

Unveiling the Latent Reactivity of Cp* Ligands (C₅Me₅[−]) toward Carbon Nucleophiles on an Iridium Complex

Alejandra Pita-Milleiro, Macarena G. Alférez, Juan J. Moreno,* María F. Espada, Celia Maya, and Jesús Campos*



Cite This: *Inorg. Chem.* 2023, 62, 5961–5971



Read Online

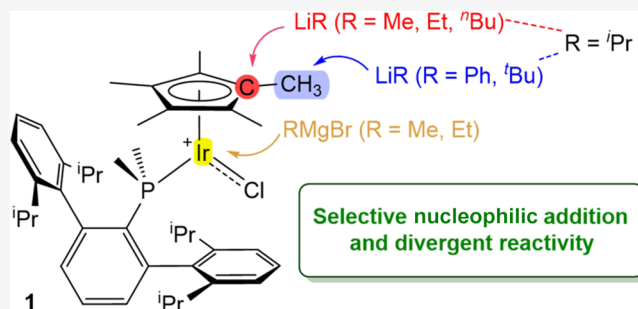
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: The divergent reactivity of the cationic iridium complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}(\text{PMe}_2\text{Ar}^{\text{Dipp2}})]^+$ ($\text{Ar}^{\text{Dipp2}} = \text{C}_6\text{H}_3\text{-2,6-}(\text{C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)_2$) toward organolithium and Grignard reagents is described. The noninnocent behavior of the Cp* ligand, a robust spectator in the majority of stoichiometric and catalytic reactions, was manifested by its unforeseen electrophilic character toward organolithium reagents LiMe, LiEt, and Li^{*n*}Bu. In these unconventional transformations, the metal center is only indirectly involved by means of the Ir(III)/Ir(I) redox cycle. In the presence of less nucleophilic organolithium reagents, the Cp* ligand also exhibits noninnocent behavior undergoing facile deprotonation, which is also concomitant with the reduction of the metal center. In turn,



the weaker alkylating agents EtMgBr and MeMgBr effectively achieve the alkylation of the metal center. These reactive iridium(III) alkyls partake in subsequent reactions: while the ethyl complex undergoes β -H elimination, the methyl derivative releases methane by a remote C–H bond activation. Computational studies, including the quantum theory of atoms in molecules (QTAIM), support that the preferential activation of the non-benzylic C–H bonds takes place via sigma-bond metathesis.

INTRODUCTION

Since the serendipitous discovery of ferrocene in 1951,^{1,2} cyclopentadienyl ligands, [C₅R₅][−], have become indisputably one of the most important ligands in organometallic chemistry and homogeneous catalysis.³ In fact, their coordination complexes extend to virtually every metal in the periodic table.^{4–6} Their versatility is evidenced as well by their variable hapticity (from η^1 to η^5)^{7,8} and synthetic flexibility. Beyond the foremost and simplest [C₅R₅][−] ligands, many versions have been developed, including mono and polyfunctionalized derivatives where R accounts for simple alkyl or aryl groups,⁹ or even bulky substituent to access extremely congested cyclopentadienyl ligands,^{10–16} heteroatom-containing fragments for cooperative reactivity with the metal,^{17,18} bridging anchors to access ansa-metalloenes,^{19–22} or chiral moieties to mediate asymmetric catalysis.²³ However, the permethylated [C₅Me₅][−] ligand (Cp*) is likely the one that has enjoyed the widest popularity.

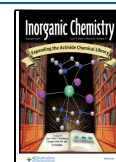
A crucial driving force for the widespread use of cyclopentadienyl ligands is their robust spectator behavior, which is particularly strong in the case of Cp*. However, even for the later ligand, there are increasing examples of its noninnocent character (Figure 1). The methyl groups of Cp* can partake in several transformations, including, but not limited to, deprotonation by an external base or a bifunctional ligand,^{24–37} hydride abstraction which tends to proceed

through single-electron processes,^{38–40} C–H oxidative addition to an adjacent transition metal in bimetallic structures,^{41–48} or direct and reversible methyl-to-metal hydride migration, which was soon identified in early transition metals^{49–52} and recently unlocked by our group as a viable process for late transition metals.⁵³ In addition, the proton-couple-electron-transfer (PCET) catalysis capitalizing on the reversible migration of the proton between the ring and the metal.^{54–60} Moreover, several radical routes have been identified for Cp*-containing species resulting as well in ligand functionalization.⁶¹

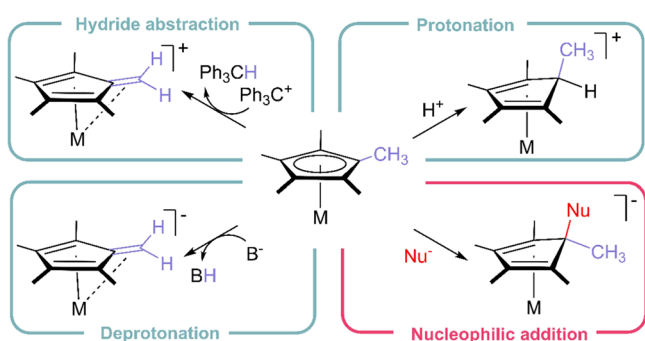
In contrast, the reactivity of the internal carbon centers of Cp* toward nucleophiles has only been observed in a limited number of cases,⁶² being more frequent on the less electron-rich and sterically hindered [C₅H₅][−] upon addition of common highly polar reagents, typically organolithium and organomagnesium compounds.^{63–73} These transformations are of high relevance for a variety of catalytic processes involving

Received: December 15, 2022

Published: April 3, 2023



(a) Some intermolecular pathways accounting for Cp* non-innocence



(b) This work: selective nucleophilic addition and divergent reactivity

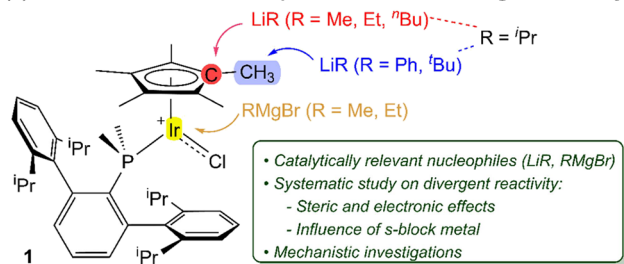


Figure 1. (a) Most common intermolecular pathways for the activation of the Cp* ligand in transition metal complexes; (b) Systematic study revealing divergent reactivity of complex **1** upon reaction with highly polarized carbon nucleophiles.

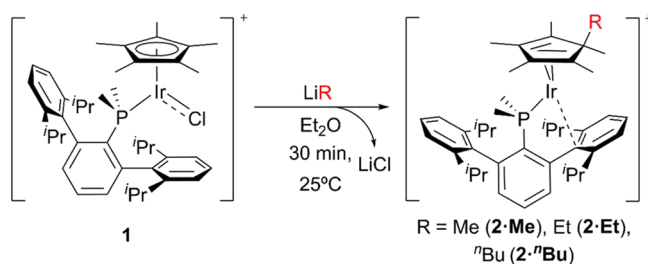
cyclopentadienyl catalysts.^{74–82} For instance, cyclopentadienyl nickel and iron complexes are very active Kumada cross-coupling catalysts with organomagnesium reagents^{83–88} or for the polymerization of the latter.⁸⁹ Organolithium and organomagnesium species are also used as initiators for olefin polymerization or diene isomerization with related catalysts.^{90,91} Besides, the use of organolithium and organomagnesium reagents in the presence of Cp*M complexes of both early^{92–100} and late-transition metals^{101–109} have been reported in many occasions, but the direct reactivity of the Cp* ligand has been overlooked in all cases. Cyclopentadienyl ligands, in particular Cp*, continue to be extensively employed in fundamental organometallic chemistry and homogeneous catalysis. On these bases, understanding these unforeseen reactions is crucial to avoid catalyst deactivation¹¹⁰ or undesired catalytic outcomes,^{111–113} and to further extend the utility of this platform beyond current capabilities, while gaining insight into the formation of active species from Cp*-bearing precatalysts in the presence of bases.^{114–116}

With this goal, we have selected our recently published terphenyl phosphine iridium compound **1** [$(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Cl})(\text{PMe}_2\text{Ar}^{\text{Dipp}2})$][BAR_F] ($\text{Ar}^{\text{Dipp}2} = \text{C}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_3\text{-}2,6\text{-iPr}_2)_2$)^{28,117} to carry out a systematic study of its reactivity toward highly polarized organolithium and organomagnesium reagents. This platform is particularly attractive for these endeavors because (i) it presents a vacant coordination site at the electrophilic Ir(III) center and a chloride ligand susceptible of participating in salt metathesis, yet both the ring and methyl groups of the Cp* can react preferentially toward nucleophiles and/or bases; (ii) the proven noninnocence of the Cp* ligand in this complex, encompassing deprotonation, reversible C–C bond formation and C–H bond breaking;²⁸ (iii) its great stability toward cyclometallation;²⁸ (iv) the possibility of accessing a bulkier analogue of Bergman's complex [$(\eta^5\text{-}$

$\text{C}_5\text{Me}_5)\text{Ir}(\text{Me})(\text{PMe}_3)(\text{ClCH}_2\text{Cl})$]^{116,118} and (v) the in general prominent position of Cp*Ir complexes in the field of C–H bond activation.^{118–124}

RESULTS AND DISCUSSION

To start this systematic study, we first examined the equimolar reaction of complex **1** with the common nucleophile LiMe. As stated above, and considering the reduced size of the methyl anion, we anticipated the methyl group to either fill the vacancy of this unsaturated Ir(III) complex or replace the chloride to access a Bergman-type complex¹¹⁸ [$(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Me})(\text{PR}_3)(\text{ClCH}_2\text{Cl})$]⁺. To our surprise, the only discernible product, which we fully characterized, is a cationic Ir(I) complex (**2·Me**) featuring a new methyl group bonded to one of the internal carbon atoms of the former Cp* ligand, as shown in Scheme 1. Analogous reactivity was found with

Scheme 1. Syntheses of Complexes **2·Me**, **2·Et**, and **2·ⁿBu** from **1** and LiMe, LiEt, and LiⁿBu, Respectively

lithium alkyls LiEt and LiⁿBu (Scheme 1), whose equimolar addition to the iridium precursor **1** led, respectively, to compounds **2·Et** and **2·ⁿBu**, in which a new hydrocarbyl fragment is installed in the exo-face of the parent Cp* ligand.

