Oxygen-Induced Dimerization of Alkyl-Manganese(II) 2,6-Bisiminopyridine Complexes. Selective Synthesis of a New Ditopic NNN-Pincer Ligand.

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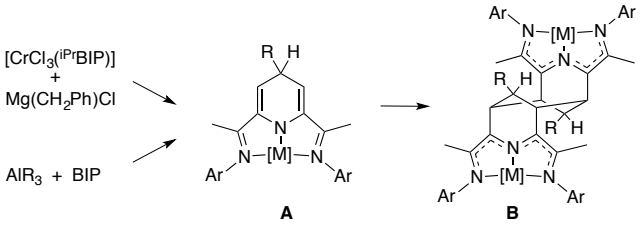
Supporting Information Placeholder

ABSTRACT: *The outcome of the reaction of manganese(II) dialkyls with 2,6-bisiminopyridine (BIP) ligands is dramatically altered by the presence of very small amounts of oxygen (< 0.5 mol %), leading to binuclear species. These arise from the dimerization of the initial product, a Mn(II) 4-alkyl-2,6-bisimino-dihydropyridinate alkyl complex. Cleavage of the binuclear Mn products with methanol affords the free dimeric bases, which can be regarded as a special type of ditopic NNN pincer ligand with an unusual tricyclic framework. The coordinative ability of the new ligands has been probed with the syntheses of Zn and Pd organometallic derivatives.*

INTRODUCTION

In the nearly two decades elapsed since the discovery of Fe and Co olefin polymerization catalysts with 2,6-bisiminopyridines (BIP),[1,2] these ligands have proved a fertile ground for new developments in Homogenous Catalysis[3] and fundamental Organometallic Chemistry.[4] Applications of BIP complexes in Catalysis have expanded from olefin polymerization[5] and oligomerization[2,6] into other domains, such as hydrogenation,[7] hydrosylilation[8] or C-C coupling reactions,[9] among others. A key factor in the catalytic ability of these complexes is the *non-innocent* character of BIP ligands *i. e.*, their ability to reversibly accept and donate electrons.[10] This feature is also responsible for the varied and complex reactivity of both BIP ligands and their complexes, particularly when they are exposed to strongly alkylating or reducing reagents, such as organolithium, organomagnesium or organoaluminum compounds. These rarely react with transition metal BIP-halide complexes to afford straightforward transmetallation products.[4,11] Most often, reactions of this type lead to reduced complexes that apparently bear the metal center in unusual low oxidation states. Analyses of the electronic structure of such compounds have shown that in most cases it is the BIP ligand, rather than the metal, which actually undergoes reduction.[12] Moreover, different types of products containing structurally modified BIP ligands have been isolated as well,[13] and similar structure alterations take place when BIP ligands react directly with organomain-group reagents.[14] One of the most common transformations of BIPs takes place when an alkyl group is transferred from a metal center (either main-group or transition) to the ligand. For example (Scheme 1), 1,4-dihydropyridinate species of type **A** are formed when the alkyl group migrates from the metal to the remote position 4 in the pyridine ring.[15,16] Further changes may also take place. An example relevant to this work is the coupling of two units of type **A** to give a dimer of type **B**. Gambarotta and co-workers[13b] isolated the first example of the latter class of compounds from the reaction of $[(^{iPr}BIP)CrCl_3]$ with $Mg(CH_2Ph)Cl$, and a few years later Budzelaar[14b,d] observed the formation of similar dimers when ligand ^{iPr}BIP reacts with aluminum trialkyls. These are rather appealing and potentially useful transformations, but their low yields or lack of selectivity render them unattractive for any practical application.

Scheme 1. Alkyl Migration followed by Dimerization of 1,4-dihydropyridinates.



Harnessing the reactivity of BIP ligands into well-behaved, selective processes might prove a productive strategy to expand the range of molecular architectures available from the basic BIP motif. However not many efforts have been oriented towards this purpose. For some years, our group has been involved in the development of the chemistry of BIP complexes into useful synthetic transformations.[15-17] We found that the reaction of mildly basic organomanganous reagents MnR_2 with BIP ligands proceeds with unusual selectivity, cleanly leading to products of type **A**.[15,16] These complexes, or the free dihydropyridines (4-R-H_2BIP) formed upon demetallation, readily undergo dehydrogenation to afford BIP's alkylated at position 4 on the pyridine ring (4-R-BIP), providing a straightforward route to ligands that would be otherwise difficult to prepare.[16] Lately, we have been interested in optimizing this methodology in order to prepare 4-R-BIP ligands in

multi-gram scale. One of such preparations afforded different type of product, arising from the hydrolysis of a Mn complex of type **B**. Repetition of the experiment showed that the formation of the dimer was fortuitous. However, this result revealed the existence of previously overlooked relationships in the chemistry of BIP-based metal alkyls. Thus, we decided to investigate the causes that led to the formation of dimeric products. Herein we report the results of our investigation and we show that these products can be used as a new type of ditopic pincer ligand in the synthesis of main group or transition metal alkyl complexes with potential uses in Catalysis.

RESULTS AND DISCUSSION

Scheme 2 presents an overview of the reactivity of BIP ligands towards Mn(II) dialkyls. As mentioned above, in an attempt to scale-up the selective alkylation of the BIP ligands on position 4 (as shown in the upper part of the Scheme), involving the allylation of ^{iPr}BIP with *in situ* generated Mn(allyl)$_2$, we obtained, after demetallation with methanol, a yellow-orange oil whose ^{1}H NMR spectrum was unexpectedly broad and complex. Crystallization by slow evaporation of a hexane solution afforded a crystalline solid more amenable of NMR analysis. The ^{1}H spectrum of this material showed that it was a mixture containing starting material (^{iPr}BIP), together with the expected products 4-allyl-^{iPr}H$_2$BIP and 4-allyl-^{iPr}BIP and a fourth, unknown component. The identity of the latter was established as the dimer (4-allyl-^{iPr}H$_2$BIP)$_2$ by X-ray diffraction analysis of a single crystal, manually selected from the mixture (Figure 1). As can be seen, its molecule contains a tricyclic core composed of a central C$_6$ carbocycle and two terminal C$_5$N heterocycles arising from the fusion of two 4-allyl-^{iPr}H$_2$BIP units through the 3 and 3' positions of their 1,4-dihydropyridine rings. This linkage removes the unsaturation from the bridgehead (3, 3') carbon atoms, yielding two independent imine-imine-enamine systems, oriented in antiparallel fashion. Overall, the molecule exhibits an inversion center, but it has no symmetry planes. Although the ^{1}H NMR spectrum of the mixture is complicated, the spectral features of the new product match the expected for such (4-allyl-^{iPr}H$_2$BIP)$_2$ dimer. Thus, the lack of symmetry planes results in the observation of two signals for the enamine and imine-bound methyl groups (δ 1.99 and 2.33 ppm), and four multiplets for the methynes of the four non-equivalent *i*-Pr groups (δ 2.92, 3.00, 3.47 and 3.54 ppm). The ^{1}H resonances of the bridgehead methynes were located at δ 3.35 and 3.96 ppm, and a broad but characteristic signal at *ca.* 7.5 ppm was identified as the enamine NH. The ESI-MS spectrum of the mixture showed an intense signal at m/z 1047.8 for the molecular ion of the protonated dimer.

