the related PCP system

reductive C-C coupling to the aryl ligand prevailed (**3.7b**).[179] The use of CO (or syngas) as a C_1 source for the synthesis of hydrocarbons and oxygenates has attracted considerable attention in the last decades.[180] A key step in the process is C-C bond formation, i. e. through migratory insertion of CO into TM—C σ-bonds. In an elegant example, Bercaw and Labinger synthesized a phosphine-functionalized aza-crown ether ligand that supports Lewis acid (Ca^{2+}, Sr^{2+}) promoted migratory insertion of CO into a Re—CH_3 bond (Scheme 32b).[181] Subsequent oxygen insertion into a related acyl rhenium complex has also been demonstrated.[182] In a different area, the first example of migratory insertion of alkenes into Au-C σ-bonds, in particular into a Au(III)—CH_3 bond, has been recently described.[183]



Scheme 32. a) Migratory insertion of CO *vs* aryl C-C reductive coupling in Rh-CH_3 complexes (ref. 179); b) Lewis-acid promoted migratory insertion (ref. 181)

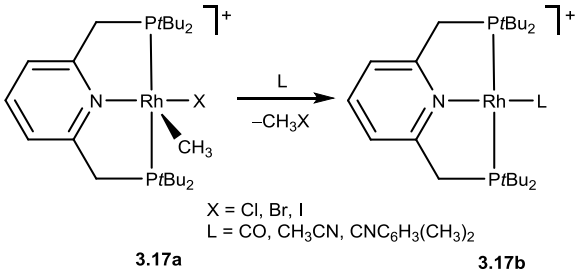
Reductive Elimination. Reductive elimination (RE) from TM-CH_3 groups is of great significance, since it can lead to either the formation of new C-C bonds in cross-coupling chemistry or C—X bonds (X = halide or pseudohalide) in catalytic hydrocarbon functionalization cycles. In TM—CH_3 complexes containing a hydride ligand RE may result in methane liberation, a process that will be further discussed as part of protonolysis reactions (*vide infra*). The simplest example of C-C coupling, the reductive elimination of ethane from TM-dimethyl complexes, has attracted considerable attention as a way to access ethane and higher hydrocarbons.[184] Due to its role in C-C cross coupling reactions, palladium complexes have played a prominent role in these investigations. It was noticed that RE in Pd(II)Me_2 species is slow and low yielding.[185] In contrast, high-valent Pd complexes seems to boost up the homocoupling. Oxidatively induced ethane formation from (dtbpy)Pd$(CH_3)_2$ (dtbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) was achieved by treatment with ferrocenium.[186] Sandford[187] and Mirica[120a] have demonstrated that the oxidatively induced formation of ethane from high-valent palladium mono-methyl complexes is more relevant than from their related di-methyl species in a potential catalytic cycle involving methane activation (Scheme 33a and 33b, respectively). Aerobic oxidation to access a Pd(III) complex and subsequent ethane release has also been reported by Mirica.[120b] Reductive ethane elimination in first-row transition metals is much less common.[188] A recent example taking place over dimethylcobalt(III) complex **3.15** seems to proceed through a concerted 2-electron process in a similar fashion as suggested for the second and third-row series (Scheme 33c).[189] C-C reductive coupling in a high-valent Ni(III) complex (**3.14**) has also been described and its implications in nickel catalyzed cross-coupling reactions studied in detail.[104]



Scheme 33. Reductive C-C coupling in TM-CH_3 complexes (refs. 187, a; 120, a, b; 189, c)

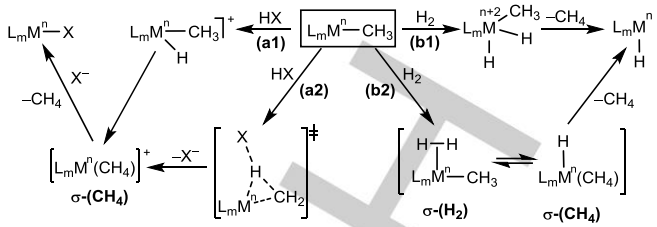
The RE of MeX (or other R-X) is comparatively less common than the reverse process, oxidative addition.[2,190] Reductive elimination of CH_3Cl was early observed as a byproduct during Shilov's methane oxidation,[191] for which an S_N2 mechanism (chloride dissociation and subsequent nucleophilic attack over the methyl ligand) was suggested.[192] Methyl chloride and iodide formation from RE in Pt,[193] Au,[137] and Rh,[194] including a tetranuclear rhodium sulfide cluster,[89e] has been documented. A reversible oxidative addition-RE of MeCl and MeI has been proposed in an iridium complex on the basis of infrared spectroscopic analysis.[195] The reversibility of the process has been achieved by Gunnoe and co-workers by fine tuning of the ligand framework of a terpyridine rhodium complex, suggesting once more an S_N2 mechanism for the RE step.[196] A detailed