The room temperature ¹H NMR spectrum of complex **2·Me** features broad resonances, suggestive of a dynamic solution process. This fluxional behavior arises from the rotation of the C₅Me₆ fragment, presumably through a tetrahedral coordination environment,^{124,125} and not from the exchange of the flanking Dipp rings of the phosphine ligand, according to exchange spectroscopy (EXSY) experiments (see Figure S4). However, at –20 °C, complex **2·Me** exhibits a rigid solution structure providing sharp, well-resolved resonances. The absence of symmetry present in **2·Me** results in a complex ¹H NMR spectrum—six singlets, each with relative intensity corresponding to 3 H, are recorded in the 1.84–0.32 ppm range for the Me groups of the newly formed C₅Me₆ diene ligand. Likewise, the four Dipp iso-propyl substituents are inequivalent and originate corresponding multiplets centered at 2.64, 2.32, 2.15, and 2.00 ppm (see Section 2.1 of the SI and Figure S2) for the methine CHMe₂ protons. As a means to compensate unsaturation, complex **2·Me** features a secondary π -arene interaction^{125,126} with the metal center revealed by the low-frequency shift of one of the ipso carbon atoms of the flanking aryl rings (120.4 ppm, cf. the 135.7 ppm value for the corresponding carbon of the noncoordinated Dipp ring) and further supported by topological analysis and Energy Decomposition Analysis - Natural Orbital for Chemical Valence (EDA-NOCV)¹²⁹ (see Sections 5.16.2 and 5.17.1 of the SI). One of the ortho carbon atoms of this ring seems to also participate in the bonding, resulting in η^2 -coordination of the arene, as its chemical shift (132.5 ppm) is significantly shifted to lower frequencies compared to its counterparts

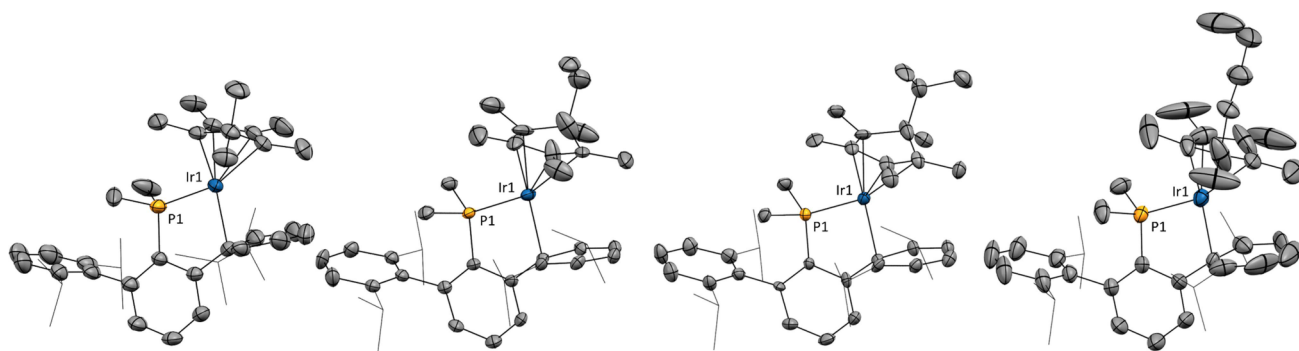


Figure 2. ORTEP diagrams of the cation of complexes **2·Me**, **2·Et**, **2·iPr**, and **2·nBu**. Hydrogen atoms are excluded for clarity and thermal ellipsoids are set at 50% probability. Wireframe is used to represent the *iso*-propyl groups.

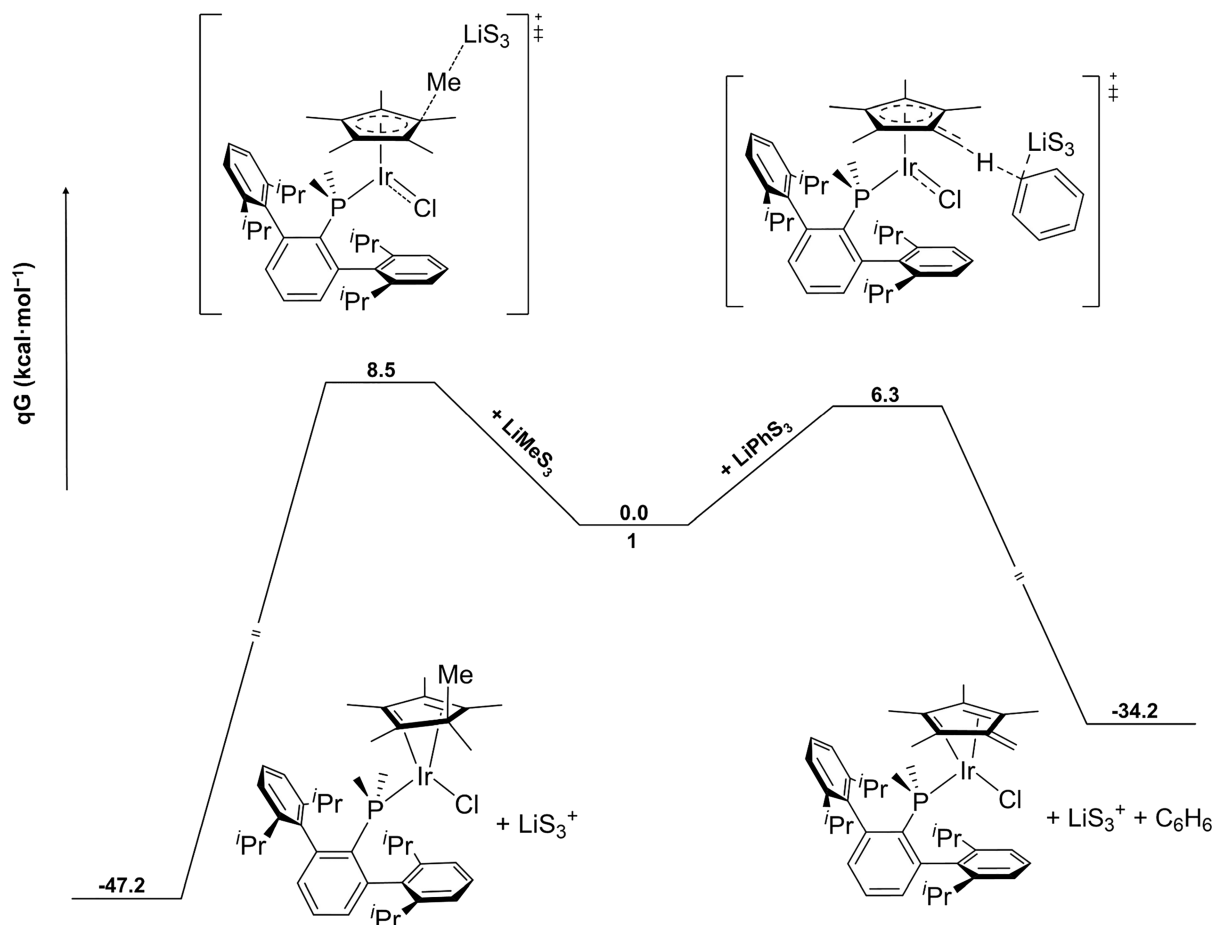


Figure 3. Free energy profiles of LiMe attacking one of the internal carbon atoms of the Cp* moiety (left) and LiPh abstracting a proton from one of the methyl groups of the Cp* moiety (right). S = Me₂O.

(141.5 ppm for the other ortho carbon within the same ring, and 146.5 and 146.9 ppm for the ones belonging to the nonbound Dipp). Interestingly, the ¹³C{¹H} NMR spectrum of complex **2·Me** also exhibits a clear difference in the chemical shift of the two pairs of carbons involved in the two formal double bonds of the C₅Me₆ unit (122.5 and 114.6 vs 78.3 and 61.9 ppm). This experimental evidence together with the longer C–C distance for the formal double bond trans to the phosphane (C34–C33: 1.431(6) vs C35–C36: 1.338(6) Å) and corresponding closer distance to the metal center (C34–Ir1: 2.118(5) and C33–Ir1: 2.163(4) vs C35–Ir1: 2.265(5) and C36–Ir1: 2.437(4) Å) support our hypothesis that the

formal coordinated diene is closer in nature to a double bond and a metalacyclopropane. This can be explained by the stronger trans influence of the phosphane, also observed in a closely related system.^{126–128} EDA-NOCV studies further sustain this idea, revealing a major contribution of the carbon atoms with the longer C–C bond distance to the principal orbital interactions (see Section 5.17.2 of the SI). These spectroscopic features are similar to those found for compounds **2·Et** and **2·nBu**, whose full characterization is included in the Supporting Information.

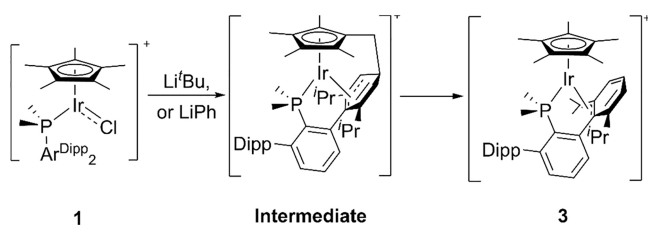
The molecular formulation of the new compounds was corroborated by X-ray diffraction studies, confirming the exo

attack on the Cp* and revealing a preferred η^1 -arene coordination in the solid state, rather than η^2 -binding as inferred from spectroscopic analysis. Thus, in complex **2·Me**, the Ir–C_{arene} bonding is characterized by an Ir–C_{ipso} bond distance of 2.249(4) Å, and by significantly longer, and therefore weaker, Ir–C_{ortho} interactions of length 2.544(5) and 2.686(4) Å (Figure 2). Similar geometric parameters are found in compounds **2·Et** and **2·ⁿBu**, with notably shorter Ir–C_{ipso} (2.231(5), **2·Et**; 2.253(5) Å, **2·ⁿBu**) distances compared to Ir–C_{ortho} (2.549(5), **2·Et**; 2.593(6) Å, **2·ⁿBu**) interactions.

We carried out Density Functional Theory studies to gain insight into the mechanism of the reactions depicted in Scheme 1. For convenience, we focused on the relatively simpler LiMe. Our attempts to rationalize this reactivity through classical foregoing routes involving reductive coupling processes between the Cp* ligand and an Ir–Me functionality failed to provide energy barriers in agreement with experimental observations (see Figures S25 and S26). This led us to explore a more unconventional reaction pathway in which the metal center does not directly participate, and, instead, the direct attack of the LiMe molecule to the exo face of the Cp* moiety takes place. The transition state of the C–C bond formation step requires surmounting a barrier of only 8.0 kcal/mol and yields a neutral Ir(I) complex at –39.2 kcal/mol relative to the reactants. Subsequent chloride release assisted by the solvated lithium atom gave complex **2·Me** through an accessible barrier (see Figures 3 and S24).