Consistent with our previous reports,[15,16] when we repeated the reaction of Mn(allyl)$_2$ with ^{iPr}BIP followed by methanolytic demetallation, dihydropyridine 4-allyl-^{iPr}H$_2$BIP and aromatized 4-allyl-^{iPr}BIP were regularly formed as the main products, but we realized that trace amounts of the dimer were formed as well. We have observed that 4-allyl-^{iPr}H$_2$BIP has no tendency to dimerize on its own, even at temperatures well above the ambient (*ca.* 80 – 90 °C), hence it can be inferred that the anomalous dimerization reaction somehow involved the conversion of the manganese dihydropyridinate complex [Mn(allyl)(4-allyl-^{iPr}HBIP)], **1a**, into **3a**, as shown in Scheme 2. Therefore we tried to promote the dimerization of **1a**, either extending the reaction time (up to 24 h)

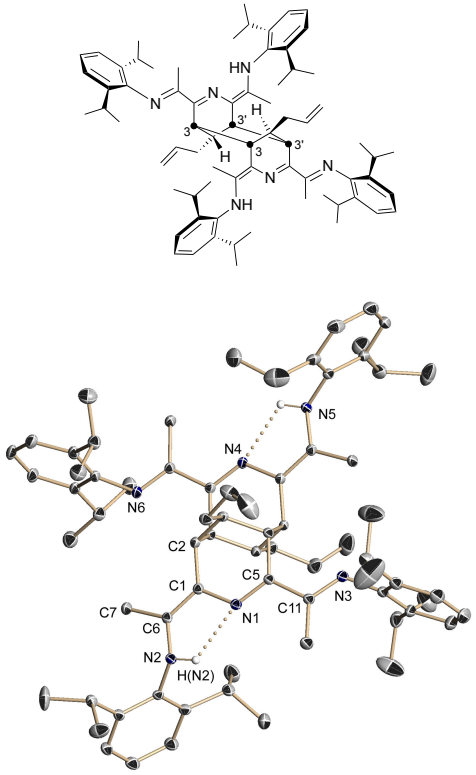
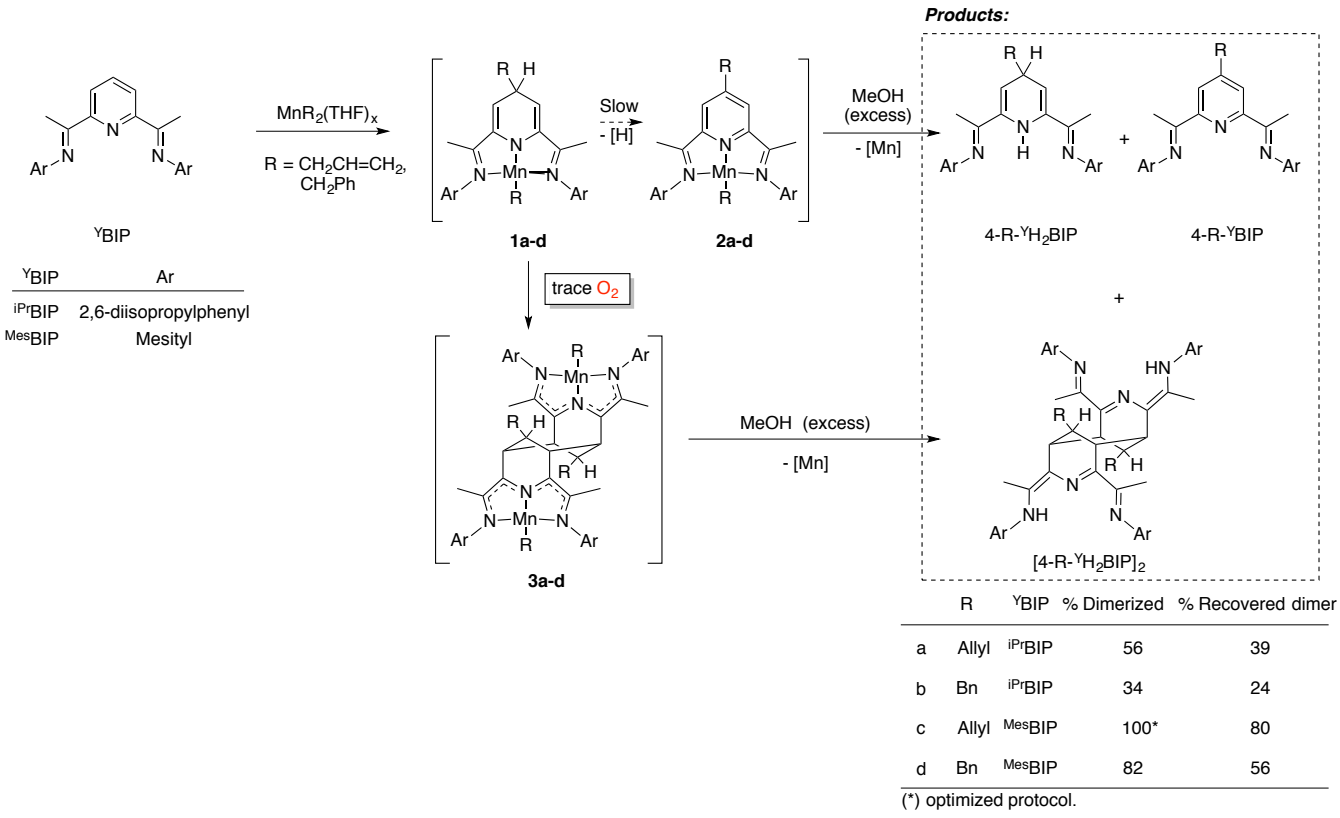


