

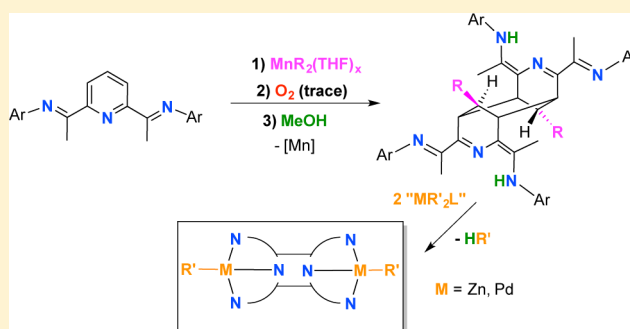
Oxygen-Induced Dimerization of Alkyl-Manganese(II) 2,6-Bisiminopyridine Complexes: Selective Synthesis of a New Ditopic NNN-Pincer Ligand

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Supporting Information

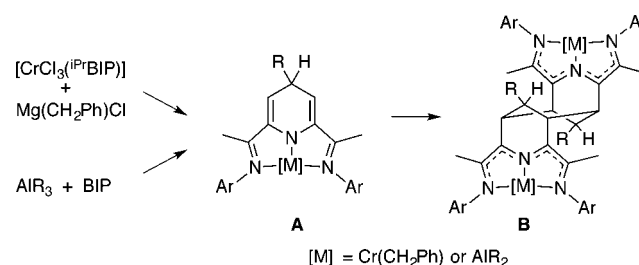
ABSTRACT: The outcome of the reaction of manganese(II) dialkyls with 2,6-bisiminopyridine (BIP) ligands is dramatically altered by the presence of very small amounts of oxygen (<0.5 mol %), leading to binuclear species. These arise from the dimerization of the initial product, a Mn(II) 4-alkyl-2,6-bisimino-dihydropyridinate 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 catalysis³ and fundamental organometallic chemistry.⁴ Applications of BIP complexes in catalysis have expanded from olefin polymerization⁵ and oligomerization^{2,6} into other domains, such as hydrogenation,⁷ hydrosilylation,⁸ or C–C coupling reactions,⁹ among others. A key factor in the catalytic ability of these complexes is the noninnocent 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 transmetalation 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 organoaluminum 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