In contrast, the less nucleophilic lithium alkyls LiPh and Li^{*t*}Bu acted instead as Brønsted-Lowry bases deprotonating one of the methyl groups of the Cp* moiety. As shown in Scheme 2, this event triggers a complex rearrangement

Scheme 2. Obtention of Complex 3, Final Product of the Reaction between Complex 1 and Li^{*t*}Bu or LiPh^a



^aConditions: alkyl lithiums were added at –78 °C; solution was left to reach room temperature.

involving reversible C–C bond formation that leads to a pseudoallylic structure, complex 3, previously reported by our group by the reaction with the much milder base NEt₃.²⁸ It is remarkable that the unexpected electrophilicity of the internal carbon atoms of the C₅Me₅ ring outcompetes the mild although well-known Brønsted-Lowry acidity of the C–H bonds, even with bases around 40 pK_a units stronger than NEt₃.

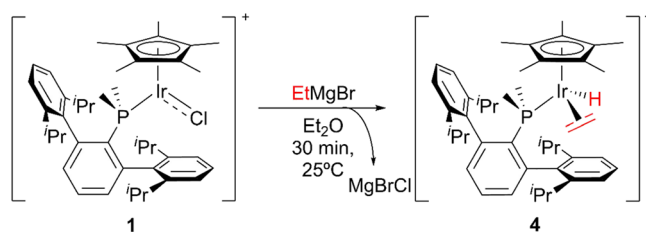
To rationalize such striking divergence in reactivity, DFT studies were performed to calculate the energy profiles for LiPh acting as a nucleophile or as a base. In agreement with the experimental observations, a lower energy barrier for the deprotonation step (6.3 kcal/mol, Figure 3) was obtained in comparison to the attack to an internal carbon atom of the Cp* (8.3 kcal/mol, see Figure S22). In both cases, square-planar Ir(I) species appear to be key intermediates. For completion, the energy barrier for the proton abstraction by

the LiMe molecule was also calculated obtaining a TS at 11.5 kcal/mol, and thus, higher than the one belonging to the methylation pathway (see Figure S23).

Bearing in mind the contrasting reactivity of alkyl lithium reagents, in particular Li^{*n*}Bu and Li^{*t*}Bu, we wondered about the outcomes of an intermediate situation in terms of steric and electronic properties of the carbon nucleophile. Thus, we examined the reactivity of **1** with one equivalent of Li^{*i*}Pr. Not surprisingly, iso-propyl lithium finds its place between the two aforementioned cases, as the reaction between complex **1** and Li^{*i*}Pr yields a mixture of complex **2·ⁱPr** and complex **3** in a ca. 1:7 ratio, along with other minor unidentified species. Although complex **2·ⁱPr** could not be isolated in pure form, we could monitor its formation, along with that of **3**, by ³¹P{¹H} NMR spectroscopy (Figure S8) and characterize it crystallographically (Figure 2). The formation of a mixture is consistent with the close DFT-calculated barriers for the deprotonation and nucleophilic attack pathways (Figure S34).

As introduced earlier, organolithium reagents have been widely used in the chemistry of Cp*-containing complexes. Nonetheless, the weaker alkylating Grignard reagents have been even more commonly used and their implications in catalysis are broader.^{90,91} Therefore, we explored the reactivity of complex **1** toward less-polarized Grignard reagents. The addition of equimolar amounts of EtMgBr to diethyl ether solutions of the cationic chloride complex **1** resulted in an instantaneous color change from dark to orange due to the formation of a new species, complex **4** (Scheme 3). In stark

Scheme 3. Synthesis of Complex 4 from 1 and EtMgBr



contrast to the reactivity exhibited by organolithium reagents, the integrity of the Cp* ligand remains intact when milder Grignard reagents are used, which represents a remarkable divergent reactivity associated to common chemicals that are on many occasions used indistinctly. The coordinatively saturated complex **4** features a ³¹P{¹H} NMR resonance at –27.0 ppm, therefore showing a large δ shift relative to that of complex **1** (6.6 ppm) and closer to free PMe₂Ar^{Dipp} (–41.3 ppm), supporting the absence of the aforementioned Ir–C_{arene} π -interactions.^{126,129,130} A distinctive low-frequency doublet in the ¹H NMR spectrum (δ –14.9 ppm, ²J_{HP} = 30.2 Hz) indicates the presence of an iridium hydride, while a coordinated ethylene molecule gives rise to two resonances at 2.18 and 1.88 ppm. X-ray diffraction studies confirmed the proposed formulation and revealed a C–C bond length of 1.426(1) Å (Figure 4) for the ethylene ligand, as expected, longer than that of noncoordinated ethylene (1.3305 Å).¹²⁹ A reasonable proposal for the mechanism of the reaction leading to complex **4** is the substitution of the chloride ligand by an ethyl group with concomitant precipitation of LiCl, followed by β -hydride elimination. Further insight into this proposed mechanism was obtained by DFT studies (see Figure S21). These revealed a low barrier (3.1 kcal/mol) for the formation

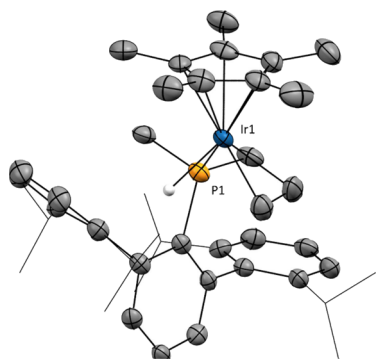
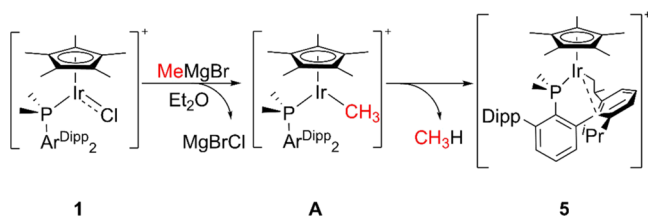


Figure 4. ORTEP diagram of the cation of complex 4. All hydrogen atoms but those of the hydride are excluded for clarity and thermal ellipsoids are set at 50% probability. Wireframe is used to represent the *iso*-propyl groups.

of an agostic interaction^{131–133} between a C–H bond of the CH₃ end of the ethyl group and the Ir atom, followed by almost barrierless β -hydride elimination ($\Delta G^\ddagger = 0.1$ kcal/mol, relative to the agostic complex). These low barriers are congruent with experimental observations, as attempts to spectroscopically detect the Ir–Et intermediate were unsuccessful even at low temperatures.

The results described above promised the obtention of the analogue of Bergman's complex reacting MeMgBr with complex 1 due to the lack of hydrogen atoms in the β position in the expected Ir–Me complex. Once more, the use of a magnesium reagent circumvented the direct nucleophilic attack to the Cp* ring, which remained unaltered, yet the observed product of this reaction was complex 5, derived from the remote and selective activation of a non-benzylic C(sp³)–H bond of one *iso*-propyl group of a lateral terphenyl ring (Scheme 4). At variance with the analogous ethyl reagent, the

Scheme 4. Synthesis of Complex 5 from 1 and MeMgBr through Proposed Intermediate Complex A



methyl fragment does not remain at the structure of 5 and instead evolves as methane, which could be observed by careful NMR monitoring (¹H NMR at 0.23 ppm). This reactivity also contrasts with the cyclometallation selectivity previously shown by this system, where the benzylic methine C–H bond is more amenable to activation.²⁸ Complex 5 was fully characterized by multinuclear NMR spectroscopy. Three distinctive ¹H multiplets, at 3.35, 0.73, and 0.22 ppm, each with relative intensity corresponding to 1 H, were assigned to the CH and the diastereotopic protons of the CH₂ of the Ir–CH₂CHCH₃ moiety, respectively. The molecular structure was authenticated by X-ray diffraction studies, which also indicate that the metal center achieves coordinative saturation by means of an η^2 -arene interaction with the flanking arene (Figure 5). Other geometrical parameters are similar to previous complexes and do not require further discussion.

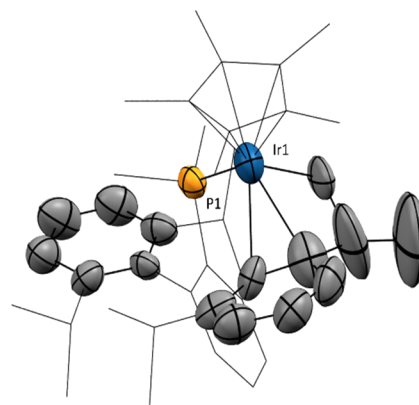


Figure 5. ORTEP diagram of the cation of complex 5. Hydrogen atoms are excluded for clarity and thermal ellipsoids are set at 50% probability. Wireframe is used to represent the Cp* ligand, the central aryl group of the phosphine, and the *iso*-propyl groups.

The mechanism of the reaction depicted in Scheme 4 was also studied through the DFT methodology. The direct attack of MeMgCl to the iridium center yielding a neutral Ir(I) complex was found to be inaccessible (Figure S28), which led us to explore an alternative mechanism. The formation of the Bergman's type Ir–CH₃ complex¹³⁴ (A in Scheme 4) commences through the magnesium-assisted chloride release ($\Delta G^\ddagger = 21.0$ kcal/mol), yielding a dicationic Ir(III) complex at 11.4 kcal/mol. This readily reacts with the generated (MeMgCl₂) moiety, alkylating the metal center with concomitant release of MgCl₂ ($\Delta G^\ddagger = 19.7$ kcal/mol) and leading to intermediate A at -17.8 kcal/mol relative to the reactants (Figure S27). For comparison, the reaction pathway of MeMgCl attacking one of the internal carbon atoms of the Cp* was also calculated. This route involves a higher-in-energy TS (28.1 kcal/mol), which explains the selectivity of the reaction between 1 and MeMgCl (Figure S27).

We evaluated three different pathways for the release of methane from intermediate A, comprising the activation of either one of the two methyl termini of an *iso*-propyl group or the methine CH. Despite benzylic C–H bonds being usually more prone to metalate, the connectivity of 5 points in a different direction, as supported by our computational studies (Figure 6). As observed experimentally, the activation of the methyl groups is kinetically favored relative to the benzylic methine, despite the latter yielding the most stable product. Notably, the activation of the distinct methyl groups follows different mechanisms: in one case, formation of an agostic interaction¹³³ leads to sigma bond metathesis (Figure S28 and Table S3). In contrast, the activation of the other methyl group, as well as for the methine CH, involved the formation of Ir(V) hydride complexes as intermediates.