study on the RE of MeX (X = Cl, Br, I) from Rh(III) pincer complexes (**3.17a** in Scheme 34) has been reported by Milstein, concluding that the steric hindrance around the metal center considerably facilitates RE (Scheme 34).[197] In this work, while RE of MeBr and MeI seemed to proceed through an S_N2 mechanism, elimination of MeCl likely involved a concerted pathway.



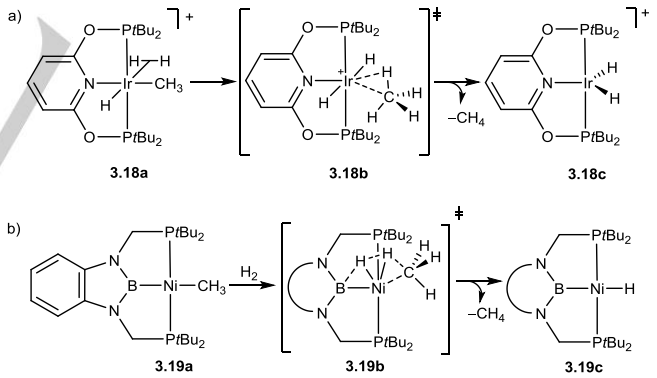
Scheme 34. Reductive elimination of MeX (X = Cl, Br, I) from a Rh(III) pincer complex from ref. 197.

Protonolysis and Hydrogenolysis. The protonoloysis of the TM—CH_3 bond to release methane has been widely used as a clean, efficient, and irreversible way of creating a vacant coordination site transition metal complexes, both for reactivity studies and to access active species in catalytic cycles.[198] Other alternative routes to abstract the methyl group and access a vacant site have been commonly employed, including the use of boranes,[41,199] trityl cation[200] or radical species.[114b,201] Protonation of the methyl ligand in (PONOP)Rh(CH_3) (PONOP = 2,6-bis(di-*tert*-butylphosphinito)-pyridine) at low temperature led to the first example of NMR-characterized σ-CH_4 complex ever reported, a landmark discovery in organometallic chemistry.[12] The existence of the analogous pincer σ-CH_4 iridium complex was later inferred on the basis of EXSY NMR and H/D scrambling experiments using (PONOP)Ir(Me).[202] A σ-CH_4 platinum complex has been suggested to be an operating intermediate in the selective deuteration of the two hydride ligands and the methyl group in $TpPtCH_3(H)_2$ (Tp = hydrido-tris(pyrazolyl)borate) using CD_3OD.[203] The mechanisms of protonolysis of Pt- and Pd—CH_3 fragments has attracted great attention.[204] It consists in the reverse reaction of methane C—H activation and thus it is of pronounced importance in the development of practical catalysts for methane functionalization. Both the direct protonation of Pt/Pd-C σ-bonds (route a2 in Scheme 35) and the stepwise protonation of the metal center and subsequent RE of methane (a1 in Scheme 35) seem to be accessible mechanisms whose prevalence depends on the electronic properties of the ligand framework (Scheme 35).[205] Tunneling effects and the significance of abnormally high kinetic isotopic effects (KIEs) have been discussed in the context of TM-CH_3 protonolysis.[206]



Scheme 35. Possible mechanisms of TM—CH_3 protonolysis (a1, a2) and hydrogenolysis (b1, b2) .

A related reaction is the hydrogenolysis of TM—CH_3 groups. In this case the proton source is H_2 instead of HX (X = halogen, OR, SR, etc.), resulting in the net substitution of the methyl ligand by a metal hydride with concomitant liberation of methane (b1 and b2 in Scheme 5). The hydrogenolysis mechanism of a pincer Ir(III)-CH_3 complex was analyzed in detail by Brookhart and co-workers (Scheme 36a). Spectroscopic studies and DFT calculations revealed that reductive elimination of methane proceeds through a σ-metathesis or σ-CAM mechanism,[207] in which the oxidation state of iridium is unaltered over the course of the transformation and where a σ-methane complex **3.18b** is an instrumental intermediate.[92b] The metal-ligand cooperative hydrogenolysis of a Ni—CH_3 bond in **3.19** has recently been disclosed and the role of the boryl ligand in assisting such transformation is supported by computational studies (Scheme 36b).[111]