Scheme 1. Alkyl Migration Followed by Dimerization of 1,4-Dihydropyridinates

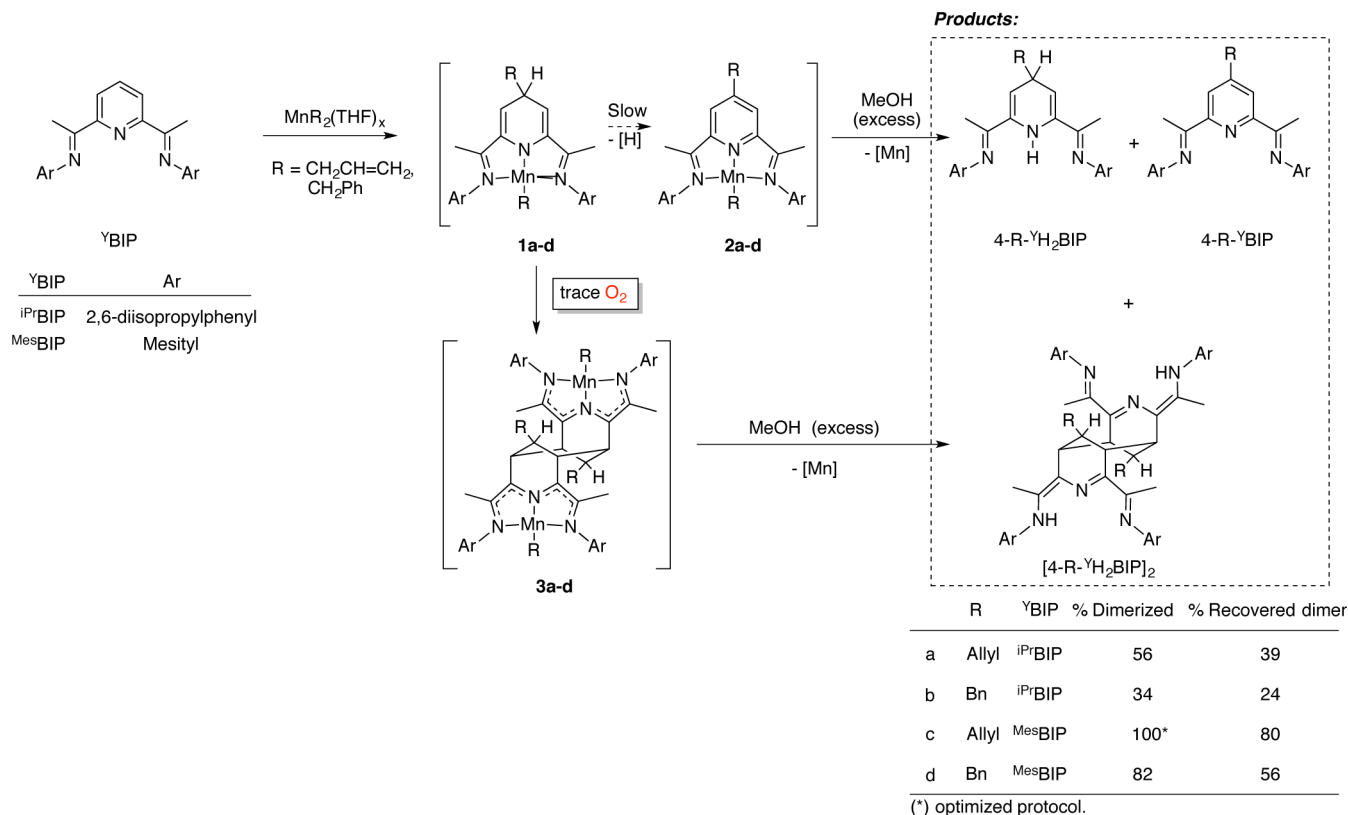


group migrates from the metal to the remote position 4 in the pyridine ring.^{15,16} Further changes may also take place. An example relevant to this work is the coupling of two units of type A to give a dimer of type B. Gambarotta and co-workers^{13b} isolated the first example of the latter class of compounds from the reaction of [(ⁱ-PrBIP)CrCl₃] with Mg(CH₂Ph)Cl, and a few years later Budzelaar^{14b,d} observed the formation of similar dimers when ligand ⁱ-PrBIP 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.

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 toward this purpose. For some years, our group has been

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



involved in the development of the chemistry of BIP complexes into useful synthetic transformations.^{15–17} We found that the reaction of mildly basic organomanganese 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 ($4\text{-R-H}_2\text{BIP}$) formed upon demetalation, 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 multigram scale. One such preparation afforded a 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 toward 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 2) involving the allylation of $i\text{-PrBIP}$ with *in situ* generated Mn(allyl)_2 , we obtained after demetalation with methanol a yellow-orange oil whose ^1H 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 ^1H spectrum of this material showed that it was a mixture containing starting material ($i\text{-PrBIP}$), together with the expected products $4\text{-allyl-}i\text{-PrH}_2\text{BIP}$ and $4\text{-allyl-}i\text{-PrBIP}$ and a fourth, unknown component. The identity of the latter was established as the dimer ($4\text{-allyl-}i\text{-PrH}_2\text{BIP}$)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 C₆ carbocycle and two terminal C₅N heterocycles arising from the fusion of two $4\text{-allyl-}i\text{-PrH}_2\text{BIP}$ 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 ^1H NMR spectrum of the mixture is complicated, the spectral features of the new product match the expected for such ($4\text{-allyl-}i\text{-PrH}_2\text{BIP}$)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 nonequivalent $i\text{-Pr}$ groups (δ 2.92, 3.00, 3.47, and 3.54 ppm). The ^1H 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 $i\text{-PrBIP}$ followed by methanolytic demetalation, dihydropyridine $4\text{-allyl-}i\text{-PrH}_2\text{BIP}$ and aromatized $4\text{-allyl-}i\text{-PrBIP}$ were regularly formed as the main products, but we realized that trace amounts of the dimer were formed as