When a pure solution of complex 5 was able to evolve at room temperature for 5 days, its ³¹P{¹H} NMR spectrum revealed the emergence of two new peaks at 9.4 and 8.2 ppm. After heating this solution at 80 °C for 5 h, conversion to the species resonating at 9.4 ppm, identified as the thermodynamically more stable complex 3, was complete. As the reaction between 1 and MeMgBr was originally carried out in a closed *J. Young* tube, one possible isomerization mechanism would be the reaction of 5 with CH₄ leading to obtaining the most stable compound 3. However, DFT calculations showed that the energy barrier would be too high ($\Delta G^\ddagger = 45.3$ kcal/mol) (Figure 6), and experimentally, we found that isomerization

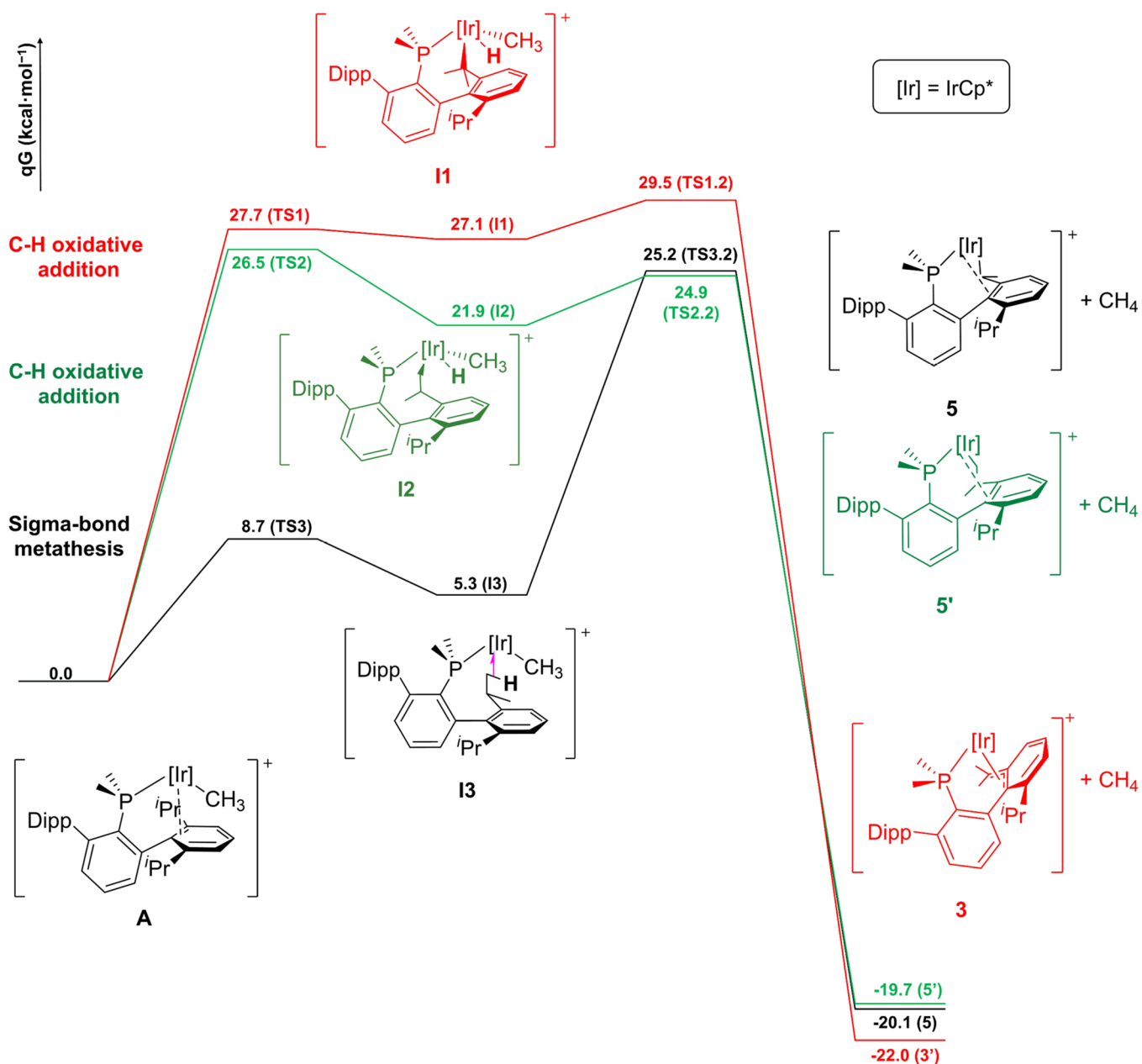


Figure 6. Three different reaction pathways for the elimination of methane from the proposed Ir(III) intermediate A. Zero energy corresponds to that of the optimized Ir(III) methylated complex. 5' is a diastereoisomer of 5.

also took place in the absence of CH_4 . Although the complex resonating at 8.2 ppm could not be isolated, its multinuclear NMR pattern perfectly fits with its assignment as a diastereoisomer of 5 (compound 5' in Figure 6) resulting from the activation of the alternative methyl group (Figures S18–S20). DFT calculations for the isomerization process are currently ongoing.

CONCLUSIONS

In conclusion, we demonstrate that the noninnocent character of the widespread Cp^* ligand in the presence of strongly polarized alkylating reagents is highly dependent on the nature of the carbon nucleophile. Thus, we identify up to three dissimilar reaction outcomes for the same Ir(III) precursor depending on the substrate employed. First, the Cp^* displays an uncommon but clear electrophilic character toward

unhindered lithium alkyls—LiMe, LiEt, Li^iBu —undergoing alkylation of one of the internal carbon atoms of the Cp^* ring through a direct nucleophilic attack to its *exo* face, leading to the formal reduction of the metal toward Ir(I) complexes. In contrast, less nucleophilic lithium reagents such as LiPh and Li^iBu act as Brønsted bases, effecting the deprotonation of a methyl group of the Cp^* ring. This event triggers a rearrangement that leads to the formation of a previously reported pseudoallylic structure. Interestingly, the use of Li^iPr , with intermediate steric and electronic properties, leads to a mixture of the aforesaid structures. In stark contrast, the use of weaker alkylating magnesium agents, which tend to exhibit similar chemistry to organolithium compounds in the context of transition metal alkylations, enables the selective alkylation of the metal center, while the Cp^* ligand remains intact.

Moreover, a series of subsequent C–H bond activation events have been disclosed for the resulting iridium complexes.

Overall, the foregoing results represent a clear illustration of both the different reactivity of some of the most common reagents in organometallic chemistry, Grignard and organolithium reagents, in many cases exchangeable, and the noninnocent behavior of the Cp* ligand, which continues to be one of the most utilized ligands in organometallic chemistry. Gaining a deep understanding of reactions where Cp* ligand is not as a mere spectator, but an active contributor, is of crucial importance for the discovery of novel transformations and the development of future catalytic processes that rely on the use of this and related ligand frameworks. Indeed, the results of this study advise taking a fresh look at the comprehensive body of work on cyclopentadienyl-based transition metal catalysts that operate in the presence of strongly polarized organometallic reagents, nucleophiles, and bases.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c04381>.

Experimental procedures; spectra; as well as XRD and computational studies (PDF)

Computational Studies coordinates (XYZ)

Accession Codes

CCDC 2214486–2214490 and 2214512 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Juan J. Moreno – Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO–CINQA), Universidad de Sevilla and Consejo Superior de Investigaciones Científicas (CSIC), 41092 Sevilla, Spain; University of Sevilla, 41092 Sevilla, Spain; orcid.org/0000-0003-1809-6170; Email: juanj.moreno@iiq.csic.es

Jesús Campos – Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO–CINQA), Universidad de Sevilla and Consejo Superior de Investigaciones Científicas (CSIC), 41092 Sevilla, Spain; University of Sevilla, 41092 Sevilla, Spain; orcid.org/0000-0002-5155-1262; Email: jesus.campos@iiq.csic.es

Authors

Alejandra Pita-Milleiro – Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO–CINQA), Universidad de Sevilla and Consejo Superior de Investigaciones Científicas (CSIC), 41092 Sevilla, Spain; University of Sevilla, 41092 Sevilla, Spain

Macarena G. Alférez – Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO–CINQA), Universidad de Sevilla and Consejo Superior de Investigaciones Científicas (CSIC), 41092 Sevilla, Spain;

University of Sevilla, 41092 Sevilla, Spain; orcid.org/0000-0001-6440-9401

María F. Espada – Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO–CINQA), Universidad de Sevilla and Consejo Superior de Investigaciones Científicas (CSIC), 41092 Sevilla, Spain; University of Sevilla, 41092 Sevilla, Spain

Celia Maya – Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO–CINQA), Universidad de Sevilla and Consejo Superior de Investigaciones Científicas (CSIC), 41092 Sevilla, Spain; University of Sevilla, 41092 Sevilla, Spain; orcid.org/0000-0002-0651-3793

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.inorgchem.2c04381>

Author Contributions

A.P.-M., J.J.M., and M.G.A. synthesized and characterized all compounds. A.P. and J.J.M. carried out computational studies. M.G.A., C.M., and M.F.E. carried out XRD studies. A.P.-M. wrote the original draft. J.C. supervised the overall project. All authors contributed to review and editing.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work has been supported by the European Research Council (ERC Starting Grant, CoopCat, 756575). We also thank Grant PID2019-110856GA-I00 funded by MCIN/AEI/10.13039/501100011033, Junta de Andalucía (P18-FR-4688) and US/JUNTA/FEDER, UE (US-1380849). J.J.M. thanks Junta de Andalucía for the postdoctoral program “Personal Investigador Doctor” (ref. DOC_00153). The authors gratefully acknowledge the financial support provided by the Consejo Superior de Investigaciones Científicas (studentship JAEINT_21_00695 granted to A.P.-M.) and the use of CESGA computational facilities.

■ REFERENCES

- (1) Kealy, T. J.; Pauson, P. L. A New Type of Organo-Iron Compound. *Nature* **1951**, *168*, 1039–1040.
- (2) Miller, A.; Tebboth, J. A.; Tremaine, F. Dicyclopentadienyliron. *J. Chem. Soc.* **1952**, 632–635.
- (3) Crabtree, R. H. NHC Ligands versus Cyclopentadienyls and Phosphines as Spectator Ligands in Organometallic Catalysis. *J. Organomet. Chem.* **2005**, 5451–5457.
- (4) Poli, R. Monocyclopentadienyl Halide Complexes of the d- and f-Block Elements. *Chem. Rev.* **1991**, *91*, 509–551.
- (5) Budzelaar, P. H. M.; Engelberts, J. J.; van Lenthe, J. H. Trends in Cyclopentadienyl–Main-Group-Metal Bonding. *Organometallics* **2003**, *22*, 1562–1576.
- (6) Evans, W. J. Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States. *Organometallics* **2016**, *35*, 3088–3100.
- (7) O’Connor, J. M.; Casey, C. P. Ring-Slippage Chemistry of Transition Metal Cyclopentadienyl and Indenyl Complexes. *Chem. Rev.* **1987**, *87*, 307–318.
- (8) Veiros, L. F. The Role of Haptotropic Shifts in Phosphine Addition to Tricarbonylmanganese Organometallic Complexes: The Indenyl Effect Revisited. *Organometallics* **2000**, *19*, 3127–3136.

