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Participation of the α,α′-Diiminopyridine Ligand System in Reduction of the Metal Center during Alkylation

Hiroyasu Sugiyama,[†] Ghazar Aharonian,[†] Sandro Gambarotta,*[,†]
Glenn P. A. Yap,[†] and Peter H. M. Budzelaar*[,‡]

Contribution from the Department of Chemistry, University of Ottawa,
Ottawa, Ontario K1N 6N5, Canada, and the Department of Inorganic Chemistry,
University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

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Abstract: The reaction of $\{[2,6\text{-(i-Pr)}_2\text{PhN}{=}\text{C(Me)}]_2(\text{C}_5\text{H}_3\text{N})\}\text{MnCl}_2$ with alkylating agents formed a dinuclear Mn(I) derivative via ligand reductive coupling. In the case of the trivalent Cr analogue, a similar reaction afforded reduction toward Cr(II) but also alkylation at the pyridine ring para position followed by an unprecedented cycloaddition that generated a tricyclic system.

Introduction

The discovery made by Gibson and co-workers,[1] Brookhart and co-workers,[2] and Bennett[3] a few years ago that an α,α′-diiminopyridine $\{[2,6\text{-(i-Pr)}_2\text{PhN}{=}\text{C(Me)}]_2(\text{C}_5\text{H}_3\text{N})\}$ ligand may provide late metals with a very high catalytic activity for olefin polymerization has marked a milestone in the neverending saga of Ziegler−Natta catalysis. Subsequent studies on the behavior of this ligand system have pointed out an unanticipated involvement of the α,α′-diiminopyridine ligand into the reactivity of its metal complexes.[4] The anionization of the ligand resulting from the direct alkylation of the pyridine ring and the consequent diminishment of the metal coordination number might be the key to explain the success of this ligand to sustain such a high level of catalytic activity. The ligand also promotes reduction of the metal center, providing examples of rare low-valent metal alkyl derivatives[4a,5,6] in principle expected to be inactive. However, the monovalent Co alkyl derivative recently reported displays catalytic activity comparable to that of the divalent precursor,[5] and thus the ability of this ligand to afford reduction of the metal center might be central to catalytic performance. Furthermore, experimental[7] and theoretical[8] studies have clearly demonstrated that this particular ligand system cannot be considered as an ancillary one since resonance structures with a considerable extent of metal-to-ligand charge transfer may play a rather significant role in the stabilization of the low-valent derivatives. Moreover, an interesting parallel can be drawn with the 1,3-diiminoarene ligand $[2,6\text{-(i-Pr)}_2\text{PhN}{=}\text{C(Me)}]_2(\text{C}_6\text{H}_4)$ that, similar to the pyridine congener, can also be alkylated but even deprotonated at one or two of the methyl groups directly attached to the imino functions.[9] Although this behavior has never been reported in the case of the α,α′-diiminopyridine ligand, these observations offer additional possibilities for explaining the unique reactivity patterns promoted by this remarkable ligand system and its ability to sustain a high level of catalytic activity.

In this paper we report the isolation and characterization of a monovalent manganese compound whose structure sheds some light on the intriguing behavior of the complexes of this remarkable ligand system. In addition, we have investigated a similar Cr(III) derivative, finding not only reduction of the metal center but also an unprecedented type of ligand reorganization and coupling.

Results and Discussion

As previously described, alkylations of $\{[2,6\text{-(i-Pr)}_2\text{PhN}{=}\text{C(Me)}]_2(\text{C}_5\text{H}_3\text{N})\}\text{MnCl}_2$ afforded Mn-alkyl derivatives formu-

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* Corresponding authors: e-mail sgambaro@science.uottawa.ca and budz@sci.kun.nl.
[†] University of Ottawa.
[‡] University of Nijmegen.

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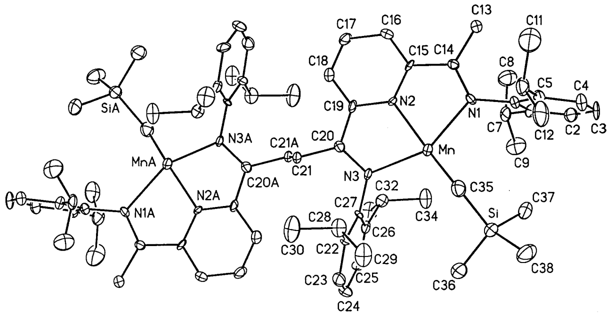


Figure 1. Thermal ellipsoid plot of **2**, drawn at 30% probability.