Figure 1. Molecular representation and ORTEP plot of the dimer [4-allyl-^{iPr}H$_2$BIP]$_2$. Selected bond distances (Å): N(1)-C(1): 1.460(3); N(1)-C(5): 1.304(3); N(2)-C(6): 1.387(3); N(3)-C(11): 1.274(3); C(1)-C(6): 1.350(4); C(5)-C(11):1.476(3); H(N2)···N(1): 2.16(2); N(2)···N(1): 2.672(3); Angle N(2)-H(N2)···N(1), 116(2)°.

prior to quenching with methanol, or heating the reaction mixture at 90 °C in a sealed ampoule. No substantial dimer formation was observed under such forcing conditions. Instead, the relative amount of 4-allyl-^{iPr}H$_2$BIP shifted to almost zero in favor of the aromatic 4-allyl-^{iPr}BIP, due to the thermally induced dehydrogenation of **1a** into **2a**. Since these observations imply that dimerization of **1a** is not spontaneous, it had to be induced by the action of an exogenous agent. Two likely candidates were light or air, the latter adventitiously admitted in the reaction flask. The former possibility was ruled out when we carried out the reaction under direct illumination from a regular incandescent lamp, with the same result as in the previous experiments. However, when a small amount of air (0.2 ml, 2 μmol of O$_2$) was intentionally injected in a cold mixture of 1.5 mmol of Mn(allyl)$_2$ and ^{iPr}BIP (-60 °C), the mixture developed a somewhat different, more reddish hue. After 90 min at room temperature, the usual workup with methanol was applied to produce a mixture containing the dimer (4-allyl-^{iPr}BIPH$_2$)$_2$, along with 4-allyl-^{iPr}H$_2$BIP and 4-allyl-^{iPr}BIP, as well as some starting material (^{iPr}BIP) in 3.5:3:1:1.5 relative ratio, *i. e.*, nearly 60 % dimerization. Independent experiments using dry oxygen instead of air led to essentially the same result. Therefore, a very small amount of dry O$_2$ (*ca.* 0.15 mol %) suffices to trigger the dimerization of a substantial fraction of the Mn intermediate complex **1a**. However, increasing the amount of O$_2$ does not improve the dimer formation, but rather causes extensive decomposition of the extremely sensitive organomanganese(II) intermediates. For example, when the oxygen dose was

Scheme 2. Selective Functionalization and Dimerization of BIP Systems by Organomanganese Reagents.



	R	YBIP	% Dimerized	% Recovered dimer
a	Allyl	iPrBIP	56	39
b	Bn	iPrBIP	34	24
c	Allyl	MesBIP	100*	80
d	Bn	MesBIP	82	56

(*) optimized protocol.

increased tenfold (2.0 ml of air, 1.5 mol O_2 %), the reaction mixture evolved into a brown suspension. No indication of the dimer was detected in the ^{1}H NMR of the crude product, which showed mainly unaltered starting material (^{iPr}BIP). Attempts to increase the dimer yield by breaking down the O_2 addition in several doses met with reproducibility problems and in general led to no clear improvement over our previous results. Separation of pure samples of the dimer (4-allyl-$^{iPr}H_2$BIP)$_2$ either by chromatography or crystallization proved a challenging task. Seeking more selective transformations, we examined the effect of oxygen on similar reactions of manganese dialkyls with BIP ligands, as shown in Scheme 2. In addition to ^{1}H NMR, the samples were analyzed by electrospray MS, which turned out to be the technique of choice for the detection of dimeric products in complicated reaction mixtures. The reaction of *in situ* generated dibenzylmanganese ($MnBn_2$) with ^{iPr}BIP in the presence of 0.15 mol % of O_2 closely resembles that of Mn(allyl)$_2$. The electrospray spectrum of the yellow oily residue obtained after quenching the reaction mixture with methanol showed a conspicuous signal at m/z = 1147.8, corresponding to the protonated molecular ion of the dimer (4-Bn-$^{iPr}H_2$BIP)$_2$, as well as other signals for ^{iPr}BIP, 4-Bn-$^{iPr}H_2$BIP and 4-Bn-^{iPr}BIP. The relative amount of benzyl dimer (4-Bn-$^{iPr}H_2$BIP)$_2$ was estimated to be *ca.* 34 % of the recovered products on the basis of the integrals of the ^{1}H NMR spectrum of the mixture. X-ray quality crystals were growth by slow evaporation of a hexane solution. The crystal structure of (4-Bn-$^{iPr}H_2$BIP)$_2$ (Figure S7, see SI) is very similar to that of its allyl analogue, with the same configuration and very close bond distances and angles.

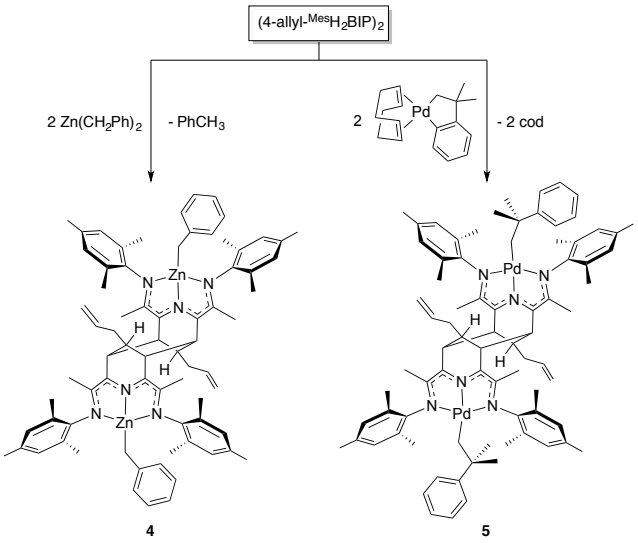
Similar reactions were carried out using ^{Mes}BIP instead of ^{iPr}BIP. The ESI-MS spectra of the crude extracts showed intense signals for the M+H$^+$ ions of the corresponding dimers, (4-allyl-$^{Mes}H_2$BIP)$_2$ (m/z = 879.6) and (4-Bn-$^{Mes}H_2$BIP)$_2$ (m/z = 979.6). Although their ^{1}H NMR spectra were even more complicated than those arising from ^{iPr}BIP, in both cases the characteristic NH signals of the dimers were observed in the low field region of the ^{1}H NMR spectra (at *ca.* 7.5 ppm) together with those of the bis(imino)-dihydropyridine and -pyridine byproducts. Integration of the dimer NH ^{1}H NMR resonances showed that the amount of monomeric byproducts accompanying (4-allyl-$^{Mes}H_2$BIP)$_2$ was particularly low. The yield of the latter was further improved when successive doses of O_2 (6 x 0.1 mL of O_2) were added to the reaction mixture at 1 h intervals. In this case, the ESI MS spectrum of the final product shows a single main signal for (4-allyl-$^{Mes}H_2$BIP)$_2$ and background impurities (Figure S1, see SI). Consistent with this, the ^{1}H NMR spectrum of the organic extract (after methanolysis) shows signals neither for the usual monomeric byproducts, nor the ^{Mes}BIP starting material. Surprisingly, this spectrum remains far more complex than expected for (4-allyl-$^{Mes}H_2$BIP)$_2$ (Figure S2). A possible explanation is that the dimer (4-allyl-$^{Mes}H_2$BIP)$_2$ occurs as a mixture of isomers arising from tautomerism of the imine-imine-enamine moieties and/or different Z/E configuration of C=N or C=C bonds. Consistent with this interpretation, an HPLC analysis of a