- (9) Deck, P. A. Perfluoroaryl-Substituted Cyclopentadienyl Complexes of Transition Metals. *Coord. Chem. Rev.* **2006**, *250*, 1032–1055.
- (10) Ruspic, C.; Moss, J. R.; Schürmann, M.; Harder, S. Remarkable Stability of Metallocenes with Superbulky Ligands: Spontaneous Reduction of Sm^{III} to Sm^{II}. *Angew. Chem., Int. Ed.* **2008**, *47*, 2121–2126.
- (11) Meyer, G. Superbulky Ligands and Trapped Electrons: New Perspectives in Divalent Lanthanide Chemistry. *Angew. Chem., Int. Ed.* **2008**, *47*, 4962–4964.
- (12) Harder, S.; Naglav, D.; Schwerdtfeger, P.; Nowik, I.; Herber, R. H. Metal Atom Dynamics in Superbulky Metallocenes: A Comparison of (Cp^{BIG})₂Sn and (Cp^{BIG})₂Eu. *Inorg. Chem.* **2014**, *53*, 2188–2194.
- (13) van Velzen, N. J. C.; Harder, S. Deca-Arylsamarocene: An Unusually Inert Sm(II) Sandwich Complex. *Organometallics* **2018**, *37*, 2263–2271.
- (14) Giesbrecht, G. R.; Gordon, J. C.; Clark, D. L.; Scott, B. L. Synthesis, Structure and Solution Dynamics of Lithium Salts of Superbulky Cyclopentadienyl Ligands. *Dalton Trans.* **2003**, *3*, 2658–2665.
- (15) Orzechowski, L.; Piesik, D. F. J.; Ruspic, C.; Harder, S. Superbulky Metallocene Complexes of the Heavier Alkaline-Earth Metals Strontium and Barium. *Dalton Trans.* **2008**, *35*, 4742–4746.
- (16) Harder, S.; Ruspic, C. Insight in Cyclopentadienyl Metal Complexes with Superbulky Ligands: The Crystal Structure of [Cp^{BIG}K]_∞. *J. Organomet. Chem.* **2009**, *694*, 1180–1184.
- (17) Blais, M. S.; Rausch, M. D. A new synthetic route to functionally substituted (η^5 -cyclopentadienyl) dicarbonyliridium compounds. *J. Organomet. Chem.* **1995**, *502*, 1.
- (18) Conway, B. G.; Rausch, M. D. Formation and reactivity of halogen derivatives of (η^5 -cyclopentadienyl)thallium. *Organometallics* **1985**, *4*, 688.
- (19) Chen, E. Y.-X.; Kruper, W. J.; Roof, G.; Wilson, D. R. “Double Activation” of Constrained Geometry and Ansa-Metallocene Group 4 Metal Dialkyls: Synthesis, Structure, and Olefin Polymerization Study of Mono- and Dicationic Aluminate Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 745–746.
- (20) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. Preparation and Structural Characterization of an Enantiomerically Pure, C₂-Symmetric, Single-Component Ziegler-Natta α -Olefin Polymerization Catalyst. *J. Am. Chem. Soc.* **1996**, *118*, 1045–1053.
- (21) Busico, V.; Cipullo, R. Influence of Monomer Concentration on the Stereospecificity of 1-Alkene Polymerization Promoted by C₂-Symmetric Ansa-Metallocene Catalysts. *J. Am. Chem. Soc.* **1994**, *116*, 9329–9330.
- (22) Wang, B. Ansa-Metallocene Polymerization Catalysts: Effects of the Bridges on the Catalytic Activities. *Coord. Chem. Rev.* **2006**, *250*, 242–258.
- (23) Mas-Roselló, J.; Herraiz, A. G.; Audic, B.; Laverny, A.; Cramer, N. Chiral Cyclopentadienyl Ligands: Design, Syntheses, and Applications in Asymmetric Catalysis. *Angew. Chem., Int. Ed.* **2021**, *60*, 13198–13224.
- (24) Bernechea, M.; Berenguer, J. R.; Lalinde, E.; Torroba, J. Facile Single or Double C-H Bond Activation on a Cp Ligand Promoted by the Presence of Alkynylphosphine Ligands. *Organometallics* **2009**, *28*, 312–320.
- (25) Fan, L.; Wei, C.; Aigbirhio, F. I.; Turner, M. L.; Gusev, O. V.; Morozova, L. N.; Knowles, D. R. T.; Maitlis, P. M. Ring-Methyl Activation in Pentamethylcyclopentadienyl Complexes. 5. Syntheses and Structures of Tetramethylfulvene Complexes of Ruthenium(II). *Organometallics* **1996**, *15*, 98–104.
- (26) Glueck, D. S.; Bergman, R. G. Deprotonation of a Cp* Methyl Group by an Iridium Anilide: Formation, Structure, and Solution Dynamics of an H₂-Tetramethylfulvene Complex. *Organometallics* **1990**, *9*, 2862–2863.
- (27) Caldwell, H.; Pregosin, P. S. Intramolecular Allylation of a Ru-Cp* Methyl Group. *Organometallics* **2008**, *27*, 1591–1595.
- (28) Moreno, J. J.; Espada, M. F.; Campos, J.; López-Serrano, J.; Macgregor, S. A.; Carmona, E. Base-Promoted, Remote C-H Activation at a Cationic (η^5 -C₅Me₅)Ir(III) Center Involving Reversible C-C Bond Formation of Bound C₅Me₅. *J. Am. Chem. Soc.* **2019**, *141*, 2205–2210.
- (29) Takemoto, S.; Morita, H.; Karitani, K.; Fujiwara, H.; Matsuzaka, H. A Bimetallic Ru₂Pt Complex Containing a Trigonal-Planar M₃-Carbido Ligand: Formation, Structure, and Reactivity Relevant to the Fischer-Tropsch Process. *J. Am. Chem. Soc.* **2009**, *131*, 18026–18027.
- (30) Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Morley, C. P. Metal Atom Synthesis and Photochemistry of Bis(η -Pentamethylcyclopentadienyl)-Tungsten Dihydride. *Chem. Commun.* **1985**, *14*, 945–946.
- (31) Riley, P. N.; Parker, J. R.; Fanwick, P. E.; Rothwell, I. P. Formation of Tantalum “Tuck-in” Complexes by Activation of Methyl C-H Bonds in Pentamethylcyclopentadiene Groups by Carbazole Ligation. *Organometallics* **1999**, *18*, 3579–3583.
- (32) Kupfer, V.; Thewalt, U.; Tišlerová, I.; Štěpnička, P.; Gyepes, R.; Kubišta, J.; Horáček, M.; Mach, K. Syntheses and Structures of Doubly Tucked-in Titanocene Complexes with Tetramethyl(Aryl)-Cyclopentadienyl Ligands. *J. Organomet. Chem.* **2001**, *620*, 39–50.
- (33) Sun, Y.; Spence, R. E. V. H.; Piers, W. E.; Parvez, M.; Yap, G. P. A. Intramolecular Ion-Ion Interactions in Zwitterionic Metallocene Olefin Polymerization Catalysts Derived from “Tucked-In” Catalyst Precursors and the Highly Electrophilic Boranes XB(C₆F₅)₂ (X = H, C₆F₅). *J. Am. Chem. Soc.* **1997**, *119*, 5132–5143.
- (34) Mori, Y.; Ando, T.; Matsumoto, T.; Yatabe, T.; Kikkawa, M.; Yoon, K.-S.; Ogo, S. Multifunctional Catalysts for H₂O₂-Resistant Hydrogen Fuel Cells. *Angew. Chem., Int. Ed.* **2018**, *57*, 15792–15796.
- (35) Rodríguez-Bárzano, A.; Blacker, A. J.; McGowan, P. C. Synthesis and Characterisation of Tetramethylfulvene Complexes of Ruthenium. *Dalton Trans.* **2013**, *42*, 16669–16671.
- (36) Holland, P. L.; Andersen, R. A.; Bergman, R. G.; Huang, J.; Nolan, S. P. Monomeric Cyclopentadienylnickel Methoxo and Amido Complexes: Synthesis, Characterization, Reactivity, and Use for Exploring the Relationship between H-X and M-X Bond Energies. *J. Am. Chem. Soc.* **1997**, *119*, 12800–12814.
- (37) Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner, K.; Bustelo, E.; Puerta, M. C.; Valerga, P. Reactions of RuCp and RuCp* Allyl Carbene Complexes: Products Derived from Activation of Phenyl, Cyclohexyl, and Methyl C-H Bonds in PPh₃, PCy₃, and Cp* Ligands. *Organometallics* **2002**, *21*, 2912–2920.
- (38) Klet, R. C.; Kaphan, D. M.; Liu, C.; Yang, C.; Kropf, A. J.; Perras, F. A.; Pruski, M.; Hock, A. S.; Delferro, M. Evidence for Redox Mechanisms in Organometallic Chemisorption and Reactivity on Sulfated Metal Oxides. *J. Am. Chem. Soc.* **2018**, *140*, 6308–6316.
- (39) Li, S.; Wang, X.; Zhang, Z.; Zhao, Y.; Wang, X. Isolation and Structural Characterization of a Mainly Ligand-Based Dimetallic Radical. *Dalton Trans.* **2015**, *44*, 19754–19757.
- (40) Meredith, J. M.; Goldberg, K. L.; Kaminsky, W.; Heinekey, D. M. η^6 -Tetramethylfulvene and μ -H₃ : η^3 -Benzene Complexes of Iridium. *Organometallics* **2012**, *31*, 8459–8462.
- (41) Einstein, F. W. B.; Jones, R. H.; Zhang, X.; Yan, X.; Nagelkerke, R.; Sutton, D. Structures of Cationic Di-Iridium Complexes Derived from (H₅-C₅Me₅)Ir(CO)₂, Including the Dication [(η^5 -C₅Me₅)-(CO)₂Ir-Ir(CO)₂(η^5 -C₅Me₅)]²⁺ and the Bridging Methylene-tetramethylcyclopentadienyl (Tetramethylfulvene) Complex [(η^5 -C₅Me₅)-(CO)Ir-Ir(CO)₂(η^5 -CH₂C₅Me₄)]⁺. *Chem. Commun.* **1989**, *19*, 1424–1426.
- (42) Wang, W.; Davis, H. B.; Einstein, F. W. B.; Pomeroy, R. K. Stepwise C-H Cleavage of Two Methyl Groups of a Pentamethylcyclopentadienyl Ligand on a Tetraosmium Cluster. *Organometallics* **1994**, *13*, 5113–5121.
- (43) Evans, W. J.; Perotti, J. M.; Ziller, J. W. Trialkylboron/Lanthanide Metallocene Hydride Chemistry: Polydentate Bridging of (HBt₃)- to Lanthanum. *Inorg. Chem.* **2005**, *44*, 5820–5825.
- (44) Takahashi, Y.; Fujita, K.; Yamaguchi, R. Mild Oxidative Addition of C-H Bonds to a Hydrido-Bridged Dinuclear Complex of

Iridium(II) Induced by the Coordination of Heteroatomic Ligands. *Eur. J. Inorg. Chem.* **2008**, *28*, 4360–4368.