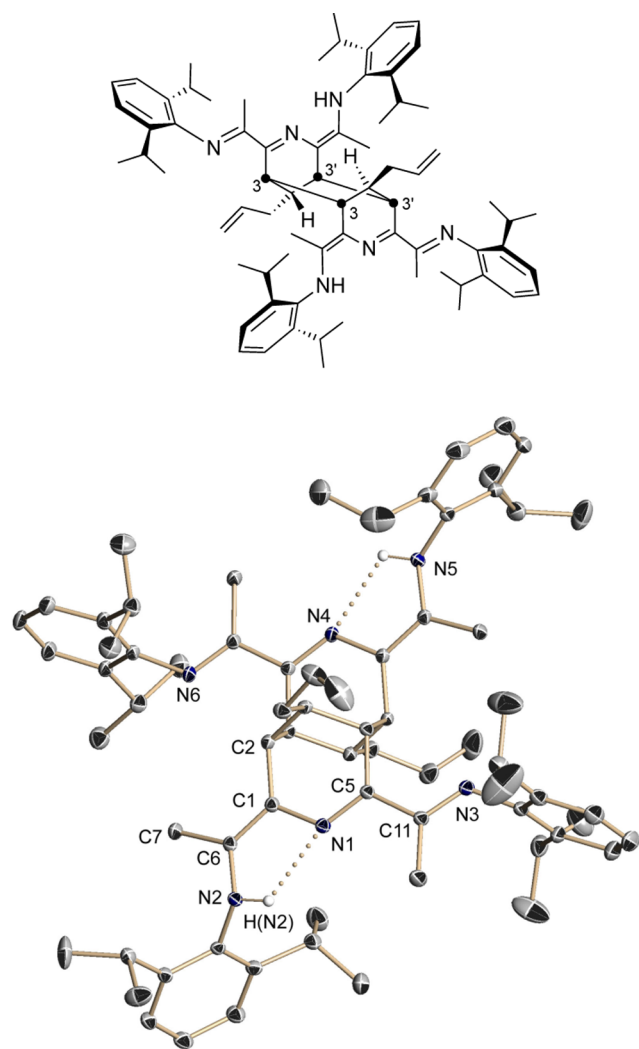


Figure 1. Molecular representation and ORTEP plot of the dimer $[4\text{-allyl-}i\text{-Pr}_2\text{H}_2\text{BIP}]_2$. Selected bond distances (Å): N(1)–C(1): 1.460(3); N(1)–C(5): 1.304(3); N(2)–C(6): 1.387(3); N(3)–C(11): 1.274(3); C(1)–C(6): 1.350(4); C(5)–C(11): 1.476(3); H(N2)⋯N(1): 2.16(2); N(2)⋯N(1):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

well. We have observed that 4-allyl- i -PrH₂BIP 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- i -PrHBIP)], **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) prior to quenching with methanol or heating the reaction mixture at 90 °C in a sealed ampule. No substantial dimer formation was observed under such forcing conditions. Instead, the relative amount of 4-allyl- i -PrH₂BIP shifted to almost zero in favor of the aromatic 4-allyl- i -PrBIP, 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,

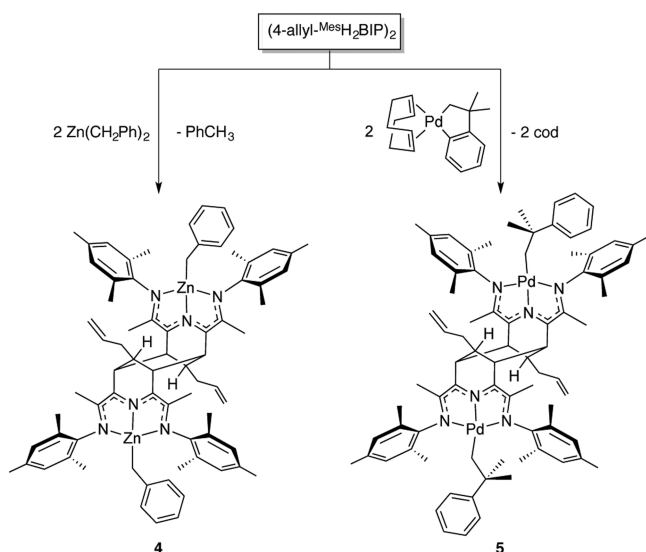
when a small amount of air (0.2 mL, 2 μ mol of O₂) was intentionally injected in a cold mixture of 1.5 mmol of Mn(allyl)₂ and ⁱ-PrBIP (−60 °C), the mixture developed a somewhat different, more reddish hue. After 90 min at room temperature, the usual workup with methanol was applied to produce a mixture containing the dimer (4-allyl-ⁱ-PrBIPH₂)₂, along with 4-allyl-ⁱ-PrH₂BIP and 4-allyl-ⁱ-PrBIP, as well as some starting material (ⁱ-PrBIP) 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 O₂ (ca. 0.15 mol %) suffices to trigger the dimerization of a substantial fraction of Mn intermediate complex 1a. However, increasing the amount of O₂ 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 increased 10-fold (2.0 mL of air, 1.5 mol O₂ %), the reaction mixture evolved into a brown suspension. No indication of the dimer was detected in the ¹H NMR of the crude product, which showed mainly unaltered starting material (ⁱ-PrBIP). Attempts to increase the dimer yield by breaking down the O₂ 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-ⁱ-PrH₂BIP)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 ¹H 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 (MnBn₂) with ⁱ-PrBIP in the presence of 0.15 mol % O₂ 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-ⁱ-PrH₂BIP)₂, as well as other signals for ⁱ-PrBIP, 4-Bn-ⁱ-PrH₂BIP, and 4-Bn-ⁱ-PrBIP. The relative amount of benzyl dimer (4-Bn-ⁱ-PrH₂BIP)₂ was estimated to be ca. 34% of the recovered products on the basis of the integrals of the ¹H NMR spectrum of the mixture. X-ray quality crystals were growth by slow evaporation of a hexane solution. The crystal structure of (4-Bn-ⁱ-PrH₂BIP)₂ (Figure S7) 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 ^{*i*-Pr}BIP. The ESI-MS spectra of the crude extracts showed intense signals for the M + H⁺ ions of the corresponding dimers, (4-allyl-^{Mes}H₂BIP)₂ (*m/z* = 879.6) and (4-Bn-^{Mes}H₂BIP)₂ (*m/z* = 979.6). Although their ¹H NMR spectra were even more complicated than those arising from ^{*i*-Pr}BIP, in both cases the characteristic NH signals of the dimers were observed in the low field region of the ¹H NMR spectra (at ca. 7.5 ppm) together with those of the bis(imino)-dihydropyridine and -pyridine byproducts. Integration of the dimer NH ¹H NMR resonances showed that the amount of monomeric byproducts accompanying (4-allyl-^{Mes}H₂BIP)₂ was particularly low. The yield of the latter was further improved when successive doses of O₂ (6 × 0.1 mL of O₂) 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}H₂BIP)₂ and background impurities (Figure S1).