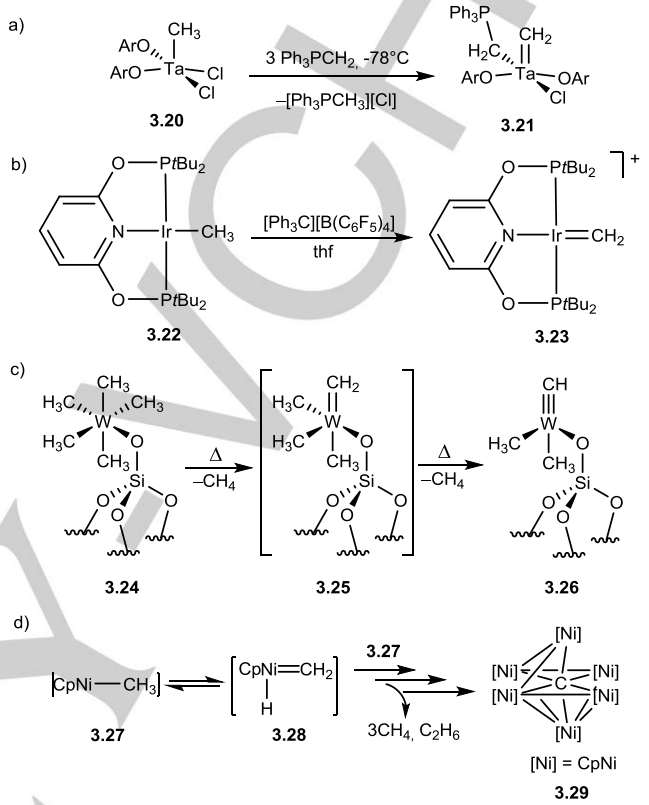


Scheme 36. Hydrogenolysis of Ir(III)—CH_3 (a) and b) Ni(II)—CH_3 (b) bonds (refs. 92, b ; 111).

Homolysis. Homolysis of TM-alkyl bonds is less common than for main group metals,[14] although the development of first-row TM catalytic cycles involving carbon-based radicals has shown the significance of this transformation as a pivotal step in many useful reactions.[208] Many metalloenzymes and, in particular methyltransferases, are proposed to involve the homolytic cleavage of TM—CH_3 bonds. This has garnered considerable efforts aiming to elucidate its mechanism and the factors that influence the process. For instance, the first Ni(III)-CH_3 complex

supported by a tetracoordinate PS_3 ligand was recently synthesized and the homolytic cleavage of the Ni—C bond by action of CO, $(PhE)_2$ (E = S, Se) or PhSH analyzed.[102] These studies are of relevance to the mechanisms of action of acetyl-CoA synthase and methyl-CoM reductase. In another example, the homolysis of Cr(III)—alkyl bonds, including Cr(III)—CH_3, was studied under ambient light in the presence of PhSSPh or O_2.[209] A palladium dimer formed by exposure of a Pd(II)—CH_3 complex to fluorescent light in CD_2Cl_2 due to homolytic cleavage of the Pd—C σ-bond and concomitant release of CH_3D.[114b] Photolysis of a (porphyrin)Rh(III)—CH_3 bond to generate (porphyrin)Rh(II) and a methyl radical has been shown to be a crucial step in the mechanism of rhodium-catalyzed hydroxylation of Si—C(sp^3) bonds.[210]