(45) Carbó, J. J.; García-López, D.; Gómez-Pantoja, M.; González-Pérez, J. I.; Martín, A.; Mena, M.; Santamaría, C. Intermetallic Cooperation in C–H Activation Involving Transient Titanium-Alkylidene Species: A Synthetic and Mechanistic Study. *Organometallics* **2017**, *36*, 3076–3083.

(46) Dyllick-Brenzinger, R.; Olsen, H. Conformational Mobility in 1,4-Bridged Cyclooctanes. Carbon-13 NMR Evidence for Facile Chirality Inversion. *J. Am. Chem. Soc.* **1981**, *103*, 704–706.

(47) Chung, C.; Tseng, W.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. Reactivity of the Tetrametallic Carbido Cluster (C₅Me₅)W₃(M₄-C)(μ -H)(CO)₁₁ with Alkyne: Isomerization of an Allyl Fragment on a Tetrametallic Cluster Framework and Ring-Methyl Activation in the C₅Me₅ Ligand. *Organometallics* **1998**, *17*, 2207–2214.

(48) Shima, T.; Hou, Z. Rare Earth/d-Transition Metal Hetero-multimetallic Polyhydride Complexes Based on Half-Sandwich Rare Earth Moieties. *Organometallics* **2009**, *28*, 2244–2252.

(49) McDade, C.; Green, J. C.; Bercaw, J. E. A Kinetic and Mechanistic Study of the Thermolysis of Bis-(Pentamethylcyclopentadienyl)Dimethyltitanium(IV). *Organometallics* **1982**, *1*, 1629–1634.

(50) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. Intramolecular Carbon-Hydrogen Bond Activation of Benzyl Ligands by Metalated Cyclopentadienyl Derivatives of Permethylhafnocene. Molecular Structure of (η^5 -C₅Me₅)(η^5 , η^1 -C₅Me₄CH₂)HfCH₂C₆H₅ and the Mechanism of Rearrangement to Its Hafnabenzocyclobutene Tautomer [Cyclic] (η^5 -C₅Me₅)₂Hf(*o*-CH₂C₆H₄). *Organometallics* **1987**, *6*, 1219–1226.

(51) Bercaw, J. E. Bis(Pentamethylcyclopentadienyl)Titanium(II) and Its Complexes with Molecular Nitrogen. *J. Am. Chem. Soc.* **1974**, *96*, 5087–5095.

(52) Cloke, F. G. N.; Day, J. P.; Green, J. C.; Morley, C. P.; Swain, A. C. Bis(η -Pentamethylcyclopentadienyl) Complexes of Molybdenum, Tungsten and Rhenium via Metal Vapour Synthesis. *Dalton Trans.* **1991**, 789–796.

(53) Alférez, M. G.; Moreno, J. J.; Hidalgo, N.; Campos, J. Reversible Hydride Migration from C₅Me₅ to RhI Revealed by a Cooperative Bimetallic Approach. *Angew. Chem., Int. Ed.* **2020**, *59*, 20863–20867.

(54) Chalkley, M. J.; del Castillo, T. J.; Matson, B. D.; Roddy, J. P.; Peters, J. C. Catalytic N₂-to-NH₃ Conversion by Fe at Lower Driving Force: A Proposed Role for Metallocene-Mediated PCET. *ACS Cent. Sci.* **2017**, *3*, 217–223.

(55) Chalkley, M. J.; del Castillo, T. J.; Matson, B. D.; Peters, J. C. Fe-Mediated Nitrogen Fixation with a Metallocene Mediator: Exploring PKa Effects and Demonstrating Electrocatalysis. *J. Am. Chem. Soc.* **2018**, *140*, 6122–6129.

(56) Chalkley, M. J.; Oyala, P. H.; Peters, J. C. Cp* Noninnocence Leads to a Remarkably Weak C–H Bond via Metallocene Protonation. *J. Am. Chem. Soc.* **2019**, *141*, 4721–4729.

(57) Quintana, L. M. A.; Johnson, S. I.; Corona, S. L.; Villatoro, W.; Goddard, W. A.; Takase, M. K.; VanderVelde, D. G.; Winkler, J. R.; Gray, H. B.; Blakemore, J. D. Proton–Hydride Tautomerism in Hydrogen Evolution Catalysis. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 6409–6414.

(58) Pitman, C. L.; Finster, O. N. L.; Miller, A. J. M. Cyclopentadiene-Mediated Hydride Transfer from Rhodium Complexes. *Chem. Commun.* **2016**, *52*, 9105–9108.

(59) Pal, S.; Kusumoto, S.; Nozaki, K. Dehydrogenation of Dimethylamine–Borane Catalyzed by Half-Sandwich Ir and Rh Complexes: Mechanism and the Role of Cp* Noninnocence. *Organometallics* **2018**, *37*, 906–914.

(60) Kefalidis, C. E.; Perrin, L.; Burns, C. J.; Berg, D. J.; Maron, L.; Andersen, R. A. Can a Pentamethylcyclopentadienyl Ligand Act as a Proton-Relay in f-Element Chemistry? Insights from a Joint Experimental/Theoretical Study. *Dalton Trans.* **2015**, *44*, 2575–2587.

(61) (a) Gusev, O.; Denisovich, L. I.; Peterleitner, M. G.; Rubezhov, A. Z.; Ustynyuk, N. A.; Maitlis, P. M. Electrochemical Generation of

19- and 20-Electron Rhodocenium Complexes and Their Properties. *J. Organomet. Chem.* **1993**, *452*, 219–222. (b) Gusev, O. V.; Peterleitner, M. G.; Ievlev, M. A.; Kal'sin, A. M.; Petrovskii, P. V.; Denisovich, L. I.; Ustynyuk, N. A. Reduction of Iridocenium Salts [Ir(η^5 -C₅Me₅)(η^5 -L)]⁺ (L = C₅H₅, C₅Me₅, C₉H₇); Ligand-to-Ligand Dimerisation Induced by Electron Transfer. *J. Organomet. Chem.* **1997**, *531*, 95–100. (c) Blaha, J. P.; Wrighton, M. S. Relative Importance of Dissociative Loss of Carbon Monoxide and Formation of Benzyl Radicals from Photoexcitation of (η^5 -C₅R₅)Fe(CO)2(η^1 -CH₂C₆H₅) and Evidence for Reaction of Carbon Monoxide with 17-Electron Radicals. *J. Am. Chem. Soc.* **1985**, *107*, 2694–2702.

(62) (a) Yao, Z.-J.; Lin, Y.-J.; Xu, B.; Jin, G.-X. Nucleophilic Addition of Carborane Anion to Ir, Rh-Coordinated Cp* Ring: C–C Bond Formation Accompanied by Reduction of Metal Center. *Dalton Trans.* **2014**, *43*, 4938–4940. (b) Moseley, K.; Kang, J. W.; Maitlis, P. M. Pentamethylcyclopentadienyl-Rhodium and -Iridium Halides. Part II. Reactions with Mono-, Di-, and Tri-Olefins. *J. Chem. Soc. A: Inorg., Phys., Theor.* **1970**, 2875–2883. (c) Razuvaev, G. A.; Maryin, V. P.; Vyshinskaya, L. I.; Ya, G.; Mal'kova, Y.; Andrianov, A.; Druzhkov, O. N. *Dokl. Akad. Nauk SSSR* **1987**, *294*, 614. [*Dokl. Chem.*, **1987**, *294* (Engl. Transl.)] (d) Kochi, T.; Nomura, Y.; Tang, Z.; Ishii, Y.; Mizobe, Y.; Hidai, M. Synthesis and Reactivities of Ir₂Ru Heterobimetallic Sulfido Clusters Derived from a Hydrogensulfido-Bridged Diiridium Complex. *Dalton Trans.* **1999**, *15*, 2575–2582.

(63) de Azevedo, C. G.; Calhorda, M. J.; de Carrondo, M. A. A. F.; Dias, A. R.; Duarte, M. T.; Galvão, A. M.; Gamelas, C. A.; Gonçalves, I. S.; da Piedade, F. M.; Romão, C. C. Nucleophilic and Electrophilic Reactions of C₅ Cyclo-Polyenes Coordinated to the [CpMoL₂]_n⁺ Fragment (n = 1,2; L = 1/2dppe, PMe₃, P(OMe)₃, CO). *J. Organomet. Chem.* **1997**, *544*, 257–276.

(64) Comte, V.; Blacque, O.; Kubicki, M. M.; Moise, C. Reactivity of the Ansa-Bridged Metallocene Dichlorides [X(η^5 -C₅H₄)₂]MCl₂ (X = SiMe₂, CMe₂; M = Mo, W) toward Metallophosphide Anions [PPh₂M'(CO)_x]⁻ (M' = Cr, Mo, W, x = 5; M' = Fe, x = 4). Formation of Heterobimetallic Complexes by Nucleophilic Substitution on a Cyclopentadienyl Ligand or on the Metal M. *Organometallics* **1997**, *16*, 5763–5769.

(65) Hughes, R. P.; Maddock, S. M.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. Reactions of Halofluorocarbons with Group 6 Complexes M(C₅H₅)₂L (M = Mo, W; L = C₂H₄, CO). Fluoroalkylation at Molybdenum and Tungsten, and at Cyclopentadienyl or Ethylene Ligands. *J. Am. Chem. Soc.* **2001**, *123*, 3279–3288.

(66) Hughes, R. P.; Maddock, S. M.; Rheingold, A. L.; Liable-Sands, L. M. Selective Fluoroalkylation of Cyclopentadienyl and Ethylene Ligands in Reactions of Perfluoroalkyl Iodides with Low-Valent Complexes of Molybdenum and Tungsten: Evidence for a Fluorocarbanion Mechanism. *J. Am. Chem. Soc.* **1997**, *119*, 5988–5989.

(67) Liu, R.; Zhou, X. Selective Transformations of Cyclopentadienyl Ligands of Transition-Metal and Rare-Earth Metal Complexes. *Chem. Commun.* **2013**, *49*, 3171–3187.