sample with UV detector showed a main and only one minor peaks characterized by very similar UV spectra (Figure S3).

Dihydropyridine dimers (4-R-H_2BIP)$_2$ can be regarded as conjugate acids of an unusual kind of ditopic pincer ligands, with two symmetrical, electronically delocalized anionic NNN donor sets. In order to confirm the identity of the (4-allyl-$^{Mes}H_2$BIP)$_2$ dimer, we prepared two organometallic derivatives thereof. As depicted in Scheme 3, the dimer was treated with two equivalents of a suitable Zn or Pd alkyl precursor. In each case, the enamine N-H functionality proved acidic enough to selectively cleave one of the metal-carbon bonds to afford the corresponding binuclear alkylmetal derivative [MR'(4-allyl-^{Mes}HBIP)]$_2$ in good yields. Dibenzylzinc reacts instantly at -40 °C, to afford a deep red-orange solution from which the zinc derivative **4** was isolated as a dark orange microcrystalline material. The reaction with the metallacycle [PdCH$_2$CMe$_2$-*o*-C$_6$H$_4$(cod)], a versatile starting material frequently used in our laboratory to prepare palladium alkyl complexes,[18] proceeds at the room temperature, selectively cleaving the Pd-aryl bond to afford complex **5**. The latter was isolated as very dark bluish-green crystals. The ^{1}H NMR spectra of the crude mixtures showed that both reactions are essentially quantitative, and cleanly afford single organometallic products without leaving substantial amounts of unreacted material. Complexes **4** and **5** are the first of their class to be fully characterized by elemental analyses, ^{1}H and ^{13}C NMR (Figures S4 and S5 in the SI), IR and X-ray diffraction (for **5**). Consistent with the extensive electron delocalization over the N_3C_2 fragments, their NMR spectra are highly symmetrical, each element of the molecule, such as the bridgehead methyne groups, the imine moieties or the Pd-bound alkyl groups giving rise to a single set of signals. This structural symmetry is confirmed by the crystal structure of the Pd complex (Figure 2), which is very similar to those of the related Cr[13b] and Al[14b] complexes reported in the literature (for a comparison of some metric parameters, see Table S2 in the SI). The lengths of the C-N and C-C bonds within the N_3C_2 fragments are similar and in between those of typical single and double bonds, in contrast with the free dimers (4-R-$^{iPr}H_2$BIP)$_2$, whose alternating long and short C-C/C-N bonds are as expected for conjugate N=C-C=N-C=C-N imino-imino-enamines. Significantly, all three Pd-N bond lengths are also very similar, the central Pd(1)-N(1) (2.025 Å) being only slightly shorter than the terminal Pd(1)-N(2) and Pd(1)-N(3) bonds (*ca.* 2.09 Å).

The requirement of oxygen to trigger the dimerization reaction marks a qualitative difference with the Cr- and Al-based literature precedents, which take place directly from the corresponding dihydropyridinate precursor.[13,14b] Woclzansky has described a number of spontaneous dimerization of *3d* transition with polydentate nitrogen-donor ligands that also proceed spontaneously, with no need of external oxidizers.[19] In our system, oxygen can be viewed as a "molecular switch" that "turns on" an alternative pathway to dimeric, tridentate pincer ligands. The need for an external trigger to switch the reaction outcome indicates that the intermediate Mn(II) dihydropyridinate complexes **1** are themselves unable to undergo dimerization, but become activated when they react with oxygen. Interestigly, the Woclzansy group has reported recently that C-C couplingmediated by aza-enolate (iminate) complexes also requires oxidation of the metal center.[20]

Scheme 3. Exchange reaction of (4-allyl-^{Mes}HBIP)$_2$ with Zn and Pd alkyls.



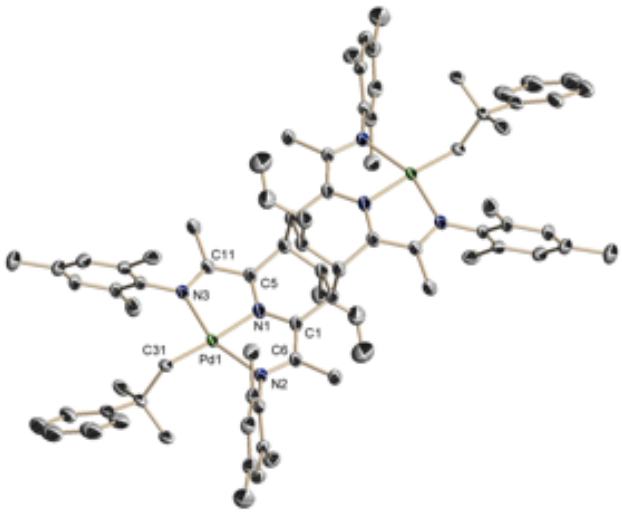
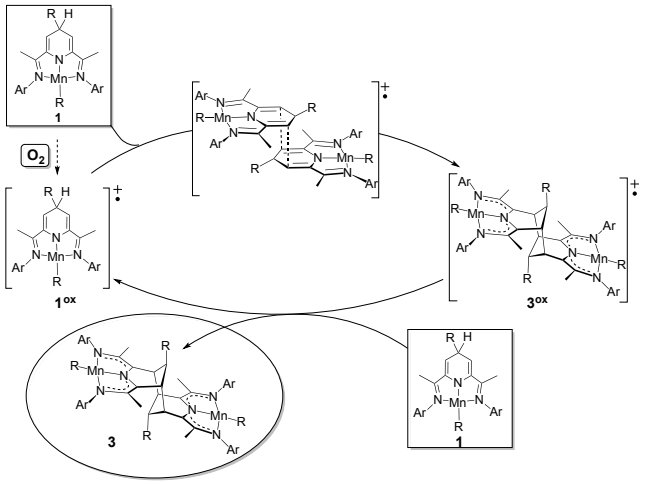