Hydrogen abstraction. The majority of reactions involving TM-CH_3 fragments proceed through the cleavage of the M-C σ-bond. There are, however, a number of examples in which the stronger C-H bond of the methyl ligand reacts while the former remains unaltered. Historically, the first isolable transition metal methylene complex, $Cp_2Ta(=CH_2)Me$, was prepared by Schrock by electrophilic abstraction of Me^- from Cp_2TaMe_3 by action of Ph_3C^+, followed by deprotonation by $Me_3P(CH_2)$ or other bases.[11,211] Formation of a methylidene terminus by abstraction of either a proton or a hydride is a prevailing transformation. This can occur by four different routes (Scheme 37): (i) intermolecular deprotonation; (ii) intermolecular hydride abstraction; (iii) intramolecular hydrogen abstraction; and (iii) α-hydrogen elimination. Deprotonation of the methyl ligand typically requires the use of a strong base, although milder bases have been reported to react in the gas phase.[212] The strategy has been widely use to access tantalum methylidene complexes.[213] More recently, Mindiola reported two elegant and related examples in which deprotonation of Ta—CH_3[214] (Scheme 37a) and Nb—CH_3[215] groups are effected by ylide $Ph_3P(CH_2)$. Less common is the intermolecular hydride abstraction from a TM-CH_3, which was recently described by our group after adding a salt of the trityl cation as hydride abstractor to [(PONOP)Ir(CH_3)] **3.22** (PONOP = 2,6-bis(di-*tert*-butylphosphinito)-pyridine) (Scheme 37b).[21] A relatively common approach to generate TM-methylidene complexes is the thermal or photochemical promoted α-hydrogen abstraction in TM-CH_3 species. Abstraction is frequently performed by another methyl (or alkyl) ligand bound to the metal center with release of methane (or the corresponding alkane),[216] but it can also occur by heteroatom-based ligand abstraction.[217] This strategy was applied by Basset to access the first tantalum methylidene species on a silica surface.[218] In a related example a polymethyl tungsten complex anchored to a silica surface leads to W-methyl/methylidyne species upon heating due to double α-hydrogen abstraction (Scheme 37c).[219] Related to this, metal-bound methyl mediated α- and β-hydrogen abstraction from amides[220] and cyclopropyl[221] ligands, respectively, with concomitant liberation of methane have also been documented. TM-CH_3 complexes can rearrange by reversible α-hydrogen elimination and formation of (H)TM=CH_2 species (Scheme 37d).[222] In an intriguing example, α-hydrogen elimination of transiently formed [CpNi—CH_3] is proposed as the first C-H activation step in a tandem process that leads to the formation of the unprecedented carbide cluster $(CpNi)_6(\mu_6\text{-}C)$ **3.29** (Scheme 37d).[223]

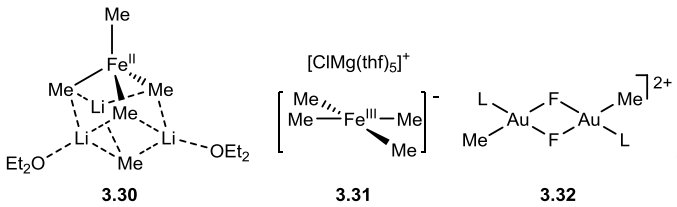


Scheme 37. Selected recent examples of TM=CH_2 formation from TM—CH_3 by: a) intermolecular deprotonation (ref. 214); b) intermolecular hydride abstraction (ref. 21); c) intramolecular hydrogen abstraction (ref. 219); d) α-hydrogen elimination (ref. 223).

3.2 TM-CH_3 as Intermediates in Catalysis

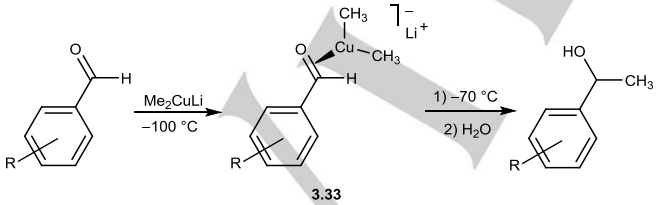
The formation of C-C bonds by stoichiometric and catalytic cross-coupling reactions has become one of the most powerful tools in chemical synthesis, with direct applications in medicinal chemistry[224] and wide use in industry.[225] In the catalytic version, the area has been largely dominated by group 10 metals and, in particular, by palladium. In contrast, the ready availability and lower prices of base metals has attracted great attention in the last decade, but the mechanisms of action of these catalysts are far less well-understood. In this section we aim to highlight some recent examples in the area where catalytically or synthetically relevant TM-CH_3 intermediates have been isolated or spectroscopically identified and have contributed importantly to build the mechanistic puzzle of C-C cross-coupling reactions. Iron-catalyzed cross-coupling systems are promising in competing with the well-established palladium catalysts.[226] Although the first example of such reactivity was reported in the 1970s, the role played by the iron salts employed was still an unsolved question. Since the early report of Kochi,[227] a reduced