Consistent with this, the ^1H NMR spectrum of the organic extract (after methanolysis) shows signals for neither the usual monomeric byproducts nor the $^{\text{Mes}}$ BIP starting material. Surprisingly, this spectrum remains far more complex than expected for $(4\text{-allyl-}^{\text{Mes}}\text{H}_2\text{BIP})_2$ (Figure S2). A possible explanation is that the dimer $(4\text{-allyl-}^{\text{Mes}}\text{H}_2\text{BIP})_2$ occurs as a mixture of isomers arising from tautomerism of the imine–imine–enamine moieties and/or different *Z/E* configuration of $\text{C}=\text{N}$ or $\text{C}=\text{C}$ bonds. Consistent with this interpretation, an HPLC analysis of a sample with UV detector showed one main peak and one minor peak characterized by very similar UV spectra (Figure S3).

Dihydropyridine dimers $(4\text{-R-H}_2\text{BIP})_2$ 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 $(4\text{-allyl-}^{\text{Mes}}\text{H}_2\text{BIP})_2$ dimer, we prepared two organometallic derivatives thereof. As depicted in Scheme 3, the dimer was

Scheme 3. Exchange Reaction of $(4\text{-Allyl-}^{\text{Mes}}\text{HBIP})_2$ with Zn and Pd Alkyls



treated with 2 equiv 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 $[\text{MR}'(4\text{-allyl-}^{\text{Mes}}\text{HBIP})_2]$ in good yields. Dibenzylzinc reacts instantly at $-40\text{ }^\circ\text{C}$ to afford a deep red-orange solution from which zinc derivative **4** was isolated as a dark orange microcrystalline material. The reaction with the metallacycle $[\text{PdCH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4(\text{cod})]$, 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 ^1H 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, ^1H and ^{13}C NMR (Figures S4 and S5), 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, with 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

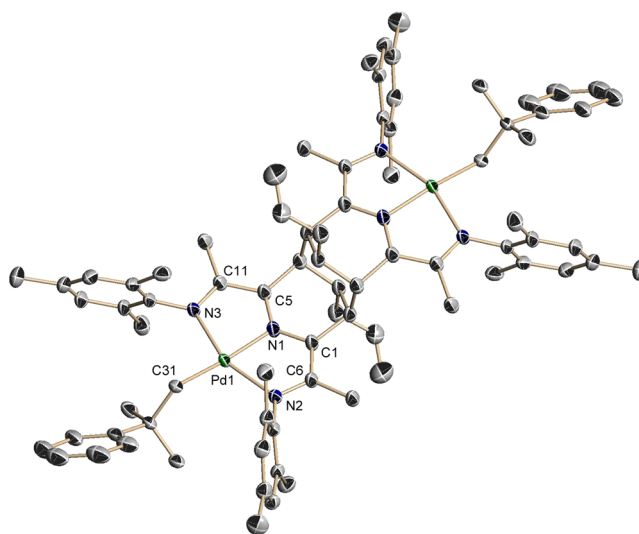
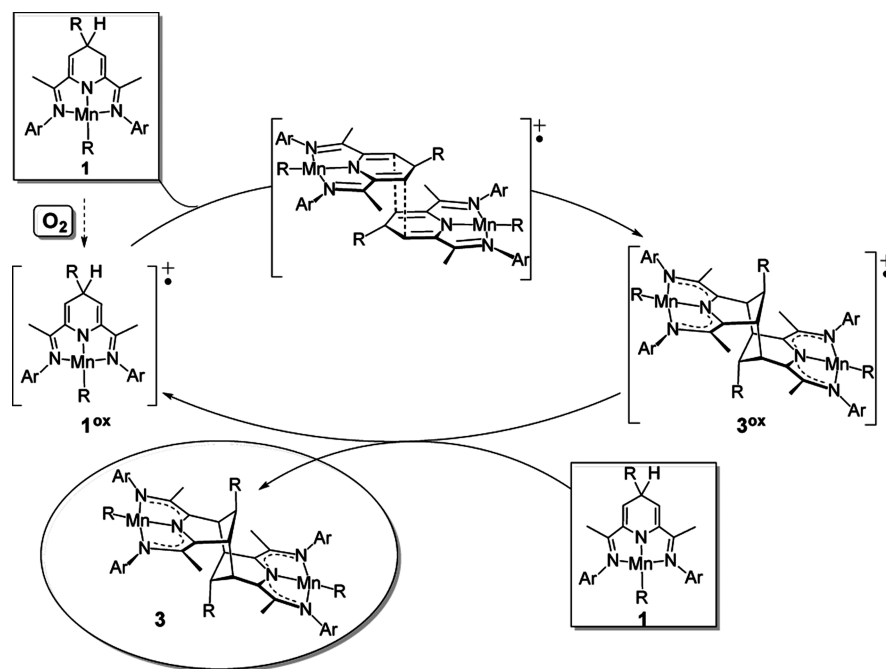