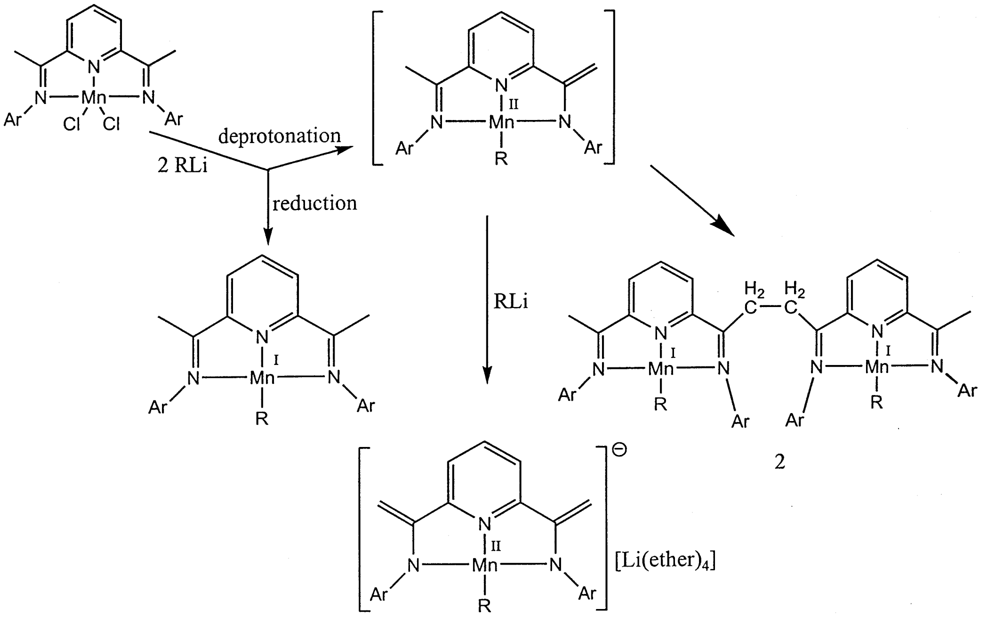
lated as $\{[2,6\text{-}(i\text{-}Pr)_2PhN{=}C(Me)]_2(C_5H_3N)\}MnMe$ and $\{[2,6\text{-}(i\text{-}Pr)_2PhN{=}C(Me)]_2(C_5H_3N)\}Mn(CH_2SiMe_3)][Li(OEt_2)_4]$ (**1**), respectively, containing the metal in the *formal* mono- and zerovalent states.[6] There was no indication in these particular cases that the diiminopyridine ligand was directly involved in assisting the reduction of the metal center as it was instead observed in the case of the vanadium analogue.[4] Simply in the case of the *formally* zerovalent **1**, the C−C distances formed by the two peripheral methyl groups attached to the imino functions were unusually short, although this was not sufficient to conclusively decide about the presence of an authentic C−C double bond. During its isolation we have observed the formation of a substantial amount of dark-colored material. After several recrystallizations from toluene/hexane mixtures we have now obtained an analytically pure crystalline solid formulated as $\{[2,6\text{-}(i\text{-}Pr)_2PhN{=}C(Me)](C_5H_3N)[2,6\text{-}(i\text{-}Pr)_2\text{-}PhN{=}C(CH_2)]\}_2[Mn(CH_2SiMe_3)]_2$ (**2**).