form of iron was believed to be the active species, but it was not until 2006 when Fürstner reported the first homoleptic tetramethyl iron(II) ferrate cluster (Scheme 38), $[(Me_4Fe)(MeLi)][Li(OEt_2)]_2$ **3.30**, obtained from reaction of LiMe with iron salts and displaying a rich reactivity.[228] More recently, Neidig and co-workers isolated and authenticated the first tetramethyliron(III) ferrate, $[Me_4Fe][ClMg(thf)_5]$ **3.31**, using only catalytically relevant reagents ($FeCl_3$, MeMgBr, thf) and being active in cross-coupling reactions after liberation of ethane.[229] Au(I)/Au(III) redox cycles have also attracted much attention in cross-coupling reactions as an alternative to palladium catalysts. In a recent report, Toste described the isolation of several alkylgold(III) difluoride species like **3.32** that mimic the speculative intermediates previously proposed in Au(I)/Au(III) C-C coupling reactions, showing that indeed they are competent for this kind of transformation.[135]



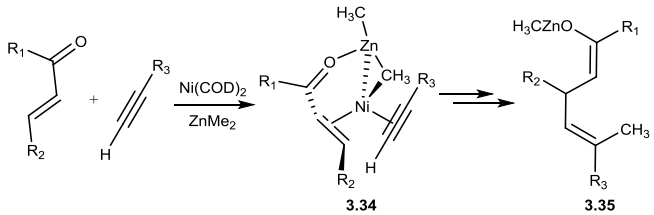
Scheme 38. Recent TM-CH_3 complexes relevant to catalytic C-C cross-coupling reactions (refs. 228, 229, and 135)

Organocopper reagents are useful alkylating tools in C-C cross-coupling chemistry.[230] However, their high reactivity has long precluded isolation of relevant intermediates and thus has shadowed our understanding of reaction mechanisms and the factors influencing activity and selectivity.[231] In a clever approach, Bertz and Ogle have successfully applied rapid-injection NMR spectroscopy (RI-NMR) during the last few years to identify and characterize a number of hitherto undetected Cu-CH_3 intermediates during C-C cross-coupling reactions (Scheme 39).[132,232] One of the structures, a cuprate-carbonyl π-complex was structurally characterized by X-ray diffraction studies.[233]



Scheme 39. Low-temperature NMR detection of an intermediate copper π-complex (**3.33**) with Gilman reagent (Me_2CuLi) (ref. 132).

Nickel-mediated oxidative cyclization of two π-components (e. g. ketone and olefin) is of particular significance, since the resulting formation of a nickelacycle is believed to be an intermediate step in several useful transformations.[234] A number of these processes involve as a third component a main group organometallic entity.[235] In this area, two recent studies from the groups of Schlegel and Montgomery (Scheme 40)[236] and Ogoshi and Kurosawa[237] deal with the role of $ZnMe_2$ and $AlMe_3$, respectively, in promoting the oxidative cyclization reaction. In both cases a bridging μ-CH_3 intermediate between Ni and either Zn or Al was suggested (*i. e.* **3.34** in Scheme 40). In the case of $AlMe_3$ that intermediate could be isolated and fully characterized by X-ray diffraction studies. However, the importance of Ni-(μ-CH_3)-Al species goes far beyond the discussed transformation and, once more, a brief historical comment is appropriate. In the early 1950s, Ziegler and co-workers observed that, without apparent reason, the reaction of triethylaluminum and ethylene to yield high molecular trialkyl aluminum species repeatedly failed. Instead, the formation of 1-butene due to chain cleavage after one olefin insertion was detected.[238] A systematic search for the reasons of the unexpected but highly useful reactivity revealed that traces of nickel were responsible and the term "nickel effect" was coined. This observation led to the foundations of Ziegler catalysts[239] and set the basis for a revolution in different areas of chemistry and, in particular, in organonickel chemistry.[240] Many exhaustive studies have pursued a mechanistic understanding of the "nickel effect". Low valent heterobimetallic Ni(0)-(μ-C)-Al species are believed to be key intermediates.[241] Recently, Hor and co-workers were able to isolate and crystallographically characterize a Ni(0)-(μ-CH_3)-Al species that mimic the presumed intermediates responsible for the "nickel effect".[242] As expected, this species was active for the olygomerization and polymerization of ethylene. Also in the field of polymerization catalysis, Mountford described the first structurally characterized $AlMe_3$ adduct of a TM-alkyl cation, closely related to the postulated resting-state species during catalytic polymerization activated by MAO (Scheme 5a).[37]