(68) Comte, V.; Blacque, O.; Kubicki, M. M.; Moise, C. Regio- and Stereochemical Aspects of the Substitution Reaction between the Molybdenocene and Tungstenocene Dichlorides (H₅-C₅H₄-R)₂MCl₂ (R = CMe₃, SiMe₃; M = Mo, W) and Metallophosphide Anions [(CO)₅M'PPh₂]⁻Li (M' = Mo, W). *Organometallics* **2001**, *20*, 5432–5439.

(69) Forschner, T. C.; Cooper, N. J. Magnesium Dihalide Promoted Addition of Grignard Reagents to the Cyclopentadienyl Rings of Tungstenocene Dichloride. *J. Am. Chem. Soc.* **1989**, *111*, 7420–7424.

(70) Basato, M.; Biffis, A.; Buscemi, G.; Callegaro, E.; Polo, M.; Tubaro, C.; Venzo, A.; Vianini, C.; Graiff, C.; Tiripicchio, A.; Benetollo, F. Reaction of Cyclopentadienyl Ruthenium Complexes with a Carborane Anion: Effect of the Spectator Ligands on the Substitution Site. *Organometallics* **2007**, *26*, 4265–4270.

(71) Basato, M.; Biffis, A.; Tubaro, C.; Graiff, C.; Tiripicchio, A. Nucleophilic Substitution on a Ru-Coordinated Cp Ring by a Carborane Anion. *Dalton Trans.* **2004**, *24*, 4092–4093.

- (72) Fischer, E. O.; Herberich, G. E. Über Die Reaktivität Des Di-Cyclopentadienyl-Kobalt(III)-Kations. *Chem. Ber.* **1961**, *94*, 1517–1523.
- (73) Fischer, E. O.; Angelici, R. J. New Cyclopentadienyl Complexes of Rhodium. *J. Am. Chem. Soc.* **1963**, *85*, 3733.
- (74) Millward, D. B.; Waymouth, R. M. Zirconocene-Mediated Cyclization of 2-Bromo α,ω -Dienes. *Organometallics* **1997**, *16*, 1153–1158.
- (75) Suzuki, N.; Kondakov, D. Y.; Takahashi, T. Zirconium-Catalyzed Highly Regioselective Carbon-Carbon Bond Formation Reactions. *J. Am. Chem. Soc.* **1993**, *115*, 8485–8486.
- (76) Dzhemilev, U. M.; D'yakov, V. A.; Khafizova, L. O.; Ibragimov, A. G. Cyclo- and Carbomagnesiation of 1,2-Dienes Catalyzed by Zr Complexes. *Tetrahedron* **2004**, *60*, 1287–1291.
- (77) Morken, J. P.; Didiuk, M. T.; Hoveyda, A. H. Zirconium-Catalyzed Asymmetric Carbomagnesiation. *J. Am. Chem. Soc.* **1993**, *115*, 6997–6998.
- (78) Negishi, E.-I.; Takahashi, T. Patterns of Stoichiometric and Catalytic Reactions of Organozirconium and Related Complexes of Synthetic Interest. *Acc. Chem. Res.* **1994**, *27*, 124–130.
- (79) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. Remarkably Pair- and Regioselective Carbon-Carbon Bond-Forming Reaction of Zirconacyclopentane Derivatives with Grignard Reagents. *J. Am. Chem. Soc.* **1991**, *113*, 6266–6268.
- (80) Farády, L.; Bencze, L.; Markó, L. Transition-Metal Alkyls and Hydrides: III. Alkyl-Olefin Exchange Reaction of Grignard Reagents Catalyzed by Nickel Chloride. *J. Organomet. Chem.* **1967**, *10*, 505–510.
- (81) Farády, L.; Markó, L. Transition Metal Alkyls and Hydrides X. Structure of Products Formed in the Reactions between Olefins and Grignard Reagents in the Presence of Nickel Chloride. *J. Organomet. Chem.* **1971**, *28*, 159–165.
- (82) Negishi, E.; Rousset, C. J.; Choueiry, D.; Maye, J. P.; Suzuki, N.; Takahashi, T. Zirconium-Catalyzed and Zirconium-Promoted Cyclization Reactions of Non-Conjugated Dienes with Alkylmagnesium Halides to Give Cycloalkylmethylmagnesium Derivatives. *Inorg. Chim. Acta* **1998**, *280*, 8–20.
- (83) Uemura, M.; Yorimitsu, H.; Oshima, K. Synthesis of Cp*CH₂PPh₂ and Its Use as a Ligand for the Nickel-Catalyzed Cross-Coupling Reaction of Alkyl Halides with Aryl Grignard Reagents. *Chem. Commun.* **2006**, *45*, 4726–4728.
- (84) Fürstner, A.; Martin, R.; Krause, H.; Seidel, G.; Goddard, R.; Lehmann, C. W. Preparation, Structure, and Reactivity of Non-stabilized Organoiron Compounds. Implications for Iron-Catalyzed Cross Coupling Reactions. *J. Am. Chem. Soc.* **2008**, *130*, 8773–8787.
- (85) Monnereau, L.; Sémeril, D.; Matt, D.; Toupet, L.; Mota, A. J. Efficient, Nickel-Catalyzed Kumada–Tamao–Corriu Cross-Coupling with a Calix[4]Arene-Diphosphine Ligand. *Adv. Synth. Catal.* **2009**, *351*, 1383–1389.
- (86) Goetz, A. E.; Garg, N. K. Regioselective Reactions of 3,4-Pyridines Enabled by the Aryne Distortion Model. *Nat. Chem.* **2013**, *5*, 54–60.
- (87) Macklin, T. K.; Snieckus, V. Directed Ortho Metalation Methodology. The N,N-Dialkyl Aryl O-Sulfamate as a New Directed Metalation Group and Cross-Coupling Partner for Grignard Reagents. *Org. Lett.* **2005**, *7*, 2519–2522.
- (88) Teo, W. J.; Wang, Z.; Xue, F.; Andy Hor, T. S.; Zhao, J. Cyclopentadienyl Nickel(II) N,C-Chelating Benzothiazolyl NHC Complexes: Synthesis, Characterization and Application in Catalytic C–C Bond Formation Reactions. *Dalton Trans.* **2016**, *45*, 7312–7319.
- (89) Tamba, S.; Fuji, K.; Meguro, H.; Okamoto, S.; Tendo, T.; Komobuchi, R.; Sugie, A.; Nishino, T.; Mori, A. Synthesis of High-Molecular-Weight Head-to-Tail-Type Poly(3-Substituted-Thiophene)s by Cross-Coupling Polycondensation with [CpNiCl(NHC)] as a Catalyst. *Chem. Lett.* **2013**, *42*, 281–283.
- (90) Yanlong, Q.; Lu, Jiaqui; Weihua, X. Studies on Olefin Isomerization Catalyzed by Transition Metals: Part IV. Isomerization of 1,5-Cyclooctadiene Catalyzed by (R-Cp)₂TiCl₂/R'MgX Systems. *J. Mol. Catal.* **1986**, *34*, 31–38.
- (91) Tao, X.; Qian, F.; Yong, L.; Qian, Y. Substituent Effect on Oligomerization of Isoprene Catalyzed by Ring-Substituted (RCp)₂TiCl₂ⁱ-C₃H₇MgCl System. *J. Mol. Catal. A: Chem.* **2000**, *156*, 121–126.
- (92) Dysard, J. M.; Tilley, T. D. Synthesis and Reactivity of H₅-Silolyl, H₅-Germolyl, and H₅-Germole Dianion Complexes of Zirconium and Hafnium. *J. Am. Chem. Soc.* **2000**, *122*, 3097–3105.
- (93) Mohapatra, S. K.; Büschel, S.; Daniliuc, C.; Jones, P. G.; Tamm, M. Selective Lithiation and Phosphate-Functionalization of [(H₇-C₇H₇)Ti(H₅-C₅H₅)] (Troticene) and Its Use for the Preparation of Early-Late Heterobimetallic Complexes. *J. Am. Chem. Soc.* **2009**, *131*, 17014–17023.
- (94) Chiu, M.; Hoyt, H. M.; Michael, F. E.; Bergman, R. G.; van Halbeek, H. Synthesis, Structural Characterization, and Quantitative Basicity Studies of Lithium Zirconimide Complexes. *Angew. Chem., Int. Ed.* **2008**, *47*, 6073–6076.
- (95) Martín, A.; Mena, M.; Morales-Varela, M. D. C.; Santamaría, C. Deprotonation of M₃-Methylidyne Groups on a Ti₃O₃ Support: A Way to Build Oxotitanocubanes Containing Alkali and Alkaline-Earth Metals. *Eur. J. Inorg. Chem.* **2004**, *9*, 1914–1921.
- (96) Hernán-Gómez, A.; Martín, A.; Mena, M.; Santamaría, C. Contact and Solvent-Separated Ion Pair Aluminium “Ate” Complexes on a Titanium Oxide Molecular Model. *Dalton Trans.* **2013**, *42*, 5076–5084.
- (97) Visser, C.; Meetsma, A.; Hessen, B. Synthesis and Trimethylsilyl C–H Activation Processes of 14-Electron Cp*Hf-(2,3-Dimethyl-1,3-Butadiene)Trimethylsilylmethyl Complexes. *Organometallics* **2002**, *21*, 1912–1918.
- (98) Kirchbauer, F. G.; Pellny, P.-M.; Sun, H.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. Synthesis and Reactions with Carbon Dioxide of Mono(σ -Alkynyl) Titanocene(III) Complexes Cp*₂Ti(C:CR) (R = Me, *t*-Bu) and the Corresponding “Ate” Complexes [Cp*₂Ti(C:CR)₂Li(THF)_n] (R = SiMe₃, *t*-Bu, Ph). *Organometallics* **2001**, *20*, 5289–5296.
- (99) García-Castro, M.; Martín, A.; Mena, M.; Yélamos, C. Coordination of [{Ti(η^5 -C₅Me₅)(μ -NH)}₃(M₃-N)] to Metal Cyclopentadienides: Cyclopentadienyl Azaheterometalloccubanes. *Organometallics* **2004**, *23*, 1496–1500.
- (100) Schock, L. E.; Marks, T. J. Organometallic Thermochemistry. Metal Hydrocarbyl, Hydride, Halide, Carbonyl, Amide, and Alkoxide Bond Enthalpy Relationships and Their Implications in Pentamethylcyclopentadienyl and Cyclopentadienyl Complexes of Zirconium and Hafnium. *J. Am. Chem. Soc.* **1988**, *110*, 7701–7715.
- (101) Golden, J. T.; Peterson, T. H.; Holland, P. L.; Bergman, R. G.; Andersen, R. A. Adduct Formation and Single and Double Deprotonation of Cp*(PMe₃)Ir(H)₂ with Main Group Metal Alkyls and Aryls: Synthesis and Structure of Three Novel Ir–Al and Ir–Mg Heterobimetallics. *J. Am. Chem. Soc.* **1998**, *120*, 223–224.
- (102) Bretschneider-Hurley, A.; Winter, C. H. Pentamethylpentaliithioruthenocene and Decalithioruthenocene. *J. Am. Chem. Soc.* **1994**, *116*, 6468–6469.
- (103) Ohashi, M.; Matsubara, K.; Iizuka, T.; Suzuki, H. Trinuclear Ruthenium Polyhydride Complexes with a Triply Bridging Ligand: [{(η^5 -C₅Me₅)Ru}₃(M₃-M)(μ -H)₃(M₃-H)] (M = Li, Mg^{Pr}, and ZnEt) and [{(η^5 -C₅Me₅)Ru}₃(M₃-M)(μ -H)₃] (M = AlEt and GaMe). *Angew. Chem., Int. Ed.* **2003**, *42*, 937–940.
- (104) Seneviratne, K. N.; Bretschneider-Hurley, A.; Winter, C. H. Synthesis, Spectroscopic Characterization, and Reactivity of Ruthenocenes Bearing Pentamagnesiated Cyclopentadienyl Ligands. *J. Am. Chem. Soc.* **1996**, *118*, 5506–5507.
- (105) Chao, S.; Robbins, J. L.; Wrighton, M. S. A New Ferrocenophane Surface Derivatizing Reagent for the Preparation of Nearly Reversible Electrodes for Horse Heart Ferri-/Ferrocytochrome c: 2,3,4,5-Tetramethyl-1-[(Dichlorosilyl)Methyl][2]Ferrocenophane. *J. Am. Chem. Soc.* **1983**, *105*, 181–188.