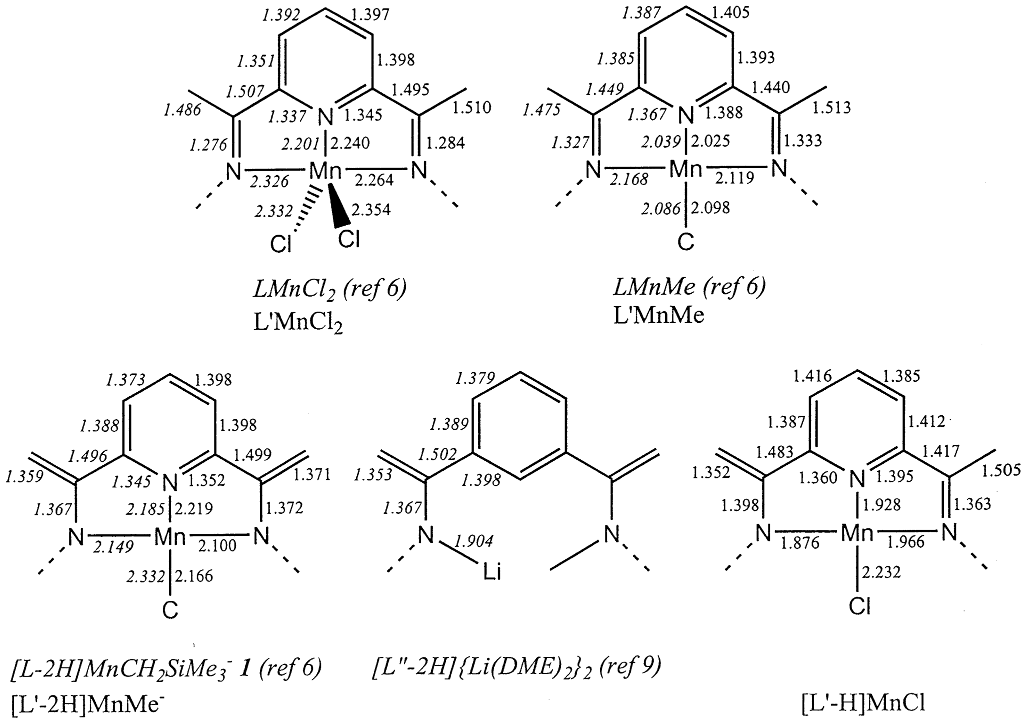
The solid-state structure revealed the connectivity and the metal oxidation state. The complex contains two monovalent $Mn{-}CH_2SiMe_3$ units each surrounded by the diiminopyridine ligand (Figure 1). The two identical moieties are connected by a C−C single bond [C(21)−C(21a) = 1.562(15) Å] between two former methyl groups, each attached to one of the two imino functions [C(21)−C(20) = 1.521(10) Å, C(20)−N(3) = 1.344(9) Å; C(14)−C(13) = 1.491(11) Å, C(14)−N(1) = 1.317(9) Å] of each Mn−ligand unit. All the other bond distances [C(14)−C(15) = 1.474(11) Å, N(2)−C(15) = 1.362(9) Å, N(2)−C(19) = 1.367(9) Å, C(19)−C(20) = 1.450(11) Å] are as expected and do not suggest the presence of any particular feature. Within each monomeric moiety the coordination geometry around the Mn atom is severely flattened tetrahedral [N(1)−Mn−N(2) = 73.1(3)°, N(1)−Mn−N(3) = 140.3(3)°, N(1)−Mn−C(35) = 108.1(3)°, N(2)−Mn−N(3) = 74.6(2)°, N(2)−Mn−C(35) = 151.0(3)°] and is defined by the three nitrogen donor atoms of the ligand [Mn−N(1) = 2.301(6) Å, Mn−N(2) = 2.073(6) Å, Mn−N(3) = 2.226(6) Å] and the C atom of the alkyl group [Mn−C(35) = 2.097(9) Å].

There are two main features in complex **2**. First, the manganese was reduced to the monovalent state. Second, the formation of the C−C bond via coupling of the two former methyl groups implies a *formal* elimination of two hydrogen atoms. This complex behavior is easily explained if we assume that the reaction may proceed through two distinct reaction pathways (Scheme 1). As a first possibility, the reaction produces a monovalent $\{[2,6\text{-}(i\text{-}Pr)_2PhN{=}C(Me)]_2(C_5H_3N)\}\text{-}MnR$ where the ligand did not undergo any transformation. This species was previously isolated and characterized for R = Me.[6] This “straight” reduction of the metal center is not terribly surprising given that alkyllithium reagents are known to be able to work as reducing agents. In a second pathway, *anionization* of the ligand may occur on a divalent manganese adduct by removing one proton from one of the two methyl groups and forming a C−C double bond at the expenses of one of the two imino functions. This process, similar to that occurring in the $[2,6\text{-}(i\text{-}Pr)_2PhN{=}C(Me)]_2(C_6H_4)$ ligand,[9] does not modify the metal oxidation state. However, subsequent reductive coupling of the C−C double bonds from two identical units forms the dimeric **2**, restores the imino functions, and provides the two electrons necessary for the reduction of the two divalent manganese atoms to the final monovalent state. The lability of the hydrogen atoms of the methyl groups attached to the imine function in diimine pyridinato complexes of Rh and Ir was previously demonstrated on the basis of the facile H,D exchange observed in the presence of NaOMe/methanol-d_1.[9b]

This behavior prompted us to reconsider the other complex previously isolated from the same reaction mixture and initially

Scheme 1




$LMnCl_2$ (ref 6)
$L'MnCl_2$

LMnMe (ref 6)
L'MnMe

*$[L\text{-}2H]MnCH_2SiMe_3^-$ **1** (ref 6)*
$[L'\text{-}2H]MnMe^-$

$[L''\text{-}2H]\{Li(DME)_2\}_2$ (ref 9)

[L'-H]MnCl

Figure 2. Observed and calculated bond lengths, in angstroms, for diiminopyridine complexes. Observed values and averaged observed values are shown in italic type.

formulated as the *zerovalent* $[\{[2,6\text{-}(i\text{-}Pr)_2PhN{=}C(Me)]_2(C_5H_3N)\}MnR][Li(ether)_4]$ (**1**).[6] It is tempting to suggest that the same divalent and monodeprotonated precursor of the dimeric **2** (Scheme 1) may alternatively undergo further deprotonation. As a result, a divalent -ate $2,6\text{-}(i\text{-}Pr)_2PhNC{=}CH_2)]_2\text{-}(C_5H_3N)\}MnR][Li(ether)_4]$ complex with manganese surrounded by a dianionic ligand might be formed. In view of the shortness of the "$C{-}CH_3$" bonds mentioned earlier, this seems more likely to be the correct formulation for **1**. However, the possibility that the complex might also be another *monovalent* species with only *one* deprotonated methyl group and the double bond equally disordered over the two positions cannot be ruled out on the basis of the analytical and crystallographic data alone.