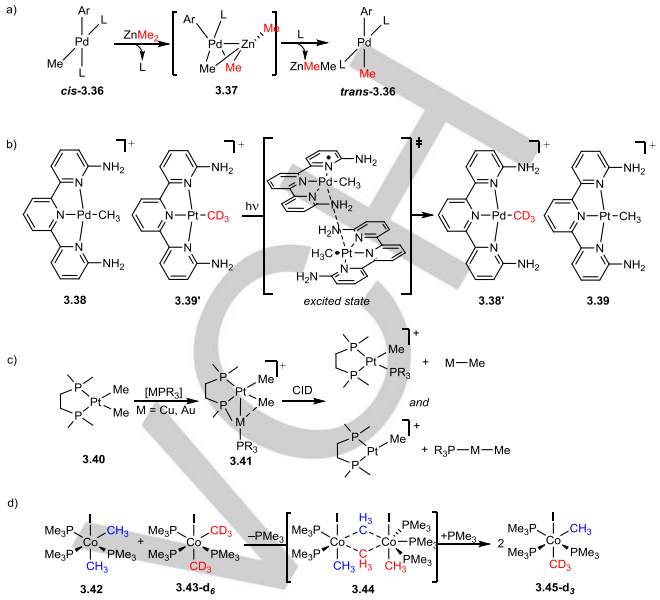


Scheme 40. Ni-(μ-CH_3)-Zn compound (**3.34**) as an intermediate during nickel-catalyzed three component addition process (ref. 236).

3.3 Reactivity of Transition Metal M(μ-CH_3)M bridging compounds

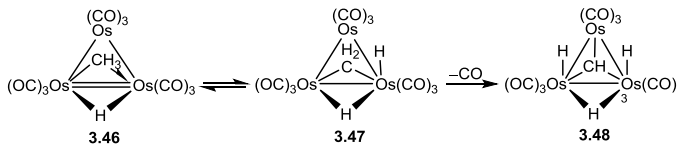
The close proximity of two metals in complexes with bridging methyl ligands leads to a rich variety of transformations of the methyl group. A fundamental process invoked in cross-coupling reactions is the transmetalation of alkyl (such as methyl) functionalities between different metal centers.[243] For instance, the role of organozinc reagents in transmetalation to palladium

in the context of Negishi coupling has been intensively studied in recent years.[244] Bimetallic Pd(II)-Zn(II) intermediates alike **3.37** (Scheme 41a) with bridging methyl ligands seem to be instrumental both for the required transmetallation and isomerization steps during C-C coupling reactions.[245] The dissimilar behaviour of $ZnMe_2$ with respect to ZnMeCl has also been analysed. In another example, a heterometallic $Pt(CH_3)$-$Sn(CH_3)_3$ species has been proposed as a key intermediate in the platinum catalyzed methyl transfer from methyl tin reagents to iridium complexes.[246] Transmetalation reactions are also employed as a convenient strategy to access mono-methyl species alike $L_nM(CH_3)X$ through metathesis of $L_nM(CH_3)_2$ and $L_nM(X)_2$. The opposite, disproportionation of mono-methyl compounds to afford dimethyl metal derivatives has been recently investigated over Pd(II) species.[185] Despite the prevalence of transmetalation reactions, detailed studies on its precise mechanisms are still scarce. Methyl transfer in the context of platinum or palladium mediated hydrocarbon oxyfunctionalization have been recently analyzed.[119,247] Studies aiming to understand the Me transfer mechanism coincide in the crucial role of the close proximity of the metal centers. A systematic investigation into methyl exchange in terpyridine Pt(II) and Pd(II) complexes driven by light suggests that an excited triplet state displaying a M—M bond is formed upon irradiation (Scheme 41b). M—C σ-bonds are weakened due to partial occupancy of antibonding $d_{x^2-y^2}$ orbitals leading to a concerted transition state featuring two bridging methyl ligands.[168b] Analogously, Pt(II)-to-Cu(I)[125b] and Pt(II)-to-Au(I)[125c] methyl transfer have been shown to proceed via heterobimetallic cationic complexes as **3.41** that exhibit some degree of M-M bond (Scheme 41c). Intermolecular methyl exchange in base metals has been recently reported in $(PMe_3)_3Co(CH_3)_2X$ (Scheme 41d).[189,248] While many potential mechanisms were experimentally ruled out, computational studies pointed out to a transient high-energy dicobalt intermediate **3.44** bearing two bridging methyl ligands as the key species. Additionally, methyl transfer from Fe(II) and Mo(II) to Sn has been described upon irradiation of $(\eta^5\text{-}C_5H_5)M(CO)_n$ Me [M = Fe, n = 2; M = Mo, n = 3] when these complexes were used as catalysts for the dehydrocoupling dimerization of $^tBu_2SnH_2$.[249]