Figure 2. ORTEP view of compound **5**. Selected bond distances (Å) and angles (°): Pd(1)-N(1): 2.025(6); Pd(1)-N(2): 2.098(6); Pd(1)-N(3): 2.077(6); Pd(1)-C(31): 2.060(7); N(1)-C(1): 1.342(9); N(1)-C(5): 1.335(10); N(2)-C(6): 1.321(9); N(3)-C(11):1.311(9); C(1)-C(6): 1.444(10); C(5)-C(11): 1.441(10). N(1)-Pd(1)-C(31): 171.6(3); N(2)-Pd(1)-N(3): 157.6(2).

The effect of oxygen in our system can be rationalized on the basis of the simplified mechanism presented in Scheme 4. We believe that oxygen initiates the process when it oxidizes a small amount of the otherwise unable to dimerize Mn(II) dihydropyridinate complex **1**, giving rise to intermediate **1^{ox}**. The latter couples then with another molecule of **1** leading to the dimer in oxidized form, **3^{ox}**. The C-C coupling reaction is probably enabled by the enhanced electrophilicity of **1^{ox}**. A redox step ensues then, which entails reduction of the dimer **3^{ox}** by a second molecule of **1**, to afford neutral dimer **3** and regenerate **1^{ox}**. In principle, a condition required for this cycle to proceed is that the potential of the **3/3^{ox}**

Scheme 4. Proposed Mechanism for the O_2-induced Dimerization Process.



redox pair should be more positive than that of **1**/**1**^{ox}, but if some **3** is in equilibrium with **3**^{ox}, the overall reaction could be driven by the irreversibility of the C-C bond formation step even if the potential of the **3**/**3**^{ox} pair is slightly less positive than that of **1**/**1**^{ox}. A preliminary DFT calculation on a simplified model (see SI) suggests that the *redox* step is indeed a reversible, nearly thermoneutral process. On the other hand, any competing process that consumes **1**^{ox} or **3**^{ox} (e. g., dehydrogenative oxidation of **1** to **2**) would irretrievably stop the dimerization process. This would explain the need to add oxygen in successive doses to drive the reaction to completion, although the very small amount of O_2 required indicates that, once started, the cycle is very efficient. The more difficult dimerization of the bulkier ^{iPr}BIP derivatives suggests that steric hindrance during the coupling of the monomeric units could be the main reason limiting the cycle propagation.

There is ample precedent for the oxidation of σ-organomanganese(II) compounds by atmospheric oxygen giving rise to Mn(III) organometallic species, often unintentionally.[21] In general, stable Mn(III) compounds isolated from such reactions incorporate halide[21a-d] or oxo ligands.[21e] This could also happen in our system, since our protocol involves the presence of magnesium halogenides. Therefore, the representations of **1**^{ox} and **3**^{ox} in Scheme 4 should be considered approximations to the actual structures, where positive charges could be counterbalanced by an additional anionic ligand (e. g., chloride or bromide). In this case, the *redox* step would become an atom transfer process rather than a pure electron transfer reaction.

CONCLUSIONS

In summary, we discovered that small amounts of oxygen modify the outcome of the reaction of manganese dialkyls with BIP ligands, leading to the formation of tricyclic dimers. At least in one specific case the O_2-induced reaction can be driven to completion, cleanly switching the selectivity of the overall process from formation of 4-R-pyridnes to the corresponding tricyclic dimer. A mild demetallation procedure allows the isolation of the free tricyclic bases (4-R- H_2BIP)$_2$, which can be transferred to different metal fragments. The ready synthesis of binuclear alkyl-zinc and –palladium complexes supported by (4-allyl-^{Mes}HBIP)$_2$ confirmed that these dimeric compounds can have interesting applications as a promising class of ditopic NNN pincer ligands. We are currently optimizing procedures in order to improve the production of (4-R-H_2BIP)$_2$ dimers and exploring their potential as ligands in Coordination/Organometallic Chemistry and in Catalysis.

EXPERIMENTAL SECTION

All manipulations were carried out under oxygen-free argon atmosphere, using conventional Schlenk techniques or a nitrogen filled glove box. Solvents were rigorously dried and degassed before using.[22] NMR spectra were recorded with Bruker 400 and 500 MHz spectrometers. The ^{1}H and ^{13}C{^{1}H} resonances of the solvent were used as internal standards but the chemical shifts are reported with respect to TMS. Spectral assignations were routinely helped with monodimensional ^{13}C (gated), DEPT135 and 2D ^{1}H-^{1}H COSY, HMBC and ^{1}H-^{13}C HSQC heterocorrelation spectra. The following measurements were carried out by the Analytical Services of the Instituto de Investigaciones Químicas: High Performance Liquid Chromatography (HPLC, Waters Alliance 2695 with detector Waters 996), Electrospray Ionization Mass Spectrometry (ESI-MS, Bruker Esquire 6000) and Elemental Analysis (LECO TruSpec CHN). High Resolution Mass spectra (HR-MS) were performed by the Spectrometry Service of the Centro de Investigación, Tecnología e Innovación de la Universidad de Sevilla, CITIUS (Universidad de Sevilla, Spain)

$MnCl_2$, $ZnCl_2$, $PdCl_2$, and benzylmagnesium chloride (2.0 M in THF or 1.0 M in Et_2O) were purchased from Sigma-Aldrich. Allylmagnesium bromide (typically 1.4 M in Et_2O) was prepared according to standard literature procedures.[23] The titer for Grignard reagents was assessed by hydrolysis and titration against HCl. $Zn(CH_2Ph)_2$[24] and $[PdCH_2CMe_2\text{-}o\text{-}C_6H_4(cod)]$ [18] were prepared as described in the literature. BIP derivatives 2,6-bis(*N*-(2,6-diisopropylphenyl)acetimidoyl)pyridine (^{iPr}BIP) and 2,6-bis(*N*-(2,4,6-trimethylphenyl)acetimidoyl)pyridine (^{Mes}BIP) were prepared by condensation of 2,6-diacetylpyridine with the corresponding anilines (2,6-diisopropylaniline or mesitidine, respectively) under azeotropic water-removal conditions.[25] Oxygen was dried for several days over P_2O_5 in a Fischer-Porter pressure bottle.