To clarify this point, we carried out DFT optimizations of the structures of $L'MnCl_2$, $L'MnCl$, $L'MnMe$, $[L' \angle H]MnCl$, $[L' \angle H]MnMe$, and $[L' - 2H]MnMe^-$, where L' is the $2,6\text{-}(HN{=}C(Me))_2C_5H_3N$ model ligand and $[L' \angle H]$ and $[L' \angle 2H]$ are its singly and doubly deprotonated forms. Figure 2 shows calculated bond lengths for the most relevant species and compares them with those observed in the X-ray structures reported previously for complexes of the "real" ligand $[2,6\text{-}(i\text{-}Pr)_2PhN{=}C(Me)]_2(C_5H_3N)$ (L).[6] The agreement is good except for the $M{-}N_{imine}$ bond lengths, which are consistently too short in the calculations by ca. 0.05−0.1 Å. This is to be expected, since a C═NH group is a much better donor than a C═NAr group for both steric and electronic reasons. Concerning the important (former) C−Me bonds, the X-ray bond lengths for **1** agree well with those predicted for $[L' - 2H]MnMe^-$ but not for an average of the bond lengths predicted for a singly deprotonated ligand (e.g., 1.429 Å for $[L' \angle H]MnCl$). Also, the similarity to the deprotonated arene analogue reported by Burger[9] (included in Figure 2) is remarkable. Thus, we believe that the formulation of **1** as an -ate complex of Mn(II) is the correct one.

Electron transfer from metal to ligand seems to be a recurring feature in diiminopyridine complexes. The calculations show that L′MnMe, although *formally* Mn(I), is best described as having a ligand radical anion antiferromagnetically coupled to a high-spin Mn(II) center. The deprotonated-ligand complexes $[L' \angle H]MnCl$ and $[L' \angle H]MnMe$ show significant spin density at the imine C and N atoms and the terminal methylene group, apparently due to electron transfer from Mn(II) to the ligand, induced by the strong ligand field of the amide functionality. Since of these atoms only the methylene carbons are sterically accessible, this might explain the observed easy dimerization. In contrast, the complex of the doubly deprotonated ligand does not show appreciable spin density at the ligand, presumably because of the weak π-acceptor character of this dianionic ligand.

The involvement of the ligand in assisting the reduction of manganese was substantially different from that observed in the case of vanadium. Thus, investigating the behavior of the chromium analogues was the next obvious step. The reaction of $CrCl_3(THF)_3$ with $[2,6\text{-}(i\text{-}Pr)_2PhN{=}C(Me)]_2(C_5H_3N)$ in toluene was a straightforward complexation affording the corresponding $\{2,6\text{-}bis[2,6\text{-}(i\text{-}Pr)_2PhN{=}C(Me)]_2(C_5H_3N)\}CrCl_3\cdot(CH_2Cl_2)_{1.33}$ (**3**) that was isolated in crystalline form from methylene chloride. The complex is isostructural with the vanadium species reported before,[4] with comparable bond distances and angles (Figure 3). Different from vanadium, however, the catalytic activity was surprisingly low (2.6 kg of PE mol^{-1} h^{-1} atm^{-1}) under the usual reaction conditions employed for this family of catalysts (MAO:Cr = 70−1000, 1 atm of ethylene, room temperature) yet producing polyethylene of comparable quality and with the usual bimodal distribution [Mw = 57 000; PD = 33]. Given the close structural analogy with the vanadium derivative, the low activity of **3** can be ascribed to either the