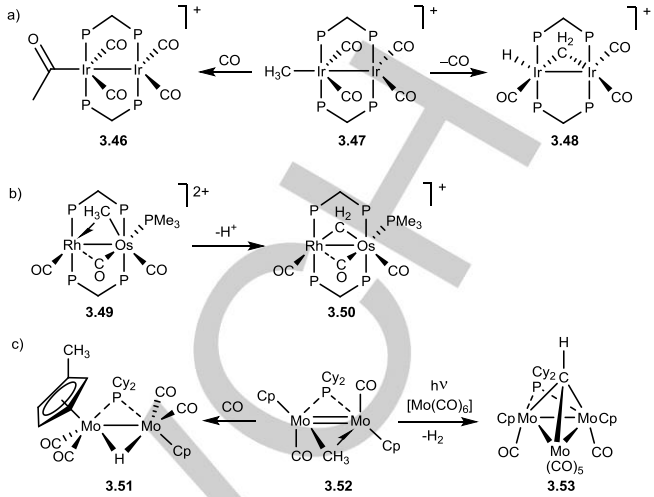
Scheme 41. Selected examples of transmetalation of methyl ligands via bimetallic intermediates. CID = Collision-Induced Dissociation (refs. 245, a; 168b, b; 125b-c, c; 248, d).

C—H bond activation in bridging μ-CH_3 ligands is significantly more prone to occur than in terminal CH_3 groups. The proximity of the two metal centers facilitates bimolecular α-hydrogen elimination to generate a μ-CH_2/hydride bimetallic species. This offers a striking scenario still to be exploited in the search for new homogeneous catalysts for hydrocarbon functionalization. Cowie has reported this bimetallic reaction in Rh/Os[22] and Ir/Ir (Scheme 42a)[250] complexes built around diphosphines, while in a related Ir/Ru system the agostic μ-CH_3 complex prevails and no α-hydrogen elimination is observed.[251] The reaction has also been described for an Os trinuclear species.[252] Although a detailed analysis of this study is beyond the scope of this article, the historical importance of the work of Shapley on osmium methyl clusters in C-H activation, and in the application of the Isotopic Perturbation of Resonance NMR technique to organometallic chemistry warrants some comments. In 1977, Calvert and Shapley reported the first direct observation of interconversion of methyl and methylene ligands in the form of the cluster compounds $[Os_3(CH_3)H(CO)_{10}]$ and $[Os_3(CH_2)(H)_2(CO)_{10}]$. Moreover, they also demonstrated that thermal loss of CO from the latter (Scheme 42) originated the methylidyne complex $[Os_3(CH)(H)_3(CO)_9]$.[252b]



Scheme 42. Interconverson of cluster-bound methyl and methylene ligands and formation of a methylidyne complex by loss of CO (ref. 245b).

This discovery was relevant to surface science, for it provided new insights to hydrocarbon adsorption and reactivity from the perspective of coordination and organometallic chemistry, furnishing a possible model for the nearly pervasive phenomenon of hydrogen atom mobility in chemisorbed hydrocarbon-derived species.[252c] Only one year later, the same authors gathered NMR evidence for the existence of agostic interactions in the methyl cluster $[Os_3(CH_3)H(CO)_{10}]$ when they performed variable temperature NMR studies of a mixture of the partially deuterated methyl and methylene isomeric complexes. The compounds were produced by the reaction of $[Os_3D_2(CO)_{10}]$ with CH_2N_2.[252d] The ^{1}H NMR spectrum of the deuterated material showed well separated CH_3, CH_2D, and CHD_2 signals with chemical shifts that varied strongly with temperature. Besides, an also abnormally large and temperature-dependent isotope effect was found for the one-bond C-H coupling constant of the three methyl isotopologues.[252d] Additional details on the applications of this interesting technique to the study of agostic interactions can be found in the first edition of Crabtree's book (reference 2), published in 1988. Bridging μ-CH_2 complexes can alternatively be formed through deprotonation of μ-CH_3 ligands (Scheme 43b), as reported by the same research group on a diphosphine Rh/Os complex.[253] Other more classic elemental reactions have also been observed in the Cowie's system, such as migratory insertion of carbon monoxide (Scheme 43a) or olefins, reductive elimination with formation of new C-C bonds or hydrogenolysis accompanied by release of methane.[22,96b,250,251,253] The latter has also been described for a Ti/Ti system.[254] Ruiz and co-workers have reported on the migratory insertion of carbon monoxide and other unsaturated species over a μ-CH_3 ligand that bridges two molybdenum centers, including the unprecedented insertion of a cyclopentadienyl ligand (Scheme 43c, left).[255] Remarkably, photolysis of solutions of binuclear Mo/Mo complexes in the presence of $[M(CO)_6]$ (M = Mo, W) result in the formation of trinuclear methylydine clusters after acceptorless dehydrogenation of the bridging μ-CH_3 ligand (Scheme 43c, right), an unknown transformation in monometallic systems.[255a,c]