General Procedure for the formation of (4-R-^{Y}H$_2$BIP)$_2$ dimers. The desired manganous alkyl reagent in THF was generated from $MnCl_2$ and Mg(R)X (R = allyl, X = Br or R = benzyl, X = Cl), as follows: The required volume of a solution containing 2.4 mmol of the Grignard reagent in Et_2O was slowly added to a stirred suspension of 150 mg (1.2 mmol) of $MnCl_2$ in THF, cooled at -70 °C. After 10 min, the cooling bath was removed. The stirring was continued at room temperature for *ca.* 30 min for R = benzyl; for R = allyl, this time was reduced to that strictly required for the $MnCl_2$ solid to disappear, *ca.* 20 min, due to the low thermal stability of the Mn(allyl)$_2$ reagent. The onset of the thermal decomposition of the Mn(allyl)$_2$ reagent is marked by the appearance of a dark ring on the walls of the vessel, near the surface of the stirred solution. At this point, the reagent must be used at once. The organomanganous reagent was transferred *via* cannula to a suspension of 1.2 mmol of the BIP ligand (^{iPr4}BIP or ^{Mes}BIP) in 20 mL of THF, vigorously stirred at -60 °C. Then, 0.2 ml of air were injected with a syringe provided with a long needle, the tip of the latter being placed close to the stirring surface. 10 min later, the mixture was allowed to warm at the room temperature, and the stirring was continued for 90 min, after which time the mixture evolved from dark purple to a somewhat redder color (the hue can vary from one experiment to other). At this point, the reaction is quenched with 5 ml of MeOH, and the solvent evaporated under vaccuum. The resulting dark brown oil was extracted in pentane (3 x 30 mL) and the extracts were filtered through a pad of Celite. The combined organic extracts were evaporated again, leaving an sticky orange oil. Attempts to separate the components either by crystallization or column chromatography were unsuccessful. However, impure crystalline samples of (4-R-^{iPr}H$_2$BIP)$_2$ (R = allyl or benzyl) can be

obtained by slow crystallization from hexane, from which single crystals suitable for X-ray diffraction were manually selected.

(4-allyl-^{iPr}H$_2$BIP)$_2$: 380 mg of a yellow oil containing (4-Allyl-^{iPr}H$_2$BIP)$_2$, 4-Allyl-^{iPr}H$_2$BIP, 4-Allyl-^{iPr}BIP and ^{iPr}BIP in an approx. relative ratio of 3.5:1:3:1.5 (56 % dimerization, 39 % absolute yield).^{1}H NMR (C_6D_6, 25 °C, 400 MHz): δ 1.11-1.21 (broad s, 48H, CH*Me*$_2$),1.99 (s, 6H, *Me*C=N), 2.09 (broad s, 4H, C*H*$_2$-CH=CH$_2$), 2.33 (s, 6H, *Me*C=N), 2.92 (m, 2H C*H*Me$_2$) 3.00 (m, 2H C*H*Me$_2$) 3.35, (broad s, 2H, 3-C*H*$_{Py}$), 3.47 (m, 2H C*H*Me$_2$) 3.54 (m, 2H, C*H*Me$_2$) 3.96 (broad s, 2H, 3-C*H*$_{Py}$), 5.04-5.11 (m, 4H, CH$_2$-CH=C*H*$_2$), 5.70-6.00 (m, 2H, C*H*$_2$-C*H*=CH$_2$), 7.00-7.17 (several signals C*H*$_{Ar}$), 7.83 (broad s, 2H, N-*H*). The signal of 4-C*H*$_{Py}$ could not be accurately assigned. ESI MS *m/z* 1047.8 ([M+H]$^+$) (Expected for $C_{72}H_{98}N_6$: 1046.8).

(4-Bn-^{iPr}H$_2$BIP)$_2$: 399 mg of a yellow oil containing (4-Bn-^{iPr}H$_2$BIP)$_2$, 4-Bn-^{iPr}H$_2$BIP, 4-Bn-^{iPr}BIP, and ^{iPr}BIP in an approx. relative ratio of 3:1:4:0.7 (34 % dimerization, 24 % absolute yield). ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz) δ 1.12-1.29 (broad s, 48H, CH*Me*$_2$),1.68 (s, 6H, *Me*C=N), 1.90 (s, 6H, *Me*C=N), 2.46 (m, 2H, C*H*Me$_2$) 2.58 (m, 2H, C*H*Me$_2$) 2.72, (broad s, 2H, 3-C*H*$_{Py}$), 3.34 (m, 2H, C*H*Me$_2$), 3.51 (m, 2H, C*H*Me$_2$), 3.76 (broad s, 2H, 3-C*H*$_{Py}$), 6.95-7.15 (several signals C*H*$_{Ar}$), 7.56 (broad s, N-*H*). Signals for 4-C*H*$_{Py}$ and PhC*H*$_2$ could not be assigned with confidence. ESI MS *m/z* 1147.8 ([M+H]$^+$) (Expected for $C_{80}H_{102}N_6$: 1146.8).

(4-Bn-^{Mes}H$_2$BIP): Yellow oil containing a mixture of (4-Bn-^{Mes}H$_2$BIP)$_2$, 4-Bn-^{Mes}H$_2$BIP, Bn-^{Mes}BIP, and ^{Mes}BIP in an approx. ratio 11:1: 1.4:6.2. (82 % dimerization, 56 % absolute yield). ESI MS m/z = 979.6 ([M+H]$^+$) (Expected for $C_{68}H_{78}N_6$, 978.6).