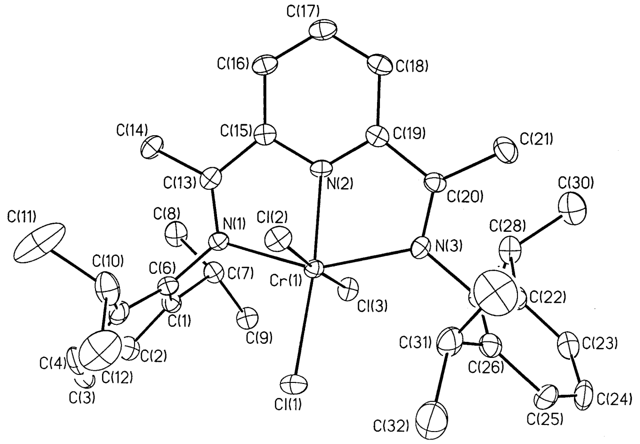
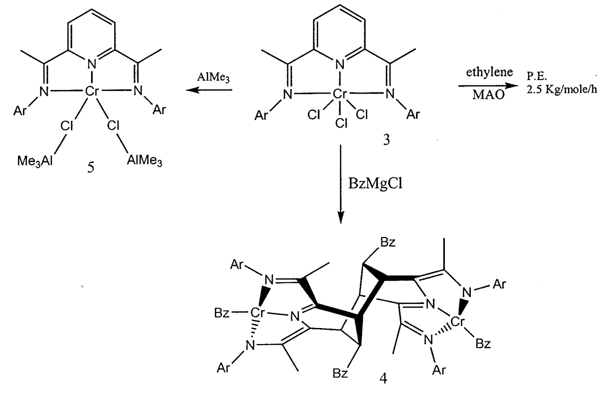


Figure 3. Thermal ellipsoid plot of **3**, drawn at 30% probability.

Scheme 2



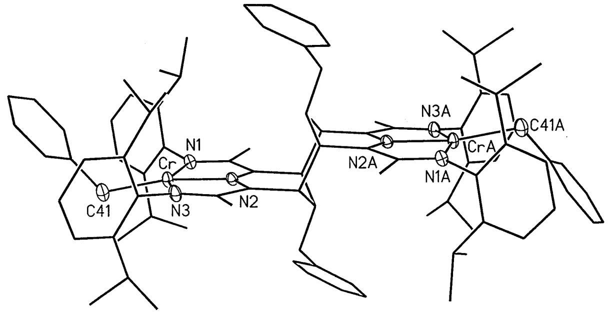


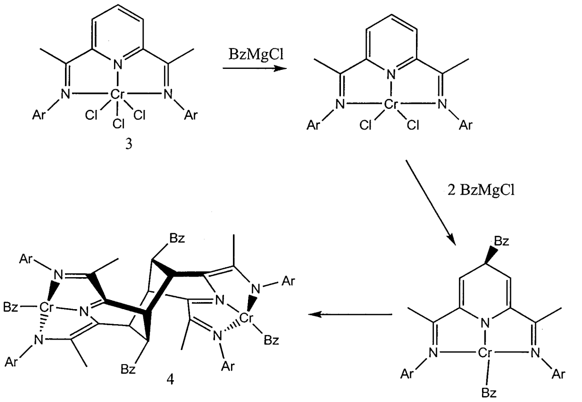
Figure 4. Thermal ellipsoid plot of **4**, drawn at 30% probability.

metal d^3 electronic configurations,[10] possibly determining instability of the M−alkyl functions, or to metal reduction with or without ligand assistance. To probe this point, we have studied the behavior of **3** with both strong and weak alkylating agents.

The reaction of **3** with 2 equiv of $PhCH_2MgCl$ triggered a very unusual transformation through which the new complex $\{[2,6\text{-(i-Pr)}_2PhNC(Me)]_2(4\text{-}PhCH_2C_5H_3N)Cr(CH_2Ph)\}_2$-(toluene) (**4**) was formed (Scheme 2). The magnetic moment clearly indicated that the two chromium atoms are in the divalent state with the two metals magnetically uncoupled. Similar reaction carried out with MeMgI only gave intractable materials.

Complex **4** is dinuclear (Figure 4) and consists of two $CrCH_2$-Ph moieties [Cr−C(41) = 2.153(4) Å] chelated by a large hexadentate dianion arising from two separate processes: (a) alkylation at the pyridine ring para position [C(17)−C(34) = 1.523(6) Å, C(16)−C(17)−C(34) = 114.1(3)°] and (b) cycloaddition to an identical ring of a second unit forming two C−C single bonds [C(18)−C(16a) = 1.563(5) Å] and linking the ring meta carbon atoms. The resulting 6,6,6-tricyclo type of frame bears one negative charge in each of the two residual π-systems present between the nitrogen atoms and the adjacent imine functions in each of the two former pyridine rings. The long C−C distances [C(13)−C(14) = 1.517(5) Å, C(20)−C(21) = 1.500(5) Å] formed by the methyl groups with the carbon atoms engaged in the formation of the two imino functions clearly indicated the presence of single bonds, thus ruling out the possibility of deprotonation as observed in the case of manganese. The C−N distances are rather short [C(13)−N(1) = 1.313(4) Å, C(20)−N(3) = 1.322(5) Å] and in good agreement with the presence of a substantial C−N double-bond character. The coordination geometry around the chromium center is nearly square-planar [N(1)−Cr−N(2) = 76.75(10)°, N(1)−Cr−N(3) = 153.09(11)°, N(1)−Cr−C(41) = 103.06(13)°, N(2)−Cr−N(3) = 76.80(1)°, N(2)−Cr−C(41) = 169.23(16)°, N(3)−Cr−C(41) = 103.84(13)°] as expected for a divalent chromium metal and is defined by the three ligand nitrogen atoms and the carbon atom of the alkyl group [Cr−N(1) = 2.114(3) Å, Cr−N(2) = 2.051(3) Å, Cr−N(3) = 2.109(3) Å, Cr−C(41) = 2.153(4) Å].