Scheme 43. Selected reactions of bridging TM-(μ-CH_3)-TM fragments from refs. 250 (a), 253 (b), and 255 (c). Bridging phosphine = dppm = μ-$Ph_2PCH_2PPh_2$; Cp = cyclopentadienyl.

4. Summary and Perspectives

One of the conspicuous accomplishments of chemistry during the past five or six decades has been the discovery of a variety of transition metal organometallic compounds that contain single or multiple metal-carbon bonds. Among them, transition metal alkyls, particularly methyl derivatives, are a prominent family that shares the benefit of a distinguished history.

The methyl group is a simple and readily accessible carbon-donor ligand. As it consists of only one carbon and three hydrogen atoms, it features slender steric properties, only surpassed by the somewhat related hydride ligand. Despite this simplicity, it forms metal-carbon bonds of diverse structure and reactivity and may be viewed as direct or indirect precursor for other one-carbon ligands such as those present in M—CH_4^+, M=CH_2, M≡CH, and even M≡C:$^-$ structures.

In the previous sections, we have attempted to offer an updated view of chemistry of TM—CH_3 complexes. Whereas synthetic procedures for the preparation of these compounds are in general straightforward, the methyl group can bond in bridging as well as terminal fashion, generating a variety of structures which resulted in much research into the synthesis and reactivity of new members of this group of complexes. The involvement of the methyl group in agostic interactions poses additional attractive peculiarities, which in the case of bridging methyl ligands may serve as models for the ready migration over metal surfaces, or for intermediates in facile C—H bond activation reactions of surface-bound methyl groups.

The reactivity of the TM—CH_3 is surprisingly rich, for in addition to cleavage of the metal-carbon bond, it can implicate, as noted earlier in this article, rupture of the stronger and less reactive carbon-hydrogen bonds. Detailed investigations on

elementary reactions at TM—CH_3 fragments are fundamental for the development of crucial transformations as, for example, the selective catalytic oxidation of methane, where the insertion of an oxygen atom into a TM—CH_3 bond is a still not well understood but essential step. Complex catalytic C-C coupling processes can also be analysed with a great level of detail by focusing on the simple methyl group. Additionally, a bright future may emerge for polynuclear species, where the possibility of forming methyl bridges has intriguingly expanded the chemistry of this fragment and, in particular, has revealed accessible ways for the activation of one (or more) of the stronger C-H σ-bonds. More fundamental studies in the future could allow for the development of catalytic versions of polymetallic activation and functionalization of C-H bonds inspired in the simple methyl ligand.

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Keywords: transition metals • coordination modes • organometallics • reactivity • M—C bonding

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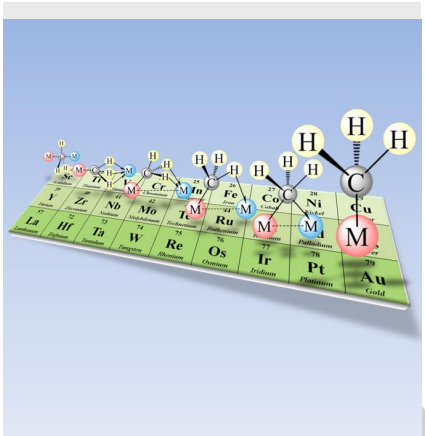
REVIEW

This review offers a concise overview on synthetic, reactivity, and bonding aspects of the chemistry of transition metal methyl compounds. After a systematic view on *d*-block elements, two further sections are specifically devoted to methyl-bridged complexes and reactivity. Citing more than 500 references, this contribution is mainly focused on the last five years.



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Methyl Complexes of the Transition Metals

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