Optimized procedure for the synthesis of (4-allyl-^{Mes}H$_2$BIP)$_2$: A solution of the Mn(II) diallyl complex in THF was prepared from $MnCl_2$ as follows: 284 mg (2.4 mmol) of $MnCl_2$ were suspended in 15 mL of THF and the mixture was stirred for 18 h. After this time, the suspension was cooled to -70 °C and 3.5 mL of a 1.4 m solution of Mg(CH$_2$CH=CH$_2$)Br in Et_2O (4.9 mmol) were slowly added with stirring. After 10 min, the resultant mixture was allowed to warm at the room temperature and the stirring was continued for 20 min. As noted before, the stirring should not be prolonged any longer because Mn(allyl)$_2$ is thermally sensitive, the onset of its decomposition being noticed by the formation of a dark material in the walls of the flask. The resulting brown suspension was transferred *via* cannula to a vigorously stirred solution of 873 mg (2.2 mmol) of ^{Mes}BIP in 30 mL of THF, at -70 °C. The mixture was stirred for 10 min, the cooling bath was removed and the stirring was continued for 70 min at the room temperature. At this point, 0.1 mL of dry O_2 was injected through a septum. No color change was noticed. After 1 h, a second 0.1 mL dose of O_2 was injected. The procedure was repeated at 1 h intervals until a total volume of 0.6 mL of O_2 had been injected. The stirring was then continued for 22 h, during which time the mixture turned dark purple. Anhydrous methanol (5 mL) was added and the volatiles were evaporated under reduced pressure. The resultant dark orange oil was extracted in pentane (3 x 20 mL) and the extracts were filtrated through a pad of Celite. The solution was then evaporated leaving a yellow solid. Attempts to crystallize this material were unsuccessful. Yield: 552 mg, 80 %. ^{1}H NMR (C_6D_6, 25 °C, 400 MHz). Due to complexity of the spectrum (Figure S2), spectral ranges for each type of signal are given: δ 1.90-2.40 (m, 4H, C*H*$_2$-CH=CH$_2$), 2.00-2.40 (m 2H, 4-C*H*$_{Py}$), 1.80-2.50 (m, 48H, Me, mesityl and imine), 3.32, 3.40, 3.56, 3.65, 4.07, 4.28 (s, total intensity 4H, 3-C*H*$_{Py}$), 4.30-5.30 (m, 4H, CH$_2$-CH=C*H*$_2$), 5.50-6.00 (m, 2H, C*H*$_2$-C*H*=CH$_2$), 6.30-6.92 (several signals C*H*$_{Ar}$), 7.59 (broad s, N-*H*).^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 100 MHz): Selected ranges: δ 12.0 – 15.3 (*Me*-C=N), 17.0 – 21.0 (*o*-*Me*$_{N\text{-}Ar}$), 30.6 – 32.0 (*p*-Me$_{N\text{-}Ar}$), 37.2 – 37.8 (*C*H$_2$, Py-*C*H$_2$CH=CH$_2$), 37.9 – 42.0 (3-*C*H$_{Py}$), 114.0 – 138.0 (*C*H$_{Ar}$), 145.7 – 148.7 (*i*-C$_{NH\text{-}Ar}$), 151.9 – 156.1 (*i*-C$_{N\text{-}Ar}$), 162.5 – 168.4 (2-*C*$_{Py}$ y Me*C*=N). ESI MS: *m/z* 879.7 ([M+H]$^+$) (expected for $C_{60}H_{74}N_6$, 878.6); EI HR-MS: *m/z* 879.6075 ([M+H]$^+$); calcd for $C_{60}H_{75}N_6^+$, 879.6053.

Synthesis of [ZnBn)$_2$-μ-(4-allyl-^{Mes}HBIP)$_2$]$_2$ (4): 200 mg (0.22 mmol) of (4-allyl-^{Mes}HBIP)$_2$ diluted in 5 mL of toluene were drop-wise added to a solution of 130 mg (0.52 mmol) of Zn(CH$_2$Ph)$_2$ in 10 mL of toluene magnetically stirred at - 40 °C. The resultant mixture turned immediately from yellow to orange-red. After 10 min, the cooling bath was removed and the stirring was continued for 16 h at the room temperature, after which time the solvent was evaporated under reduced pressure. The oily residue was extracted in 15 mL of hexane, filtered and evaporated again to 2/3 of the initial volume. Then, the remaining orange solution was stored in absence of light at -20 °C. Four days later, a microcrystaline solid had formed. After filtration and drying under vaccuum 190 mg (73 %) of **4** were isolated. ^{1}H NMR (C_6D_6, 25 °C, 400 MHz): δ 1.64 (m, 2H, 4-C*H*$_{Py}$), 1.72 (s, 16H, *Me*-C=N, C*H*$_2$-CH=CH$_2$), 1.95 (s, 4H, C*H*$_2$ Zn-Bn), 2.07, 2.08 (s, 24H, *o*-*Me*$_{N\text{-}Ar}$), 2.26 (s, 12H, *p*-*Me*$_{N\text{-}Ar}$), 2.79 (broad s, 4H, 3-C*H*$_{Py}$), 4.91 (s, 2H, CH$_2$-CH=CH*H*), 4.94 (d, 2H, $^3J_{HH}$ = 5.0 Hz, CH$_2$-CH=C*H*H), 5.66 (m, 2H, CH$_2$-C*H*=CH$_2$), 6.17 (d, $^3J_{HH}$ = 7.1 Hz, 4H, *o*-C*H*$_{Ar}$ Zn-Bn), 6.79 (t, 2H, $^3J_{HH}$ = 6.0 Hz, *p*-C*H*$_{Ar}$ Zn-Bn), 6.86 (t, $^3J_{HH}$ = 7.9 Hz, 4H, *m*-C*H*$_{Ar}$ Zn-Bn), 6.87 (s, 4H, *m*-C*H*$_{N\text{-}Ar}$), 6.88 (s, 4H, *m*-C*H*$_{N\text{-}Ar}$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 100 MHz): δ 15.4 (*Me*-C=N), 18.4, 18.7 (*o*-*Me*$_{N\text{-}Ar}$), 19.9 (*C*H$_2$ Zn-Bn), 21.0 (*p*-*Me* N-Aryl), 30.2 (4-*C*H$_{Py}$), 37.7 (*C*H$_2$-CH=CH$_2$), 44.0 (3-CH$_{Py}$), 116.2 (CH$_2$-CH=*C*H$_2$), 120.4 (*p*-*C*H$_{Ar}$ Zn-Bn), 124.3 (2-*C*$_{Py}$), 126.9 (*m*-*C*H$_{Ar}$ Zn-Bn), 127.7 (*o*-*C*H$_{Ar}$ Zn-Bn, partially overlaped by C_6D_6), 129.4 (*m*-*C*H$_{N\text{-}Ar}$), 129.7, 131.4 (*o, o'*-*C*$_{N\text{-}Ar}$), 133.7 (*p*-*C*$_{N\text{-}Ar}$), 137.3 (CH$_2$-*C*H=CH$_2$), 145.5 (*i*-*C*$_{N\text{-}Ar}$), 148.4 (*i*-*C*$_{Ar}$ Zn-Bn), 164.2 (Me-*C*=N). Anal calcd. for $C_{74}H_{86}N_6Zn_2$: C, 74.67; H, 7.28; N, 7.06. Found: C, 74.77; H, 7.92; N, 7.33.