Figure 2. ORTEP view of compound **5**. Selected bond distances (Å) and angles (deg): Pd(1)–N(1): 2.025(6); Pd(1)–N(2): 2.098(6); Pd(1)–N(3): 2.077(6); Pd(1)–C(31): 2.060(7); N(1)–C(1): 1.342(9); N(1)–C(5): 1.335(10); N(2)–C(6): 1.321(9); N(3)–C(11): 1.311(9); C(1)–C(6): 1.444(10); C(5)–C(11): 1.441(10).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

similar to those of the related $\text{Cr}^{13\text{b}}$ and $\text{Al}^{14\text{b}}$ complexes reported in the literature (for a comparison of some metric parameters, see Table S2). 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 those of free dimers $(4\text{-R-}^i\text{PrH}_2\text{BIP})_2$, whose alternating long and short C-C/C-N bonds are as expected for conjugate $\text{N}=\text{C}-\text{C}=\text{N}-\text{C}=\text{C}-\text{N}$ 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 dihydropyridine precursor.^{13,14b} Wocłzansky has described a number of spontaneous dimerizations of 3d transition metal complexes with polydentate nitrogen-donor ligands that also proceed 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 intermediate Mn(II) dihydropyridinate complexes **1** are themselves unable to undergo dimerization but become activated when they react with oxygen. Interestingly, the Wocłzansky group has reported recently that C-C coupling mediated by aza-enolate (iminate) complexes also requires oxidation of the metal center.²⁰

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 Mn(II) dihydropyridinate complex **1** that is otherwise unable to dimerize, giving rise to intermediate **1^{ox}**.

Scheme 4. Proposed Mechanism for the O₂-Induced Dimerization Process

The latter then couples 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}** redox pair should be more positive than that of **1/1^{ox}**, but if some **3** is in equilibrium with **3^{ox}**, then 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 [Supporting Information](#)) suggests that the redox step is indeed a reversible, nearly thermoneutral process. However, 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 O₂ required indicates that once started the cycle is very efficient. The more difficult dimerization of the bulkier *i*-PrBIP 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

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 O₂-induced reaction can be driven to completion, cleanly switching the selectivity of the overall process from formation of 4-R-pyridines to the corresponding tricyclic dimer. A mild demetalation procedure allows the isolation of the free tricyclic bases (4-R-H₂BIP)₂, which can be transferred to different metal fragments. The ready synthesis of binuclear alkyl–zinc and –palladium complexes supported by (4-allyl-MesHBIP)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-H₂BIP)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 glovebox. Solvents were rigorously dried and degassed before using.²² NMR spectra were recorded with Bruker 400 and 500 MHz spectrometers. The ¹H and ¹³C{¹H} resonances of the solvent were used as internal standards, but the chemical shifts are reported with respect to TMS. Spectral assignments were routinely helped with monodimensional ¹³C (gated), DEPT135 and 2D ¹H–¹H COSY, and HMBC and ¹H–¹³C 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).

MnCl₂, ZnCl₂, PdCl₂, and benzylmagnesium chloride (2.0 M in THF or 1.0 M in Et₂O) were purchased from Sigma-Aldrich. Allylmagnesium bromide (typically 1.4 M in Et₂O) was prepared

according to standard literature procedures.²³ The titer for Grignard reagents was assessed by hydrolysis and titration against HCl.