Scheme 3



The formation of **4** is a complex reaction that can be rationalized in three main steps (Scheme 3). The first step is probably reduction of the metal center by 1 equiv of alkylating agent. Easy reduction is in line with the results obtained with Mn[6] and Co[5] and is also observed for Cr in combination with Me_3Al (vide infra). Reaction with a further 2 equiv of BzMgCl then results in alkylation at the metal atom and at the pyridine para position, the latter being related to the ortho coupling previously observed with vanadium.[4a] Whether ring alkylation involves direct attack of BzMgCl at the pyridine ring or alkylation at Cr followed by migration to the ring cannot be established at this point. In this respect, it should be mentioned that the ability of uncoordinated pyridine ring to undergo nucleophilic attack is well established.[11] Finally, the square-planar Cr(II) product dimerizes to the observed tricyclic structure. In support of this interpretation, calculations on model system [L′ + H]CrMe (where [L′ + H] has a hydrogen atom added to C_{para}) predict that the highest spin density on the ligand is at the pyridine meta carbons (Figure S-1 in Supporting Information). Also, the X-ray structure reported for [2,6-

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[10] Margl, P.; Deng, L.; Ziegler, T. *Organometallics* **1999**, *18*, 5701.

[11] See for example (a) Gilman, H.; Gregory, W. A.; Spatz, S. M. *J. Org. Chem.* **1951**, *16*, 1788. (b) Nunn, A. J.; Schofiel, K. *J. Chem. Soc.* **1952**, 589.

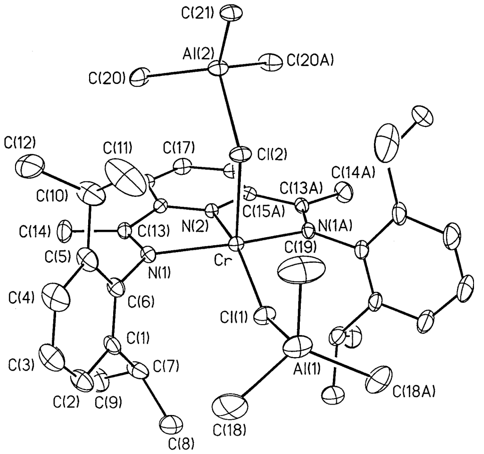

Figure 5. Thermal ellipsoid plot of **5**, drawn at 30% probability.

(i-Pr)$_2$PhN═C(Me)]$_2$(C$_5$H$_3$N)CoCH$_2$SiMe$_3$ shows a close contact (3.5 Å) between the pyridine rings of two neighboring molecules,[5a] indicating that a close approach of these rings is sterically feasible. Driving force for the dimerization would then be the conversion of one net C−C π-bond per monomer to a σ-bond, coupled with a delocalization of the ligand negative charge to the imine nitrogens.

From what is presented above, it appears that reduction is a rather general trend in this chemistry. It may be that reduction initially takes place at the ligand, forming a ligand radical anion. This may result in a stable situation (as in {[2,6-(i-Pr)$_2$PhN═C(Me)]$_2$(C$_5$H$_3$N)}MnMe and complex **2**), whereas in others the radical anion can in turn reduce the metal (as has presumably happened in the formation of **4**). On the other hand, the *nature* of the transition metal seems to determine the type of further transformations undergone by the ligand. Thus, this intriguing behavior does not necessarily have implications for the catalytic performances of these species and questions remain open about the role of the Al cocatalyst (a mild alkylating agent). Supporting a very high catalytic activity is a primary characteristic of the diiminopyridine ligand. However, the effect of the reduction of the metal center on the catalytic activity of this family of complexes is unclear and controversial in the case of the Co supercatalyst.[1e,5] In the case of the highly active vanadium,[4] the MAO cocatalyst alkylated the pyridine ortho position and anionized the ligand, but no reduction toward the inactive divalent state apparently occurred under these conditions. Thus, we were puzzled by the low catalytic activity displayed by **3**. In other words, the low activity may be the result of (1) metal reduction, (2) the d^3 electronic configuration, or (3) some ligand transformation. To probe these possibilities we have thus reacted **3** with Me$_3$Al and isolated the resulting complex. To keep the conditions as close as possible to those employed for the polymerization, the reaction was carried out in toluene with Me$_3$Al. The reaction of **3** with Me$_3$Al afforded a dark-brown compound that was isolated in crystalline form as extremely air-sensitive paramagnetic and pyrophoric crystals. The formulation of {[2,6-(i-Pr)$_2$PhN═C(Me)]$_2$(C$_5$H$_3$N)}Cr(μ-ClAlMe$_3$)$_2$ (toluene) **(5)** was provided by the X-ray crystal structure and was in good agreement with analytical and magnetism data.