Synthesis of [PdCH$_2$CMe$_2$Ph)$_2$-μ-(4-allyl-^{Mes}HBIP)$_2$] (5): Solid samples of [PdCH$_2$CMe$_2$-*o*-C$_6$H$_4$(cod)] (279 mg, 0.74 mmol) and (4-allyl-^{Mes}HBIP)$_2$ (320 mg, 0.36 mmol) were mixed, and dissolved in 30 mL of Et_2O. The resultant solution was magnetically stirred during 4 h at 23 °C. A ^{1}H NMR spectrum prepared from an aliquot sample of the solution showed that the reaction was complete. The solution was evaporated to dryness leaving a green oily solid. This was extracted in hexane (10 mL), filtrated and the resultant solution was concentrated to 2/3 of its original volume. Compound **5** crystallized as dark bluish-green blocks when this solution was allowed to rest at -20 °C for 48 h. After filtration, the crystals were washed three times with a mixture diethyl-ether/hexane (1:10) at -25 °C and dried under vaccuum. Yield, 280 mg (57%). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz) δ 0.32 (s, 4H, C*H*$_2$ Pd-R), 0.66 (s, 12H, C*Me*$_2$ Pd-R), 1.55 (s, 12H, *Me*-C=N), 1.98-2.01 (broad s, 6H, 4-CH$_{Py}$, C*H*$_2$-CH=CH$_2$), 2.28, 2.29 (s, 24H, *o*-*Me*$_{N\text{-}Ar}$), 2.33 (s, 12H, *p*-*Me*$_{N\text{-}Ar}$), 2.36 (s, 4H, 3-C*H*$_{Py}$), 5.10 (dd, 2H, $^3J_{HH}$ = 10.1, $^2J_{HH}$ = 2.1 Hz, CH$_2$-CH=CH*H*), 5.21 (dd, 2H, $^3J_{HH}$ = 16.8, $^2J_{HH}$ = 2.1 Hz, CH$_2$-CH=C*H*H), 5.95 (m, 2H, CH$_2$-C*H*=CH$_2$), 6.39 (d, 4H, $^3J_{HH}$ = 6.9 Hz, *o*-C*H*$_{Ar}$ Pd-R), 6.83-6.91 (m, 14H, C*H*$_{N\text{-}Ar}$, C*H*$_{Ar}$ Pd-R).^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz) δ 15.9 (*Me*-C=N), 18.7, 18.9 (*o*-*Me*$_{N\text{-}Ar}$), 21.0 (*p*-*Me*$_{N\text{-}Ar}$), 29.9 (4-*C*H$_{Py}$), 30.2 (C*Me*$_2$ Pd-R), 37.6 (*C*H$_2$-CH=CH$_2$), 39.4 (*C*H$_2$ Pd-R), 41.6 (*C*Me$_2$ Pd-R), 42.9 (3-*C*H$_{Py}$), 116.3 (CH$_2$-CH=*C*H$_2$), 124.0 (*p*-*C*H$_{Ar}$ Pd-R), 125.2 (*m*-*C*H$_{Ar}$ Pd-R and 2-*C*$_{Py}$), 127.5 (*o*-*C*H$_{Ar}$ Pd-R), 128.9 (*m*-*C*H$_{N\text{-}Ar}$), 131.9, 132.0 (*o*-*C*$_{N\text{-}Ar}$), 134.4 (*p*-*C*$_{N\text{-}Ar}$), 137.9 (CH$_2$-*C*H=CH$_2$), 144.3 (*i*-*C*$_{N\text{-}Ar}$), 155.0 (*i*-*C*$_{Ar}$ Pd-R), 175.1 (Me-*C*=N). Anal. Calcd for $C_{80}H_{98}N_6Pd_2$: C, 70.83; H, 7.28; N, 6.28. Found: C, 70.91; H, 7.47; N, 5.92.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Additional figures showing NMR and mass spectra and HPLC plots.

Crystallographic details and ORTEP plots for [4-allyl-^{iPr}H$_2$BIP]$_2$, (4-allyl-^{Mes}H$_2$BIP)$_2$ and **5** with full numbering schemes.

Crystallographic data for [4-allyl-^{iPr}H$_2$BIP]$_2$ (4-allyl-^{Mes}H$_2$BIP)$_2$ and **5** (CIF)

DFT calculation details.

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Notes

The authors declare no competing financial interest.

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FOR TABLE OF CONTENTS

Oxygen-Induced Dimerization of Alkyl-Manganese(II) 2,6-Bisiminopyridine Complexes. Selective Synthesis of a New Ditopic NNN-Pincer Ligand.

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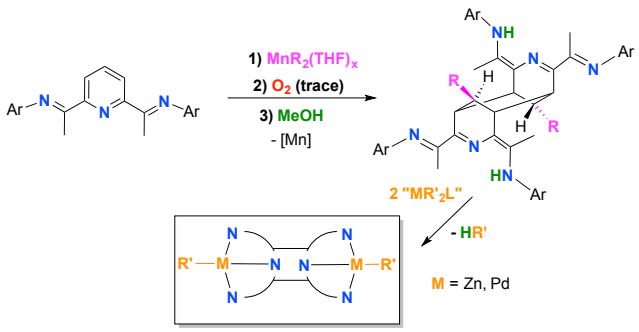

An oxygen trace suffices to drive the reaction of 2,6-bisiminopyridines with organomanganous reagents into self-coupling, affording tricyclic dimers that can be used as ditopic NNN pincer ligands.