$\text{Zn}(\text{CH}_2\text{Ph})_2$ ²⁴ and $[\text{PdCH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4(\text{cod})]$ ¹⁸ were prepared as described in the literature. BIP derivatives 2,6-bis(*N*-(2,6-diisopropylphenyl)acetimidoyl)pyridine (*i*-Pr²BIP) 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.^{1a} Oxygen was dried for several days over P_2O_5 in a Fischer–Porter pressure bottle.

General Procedure for the Formation of (4-*R*-^YH₂BIP)₂ Dimers. The desired manganous alkyl reagent in THF was generated from MnCl_2 and $\text{Mg}(\text{R})\text{X}$ (*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 $\text{Mn}(\text{allyl})_2$ reagent. The onset of the thermal decomposition of the $\text{Mn}(\text{allyl})_2$ 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 (*i*-Pr²BIP or ^{Mes}BIP) in 20 mL of THF, vigorously stirred at -60°C . Then, 0.2 mL of air was injected with a syringe provided with a long needle, the tip of the latter being placed close to the stirring surface. Then, 10 min later, the mixture was allowed to warm at 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 vacuum. The resulting dark brown oil was extracted in pentane (3×30 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*-^YH₂BIP)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-ⁱ-Pr²H₂BIP)₂. A yellow oil (380 mg) containing (4-allyl-ⁱ-Pr²H₂BIP)₂, 4-allyl-ⁱ-Pr²H₂BIP, 4-allyl-ⁱ-PrBIP, and ⁱ-PrBIP in an approximately relative ratio of 3.5:1.3:1.5 (56% dimerization, 39% absolute yield). ¹H NMR (C_6D_6 , 25°C , 400 MHz) δ 1.11–1.21 (broad s, 48H, CHMe_2), 1.99 (s, 6H, $\text{MeC}\equiv\text{N}$), 2.09 (broad s, 4H, $\text{CH}_2\text{-CH}=\text{CH}_2$), 2.33 (s, 6H, $\text{MeC}\equiv\text{N}$), 2.92 (m, 2H CHMe_2), 3.00 (m, 2H CHMe_2), 3.35 (broad s, 2H, 3- CH_{Py}), 3.47 (m, 2H CHMe_2), 3.54 (m, 2H, CHMe_2), 3.96 (broad s, 2H, 3- CH_{Py}), 5.04–5.11 (m, 4H, $\text{CH}_2\text{-CH}=\text{CH}_2$), 5.70–6.00 (m, 2H, $\text{CH}_2\text{-CH}=\text{CH}_2$), 7.00–7.17 (several signals CH_{Ar}), 7.83 (broad s, 2H, *N*-H). The signal of 4- CH_{Py} could not be accurately assigned. ESI MS m/z 1047.8 ($[\text{M} + \text{H}]^+$) (expected for $\text{C}_{77}\text{H}_{98}\text{N}_6$: 1046.8).

(4-Bn-ⁱ-Pr²H₂BIP)₂. A yellow oil (399 mg) containing (4-Bn-ⁱ-Pr²H₂BIP)₂, 4-Bn-ⁱ-Pr²H₂BIP, 4-Bn-ⁱ-PrBIP, and ⁱ-PrBIP in an approximately relative ratio of 3:1.4:0.7 (34% dimerization, 24% absolute yield). ¹H NMR (CDCl_3 , 25°C , 400 MHz) δ 1.12–1.29 (broad s, 48H, CHMe_2), 1.68 (s, 6H, $\text{MeC}\equiv\text{N}$), 1.90 (s, 6H, $\text{MeC}\equiv\text{N}$), 2.46 (m, 2H, CHMe_2), 2.58 (m, 2H, CHMe_2), 2.72 (broad s, 2H, 3- CH_{Py}), 3.34 (m, 2H, CHMe_2), 3.51 (m, 2H, CHMe_2), 3.76 (broad s, 2H, 3- CH_{Py}), 6.95–7.15 (several signals CH_{Ar}), 7.56 (broad s, *N*-H). Signals for 4- CH_{Py} and PhCH_2 could not be assigned with confidence. ESI MS m/z 1147.8 ($[\text{M} + \text{H}]^+$) (Expected for $\text{C}_{80}\text{H}_{102}\text{N}_6$: 1146.8).

(4-Bn-^{Mes}H₂BIP). A yellow oil containing a mixture of (4-Bn-^{Mes}H₂BIP)₂, 4-Bn-^{Mes}H₂BIP, Bn-^{Mes}BIP, and ^{Mes}BIP in an approximately ratio 11:1.4:6.2. (82% dimerization, 56% absolute

yield). ESI MS m/z = 979.6 ($[\text{M} + \text{H}]^+$) (Expected for $\text{C}_{68}\text{H}_{78}\text{N}_6$: 978.6).