The structure of **5** (Figure 5) consists of a simple diimine pyridinato CrCl$_2$ complex where each of the two chlorine atoms bridge one Me$_3$Al unit [Cr−Cl(1) = 2.3435(9) Å, Cr−Cl(2) = 2.5415(8) Å, Cl(1)−Al(1) = 2.348(2) Å, Cl(2)−Al(2) = 2.313(2) Å]. The ligand system is apparently intact. No special deformation is observed in the pyridine ring. The long C−C distances [C(13)−C(14) = 1.510(3) Å] formed by the methyl group with the imino carbon atoms [C(13)−N(1) = 1.295(3) Å] clearly indicated that no deprotonation occurred in this case. The coordination geometry around the chromium center is square pyramidal and very similar to those of the Co and Fe supercatalysts [N(1)−Cr−N(2) = 76.82(4)°, N(1)−Cr−N(1a) = 151.63(8)°, N(1)−Cr−Cl(1) = 100.45(4)°, N(2)−Cr−Cl(1) = 59.23(6)°] with the metal center being coplanar with the three N-donor atoms and one of the two chlorine atoms. The second chlorine lies on the axis nearly perpendicular to the molecular plane [Cl(2)−Cr−N(1) = 96.79(4)°, Cl(2)−Cr−N(2) = 97.40(6)°, Cl(2)−Cr−Cl(1) = 103.37(3)°].

Given the fact that the ligand in **5** is apparently intact and neutral, the connectivity clearly assigned a formal divalent oxidation state to the chromium atom. This is also in good agreement with the magnetic moment that was as expected for the d^4 high-spin electronic configuration. Thus, the formation of the divalent **5** clearly indicates that even a mild alkylating agent may promote the reduction of the metal center. This is especially striking in the case of trivalent Cr when we consider the unusually high stability and chemical inertness of the Cl$_2$CrMe moiety[12] capable of resisting the attack of HCl and whose stability should increase even further while in combination with the diiminato ligand. Thus, ligand involvement in the reduction remains a distinct possibility. Given also that **5,** while in combination with a variety of cocatalyts, is totally inactive toward olefin polymerization, the easy reduction of the metal center explains the lack of activity of **3**.

Conclusions

In this paper we have described the isolation of new complexes of the popular diiminopyridinato ligand system where the ligand has undergone two different types of unprecedented transformations. The first, C−C bond formation as observed in the case of **2**, proceeds via deprotonation of a methyl group forming a C−C double bond. This reductive coupling is accompanied by a *formal* reduction of the metal oxidation state. The second consists of pyridine ring alkylation that, in the particular case of chromium, also triggered a complex rearrangement and dimerization. Even in this case, the metal was reduced. In both scenarios the ligand became anionic. Reduction of the metal center as observed in the case of vanadium, chromium, manganese, and cobalt seems to be a trend in the organometallic derivatives of this ligand. In turn, the stabilization of low-valent metal alkyls may be explained by a great ability of this ligand system to accept and efficiently delocalize electronic charge. The reduction of the metal center as observed in the case of the treatment of **3** with Me$_3$Al is particularly eloquent and reiterates that destabilization of higher-valent metal alkyls occurs in favor of lower oxidation states. Thus questions continue to rise about the nature of the catalytically active species and metal oxidation state, given that in the case of early transition metals lower oxidation states are commonly expected to be less active if active at all. Thus, further studies aimed at elucidating the effect of this particular ligand system on the stability of the M−C bond will be central both to understand

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the catalytic performance of this family of catalysts and to the design of even more potent catalysts.

Experimental Section

All operations were performed under inert atmosphere by using standard Schlenk-type techniques. $MnCl_2(THF)_2$,[13] $CrCl_3(THF)_3$,[13] [2,6-(i-Pr)$_2$PhN═C(Me)]$_2$(C_5H_3N),[14] $LiCH_2Si(CH_3)_3$[15] and {[2,6-(i-Pr)$_2$PhN═C(Me)]$_2$(C_5H_3N)}$MnCl_2$[6] were prepared according to published procedures. A solution of $PhCH_2MgCl$ in ether was prepared and titrated according to standard procedures. Infrared spectra were recorded on a Mattson 9000 and Nicolet 750-Magna FTIR instruments from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. Magnetic moments were calculated following standard methods,[16] and corrections for underlying diamagnetism were applied to data.[17] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination were obtained with a Bruker diffractometer equipped with a Smart CCD area detector.