- (106) Sun, X.; Singh, A. K.; Yadav, R.; Jin, D.; Haimerl, M.; Scheer, M.; Roesky, P. W. Triple-Decker Complexes Incorporating Three Distinct Deck Architectures. *Chem. Commun.* **2022**, *58*, 673–676.
- (107) Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. Synthesis, Structure, and Redox Chemistry of Heteropolymetallic Carbon Complexes with MC_2M' , MC_4M' , and $MC_4M'C_4M$ Linkages. Transmetalations of Lithiocarbon Complexes ($\eta^5-C_5Me_5$)Re(NO)(PPh₃)(C≡CLi) and ($\eta^5-C_5Me_5$)Re(NO)-(PPh₃)(C≡CC≡CLi). *J. Am. Chem. Soc.* **1995**, *117*, 11922–11931.
- (108) Herring, F. G.; Legzdins, P.; Richter-Addo, G. B. Organometallic Nitrosyl Chemistry. 40. Reduction Behavior of the Complexes Cp^{*}M(NO)X₂ (Cp^{*} = Cp ($\eta^5-C_5Me_5$) or Cp^{*}($\eta^5-C_5Me_5$); M = Mo or W; X = Cl, Br, or I): Synthesis and Characterization of the [Cp^{*}Mo(NO)X₂] Radical Anions. *Organometallics* **1989**, *8*, 1485–1493.
- (109) Glassman, T. E.; Liu, A. H.; Schrock, R. R. Bimetallic Hydrazido(3- and 4-) and Nitrido Complexes of Tungsten Containing the W($\eta^5-C_5Me_5$)Me₃ Core. *Inorg. Chem.* **1991**, *30*, 4723–4732.
- (110) Crabtree, R. H. Deactivation in Homogeneous Transition Metal Catalysis: Causes, Avoidance, and Cure. *Chem. Rev.* **2015**, *115*, 127–150.
- (111) Maimone, T. J.; Milner, P. J.; Kinzel, T.; Zhang, Y.; Takase, M. K.; Buchwald, S. L. Evidence for in Situ Catalyst Modification during the Pd-Catalyzed Conversion of Aryl Triflates to Aryl Fluorides. *J. Am. Chem. Soc.* **2011**, *133*, 18106–18109.
- (112) Milner, P. J.; Maimone, T. J.; Su, M.; Chen, J.; Müller, P.; Buchwald, S. L. Investigating the Dearomative Rearrangement of Biaryl Phosphine-Ligated Pd(II) Complexes. *J. Am. Chem. Soc.* **2012**, *134*, 19922–19934.
- (113) Sather, A. C.; Lee, H. G.; de La Rosa, V. Y.; Yang, Y.; Müller, P.; Buchwald, S. L. A Fluorinated Ligand Enables Room-Temperature and Regioselective Pd-Catalyzed Fluorination of Aryl Triflates and Bromides. *J. Am. Chem. Soc.* **2015**, *137*, 13433–13438.
- (114) Thomsen, J. M.; Sheehan, S. W.; Hashmi, S. M.; Campos, J.; Hintermair, U.; Crabtree, R. H.; Brudvig, G. W. Electrochemical Activation of Cp^{*} Iridium Complexes for Electrode-Driven Water-Oxidation Catalysis. *J. Am. Chem. Soc.* **2014**, *136*, 13826–13834.
- (115) Sharninghausen, L. S.; Campos, J.; Manas, M. G.; Crabtree, R. H. Efficient Selective and Atom Economic Catalytic Conversion of Glycerol to Lactic Acid. *Nat. Commun.* **2014**, *5*, 5084.
- (116) Campos, J.; Hintermair, U.; Brewster, T. P.; Takase, M. K.; Crabtree, R. H. Catalyst Activation by Loss of Cyclopentadienyl Ligands in Hydrogen Transfer Catalysis with Cp^{*}Ir(III) Complexes. *ACS Catal.* **2014**, *4*, 973–985.
- (117) Moreno, J. J.; Espada, M. F.; Maya, C.; Campos, J.; López-Serrano, J.; Macgregor, S. A.; Carmona, E. Isomerization of a Cationic ($\eta^2-C_3Me_3$)Ir(III) Complex Involving Remote C–C and C–H Bond Formation. *Polyhedron* **2021**, *207*, No. 115363.
- (118) Arndtsen, B. A.; Bergman, R. G. Unusually Mild and Selective Hydrocarbon C–H Bond Activation with Positively Charged Iridium(III) Complexes. *Science* **1995**, *270*, 1970–1973.
- (119) Labinger, J. A.; Bercaw, J. E. Understanding and Exploiting C–H Bond Activation. *Nature* **2002**, *417*, 507–514.
- (120) Balcells, D.; Clot, E.; Eisenstein, O. C–H Bond Activation in Transition Metal Species from a Computational Perspective. *Chem. Rev.* **2010**, *110*, 749–823.
- (121) Klei, S. R.; Tilley, T. D.; Bergman, R. G. The Mechanism of Silicon–Hydrogen and Carbon–Hydrogen Bond Activation by Iridium(III): Production of a Silylene Complex and the First Direct Observation of Ir(III)/Ir(V) C–H Bond Oxidative Addition and Reductive Elimination. *J. Am. Chem. Soc.* **2000**, *122*, 1816–1817.
- (122) Carlsen, R.; Wohlgemuth, N.; Carlson, L.; Ess, D. H. Dynamical Mechanism May Avoid High-Oxidation State Ir(V)–H Intermediate and Coordination Complex in Alkane and Arene C–H Activation by Cationic Ir(III) Phosphine. *J. Am. Chem. Soc.* **2018**, *140*, 11039–11045.
- (123) Hoyano, J. K.; Graham, W. A. G. Oxidative Addition of the Carbon-Hydrogen Bonds of Neopentane and Cyclohexane to a Photochemically Generated Iridium(I) Complex. *J. Am. Chem. Soc.* **1982**, *104*, 3723–3725.
- (124) Janowicz, A. H.; Bergman, R. G. C–H Activation in Completely Saturated Hydrocarbons: Direct Observation of M + R–H → M(R)(H). *J. Am. Chem. Soc.* **1982**, *104*, 352–354.
- (125) Marinelli, G.; Rachidi, I. E. I.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. Alkyne Hydrogenation by a Dihydrogen Complex: Synthesis and Structure of an Unusual Iridium-Butyne Complex. *J. Am. Chem. Soc.* **1989**, *111*, 2346–2347.
- (126) Knies, M.; Kaiser, M.; Isaeva, A.; Müller, U.; Doert, T.; Ruck, M. Front Cover: The Intermetallic Cluster Cation (CuBi₈)³⁺. *Chem. Eur. J.* **2018**, *24*, 1.
- (127) Moreno, J. J.; Espada, M. F.; Krüger, E.; López-Serrano, J.; Campos, J.; Carmona, E. Ligand Rearrangement and Hemilability in Rhodium(I) and Iridium(I) Complexes Bearing Terphenyl Phosphines. *Eur. J. Inorg. Chem.* **2018**, *2018*, 2309–2321.
- (128) Martin, R.; Buchwald, S. L. Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling Reactions Employing Dialkylbiaryl Phosphine Ligands. *Acc. Chem. Res.* **2008**, *41*, 1461–1473.
- (129) Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. *J. Comput. Chem.* **2001**, *22*, 931–967.
- (130) Marín, M.; Moreno, J. J.; Navarro-Gilabert, C.; Álvarez, E.; Maya, C.; Peloso, R.; Nicasio, M. C.; Carmona, E. Synthesis, Structure and Nickel Carbonyl Complexes of Dialkylterphenyl Phosphines. *Chem. – Eur. J.* **2019**, *25*, 260–272.
- (131) Ortega-Moreno, L.; Fernández-Espada, M.; Moreno, J. J.; Navarro-Gilabert, C.; Campos, J.; Conejero, S.; López-Serrano, J.; Maya, C.; Peloso, R.; Carmona, E. Synthesis, Properties, and Some Rhodium, Iridium, and Platinum Complexes of a Series of Bulky m-Terphenylphosphine Ligands. *Polyhedron* **2016**, *116*, 170–181.
- (132) Craig, N. C.; Groner, P.; McKean, D. C. Equilibrium Structures for Butadiene and Ethylene: Compelling Evidence for Π -Electron Delocalization in Butadiene. *J. Phys. Chem. A* **2006**, *110*, 7461–7469.
- (133) Brookhart, M.; Green, M. L. H.; Parkin, G. Agostic Interactions in Transition Metal Compounds. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 6908–6914.
- (134) Ortega-Moreno, L.; Fernández-Espada, M.; Moreno, J. J.; Navarro-Gilabert, C.; Campos, J.; Conejero, S.; López-Serrano, J.; Maya, C.; Peloso, R.; Carmona, E. Synthesis, Properties, and Some Rhodium, Iridium, and Platinum Complexes of a Series of Bulky m-Terphenylphosphine Ligands. *Polyhedron* **2016**, *116*, 170–181.