Optimized Procedure for the Synthesis of (4-Allyl-^{Mes}H₂BIP)₂. A solution of the Mn(II) diallyl complex in THF was prepared from MnCl_2 as follows: MnCl_2 (284 mg, 2.4 mmol) was 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 $\text{Mg}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Br}$ in Et_2O (4.9 mmol) was 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 $\text{Mn}(\text{allyl})_2$ 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 removed, and the stirring 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 (3×20 mL), and the extracts were filtered 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%. ¹H 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, $\text{CH}_2\text{-CH}=\text{CH}_2$), 2.00–2.40 (m 2H, 4- CH_{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- CH_{Py}), 4.30–5.30 (m, 4H, $\text{CH}_2\text{-CH}=\text{CH}_2$), 5.50–6.00 (m, 2H, $\text{CH}_2\text{-CH}=\text{CH}_2$), 6.30–6.92 (several signals CH_{Ar}), 7.59 (broad s, *N*-H). ¹³C{¹H} NMR (C_6D_6 , 25°C , 100 MHz): Selected ranges: δ 12.0–15.3 ($\text{Me-C}\equiv\text{N}$), 17.0–21.0 (*o*- $\text{Me}_{\text{N-Ar}}$), 30.6–32.0 (*p*- $\text{Me}_{\text{N-Ar}}$), 37.2–37.8 (CH_2 , $\text{Py-CH}_2\text{CH}=\text{CH}_2$), 37.9–42.0 (3- CH_{Py}), 114.0–138.0 (CH_{Ar}), 145.7–148.7 (*i*- $\text{C}_{\text{NH-Ar}}$), 151.9–156.1 (*i*- $\text{C}_{\text{N-Ar}}$), 162.5–168.4 (2- C_{Py} and $\text{MeC}\equiv\text{N}$). ESI MS: m/z 879.7 ($[\text{M} + \text{H}]^+$) (expected for $\text{C}_{60}\text{H}_{74}\text{N}_6$: 878.6). EI HR-MS: m/z 879.6075 ($[\text{M} + \text{H}]^+$); Calcd for $\text{C}_{60}\text{H}_{75}\text{N}_6^+$: 879.6053.

Synthesis of [ZnBn]₂-μ-(4-allyl-^{Mes}H₂BIP)₂ (4). (4-Allyl-^{Mes}H₂BIP)₂ (200 mg, 0.22 mmol) diluted in 5 mL of toluene was dropwise added to a solution of 130 mg (0.52 mmol) of $\text{Zn}(\text{CH}_2\text{Ph})_2$ 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 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 the absence of light at -20°C . Four days later, a microcrystalline solid had formed. After filtration and drying under vacuum 190 mg (73%) of **4** were isolated. ¹H NMR (C_6D_6 , 25°C , 400 MHz) δ 1.64 (m, 2H, 4- CH_{Py}), 1.72 (s, 16H, $\text{Me-C}\equiv\text{N}$, $\text{CH}_2\text{-CH}=\text{CH}_2$), 1.95 (s, 4H, CH_2 Zn-Bn), 2.07, 2.08 (s, 24H, *o*- $\text{Me}_{\text{N-Ar}}$), 2.26 (s, 12H, *p*- $\text{Me}_{\text{N-Ar}}$), 2.79 (broad s, 4H, 3- CH_{Py}), 4.91 (s, 2H, $\text{CH}_2\text{-CH}=\text{CH}_2$), 4.94 (d, 2H, $^3J_{\text{HH}} = 5.0$ Hz, $\text{CH}_2\text{-CH}=\text{CH}_2$), 5.66 (m, 2H, $\text{CH}_2\text{-CH}=\text{CH}_2$), 6.17 (d, 4H, $^3J_{\text{HH}} = 7.1$ Hz, *o*- CH_{Ar} Zn-Bn), 6.79 (t, 2H, $^3J_{\text{HH}} = 6.0$ Hz, *p*- CH_{Ar} Zn-Bn), 6.86 (t, 4H, $^3J_{\text{HH}} = 7.9$ Hz, *m*- CH_{Ar} Zn-Bn), 6.87 (s, 4H, *m*- $\text{CH}_{\text{N-Ar}}$), 6.88 (s, 4H, *m*- $\text{CH}_{\text{N-Ar}}$). ¹³C{¹H} NMR (C_6D_6 , 25°C , 100 MHz) δ 15.4 ($\text{Me-C}\equiv\text{N}$), 18.4, 18.7 (*o*- $\text{Me}_{\text{N-Ar}}$), 19.9 (CH_2 Zn-Bn), 21.0 (*p*- $\text{Me}_{\text{N-Ar}}$), 30.2 (4- CH_{Py}), 37.7 ($\text{CH}_2\text{-CH}=\text{CH}_2$), 44.0 (3- CH_{Py}), 116.2 ($\text{CH}_2\text{-CH}=\text{CH}_2$), 120.4 (*p*- CH_{Ar} Zn-Bn), 124.3 (2- C_{Py}), 126.9 (*m*- CH_{Ar} Zn-Bn), 127.7 (*o*- CH_{Ar} Zn-Bn, partially overlapped by C_6D_6), 129.4 (*m*- $\text{CH}_{\text{N-Ar}}$), 129.7, 131.4 (*o*,*o'*- $\text{C}_{\text{N-Ar}}$), 133.7 (*p*- $\text{C}_{\text{N-Ar}}$), 137.3 ($\text{CH}_2\text{-CH}=\text{CH}_2$), 145.5 (*i*- $\text{C}_{\text{N-Ar}}$), 148.4 (*i*- C_{Ar} Zn-Bn), 164.2 ($\text{Me-C}\equiv\text{N}$). Anal. Calcd. for $\text{C}_{74}\text{H}_{86}\text{N}_6\text{Zn}_2$: C, 74.67; H, 7.28; N, 7.06. Found: C, 74.77; H, 7.92; N, 7.33.

Synthesis of [PdCH₂CMe₂Ph]₂-μ-(4-allyl-Mes^{HBIP})₂ (5). Solid samples of [PdCH₂CMe₂-o-C₆H₄(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 Et₂O. The resultant solution was magnetically stirred during 4 h at 23 °C. A ¹H 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 vacuum. Yield, 280 mg (57%). ¹H NMR (CD₂Cl₂, 25 °C, 400 MHz) δ 0.32 (s, 4H, CH₂ Pd-R), 0.66 (s, 12H, CMe₂ Pd-R), 1.55 (s, 12H, Me-C≡N), 1.98–2.01 (broad s, 6H, 4-CH₂Py, CH₂-CH=CH₂), 2.28, 2.29 (s, 24H, o-Me_{N-Ar}), 2.33 (s, 12H, p-Me_{N-Ar}), 2.36 (s, 4H, 3-CH₂Py), 5.10 (dd, 2H, ³J_{HH} = 10.1, ²J_{HH} = 2.1 Hz, CH₂-CH=CHH), 5.21 (dd, 2H, ³J_{HH} = 16.8, ²J_{HH} = 2.1 Hz, CH₂-CH=CHH), 5.95 (m, 2H, CH₂-CH=CH₂), 6.39 (d, 4H, ³J_{HH} = 6.9 Hz, o-CH_{Ar} Pd-R), 6.83–6.91 (m, 14H, CH_{N-Ar}, CH_{Ar} Pd-R). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C, 100 MHz) δ 15.9 (Me-C≡N), 18.7, 18.9 (o-Me_{N-Ar}), 21.0 (p-Me_{N-Ar}), 29.9 (4-CH₂Py), 30.2 (CMe₂ Pd-R), 37.6 (CH₂-CH=CH₂), 39.4 (CH₂ Pd-R), 41.6 (CMe₂ Pd-R), 42.9 (3-CH₂Py), 116.3 (CH₂-CH=CH₂), 124.0 (p-CH_{Ar} Pd-R), 125.2 (m-CH_{Ar} Pd-R and 2-C_{Py}), 127.5 (o-CH_{Ar} Pd-R), 128.9 (m-CH_{N-Ar}), 131.9, 132.0 (o-C_{N-Ar}), 134.4 (p-C_{N-Ar}), 137.9 (CH₂-CH=CH₂), 144.3 (i-C_{N-Ar}), 155.0 (i-C_{Ar} Pd-R), 175.1 (Me-C≡N). Anal. Calcd for C₈₀H₉₈N₆Pd₂: C, 70.83; H, 7.28; N, 6.28. Found: C, 70.91; H, 7.47; N, 5.92.

■ ASSOCIATED CONTENT

■ Supporting Information

(CIF) The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00538.

Additional figures showing NMR and mass spectra and HPLC plots, crystallographic details and ORTEP plots for [4-allyl-ⁱ-PrH₂BIP]₂, (4-allyl-Mes^{HBIP})₂, and 5 with full numbering schemes, and DFT calculation details (PDF)

Crystallographic data for [4-allyl-ⁱ-PrH₂BIP]₂, (4-allyl-Mes^{HBIP})₂, and 5 (CIF)

DFT calculations details and coordinates for optimized structures (XYZ)

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Notes

The authors declare no competing financial interest.

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