Isolation of {[2,6-(i-Pr)$_2$PhNC(═CH_2)]$_2$(C_5H_3N)}Mn(CH_2SiMe_3)]-[Li(OEt_2)$_4$] (1) and {[2,6-(i-Pr)$_2$PhN═C(Me)](C_5H_3N)[2,6-(i-Pr)$_2$PhN═C(CH_2)]}$_2$[Mn(CH_2SiMe_3)]$_2$ (2). Solid $LiCH_2Si(CH_3)_3$ was added (0.32 g, 3.4 mmol) to an orange suspension of {[2,6-(i-Pr)$_2$PhN═C(Me)]$_2$-(C_5H_3N)}$MnCl_2$ (1.0 g, 1.7 mmol) in toluene (80 mL) at room temperature. A fast reaction was observed during which the color of the mixture changed from orange to dark brown. The suspension was stirred for an additional 4 h, after which, the solvent was removed in vacuo. The resulting brown residue was dissolved in freshly distilled diethyl ether (80 mL), centrifuged to eliminate a small amount of pale colored solid, and the resulting solution was concentrated to about 50 mL. Dark blue-black solid precipitated upon standing overnight at room temperature. The dark brown mother liquor was placed at 4 °C, in which yellow-brown crystals of **1** were isolated (0.6 g, 0.6 mmol, 35%). Anal. Calcd (Found) for $C_{53}H_{94}LiMn\ N_3O_4Si$: C 68.65 (68.86), H 10.22-(10.34), N 4.53 (4.27). IR (Nujol mull, cm^{-1}) ν 1912 (w), 1851 (w), 1790 (w), 1643 (s), 1589 (s), 1570 (m), 1364 (s), 1321 (w), 1261 (s), 1192 (w), 1094 (s), 1021 (s), 929 (w), 861 (m), 802 (s), 721 (m), 691 (m), 663 (m). $\mu_{eff} = 3.91\mu_{BM}$. The solid separated from the solution was dissolved in toluene and layered with hexane, affording dark crystals of **2** (0.55 g, 0.44 mmol, 52%). Anal. Calcd. (Found) for $C_{74}H_{106}N_6Si_2Mn_2$: C 71.35 (71.64), H 8.58 (8.67), N 6.75 (6.27). IR (Nujol mull, cm^{-1}): 1646 (s), 1566 (m), 1531 (s), 1495 (s), 1366 (s), 1317 (w), 1268 (s), 1251 (s), 1229 (s), 1194 (w), 1164 (s), 1136 (w), 1111 (s), 1092 (s), 1046 (s), 1026 (s), 993 (s), 956 (s), 875 (s), 823 (s), 785 (m), 773 (w), 764 (m), 748 (s), 727 (s), 692 (s), 671 (w), 619 (w). $\mu_{eff} = 5.65\mu_{BM}$.

Preparation of {2,6-bis[2,6-(i-Pr)$_2$PhN═C(Me)]$_2$(C_5H_3N)}$CrCl_3$·(CH_2Cl_2)$_{1.33}$ (3). A solution of 2,6-bis[1-(2,6-diisopropylphenylimino)-ethyl]pyridine (2.0 g, 4.16 mmol) in toluene (100 mL) was treated with $CrCl_3(THF)_3$ (1.55 g, 4.16 mmol). The mixture was refluxed overnight (110 °C). The solution was evaporated to dryness and the solvent was replaced with 20 mL of methylene chloride, upon which the color of the solution changed to dark green. The solution was filtered and layered with hexane, yielding green crystals of **3** over a period of 2 weeks. (2.4 g, 3.3 mmol, yield 79%). IR (Nujol mull, cm^{-1}): 3168 (m), 2954 (s), 2879 (s), 1620 (w), 1576 (m), 15.14 (m), 1464 (s), 1379 (s), 1323 (w), 1259 (m), 1209 (w), 1171 (w), 1149 (w), 1101 (m), 1055 (w), 1039 (m), 982 (w), 935 (w), 891 (w), 839 (w), 796 (s), 777 (m), 760 (w), 723 (m), 700 (w), 654 (w). Analytical data for the formula $C_{33}H_{43}N_3Cl_3Cr$ (without solvent) were obtained upon crushing the crystalline solid and gently heating in vacuo for 1 h. Anal. Calcd (Found): C 61.92 (61.73), H 6.77 (6.61), N 6.56 (6.48). $\mu_{eff} = 3.83\mu_{BM}$.

Preparation of {[2,6-(i-Pr)$_2$PhNC(Me)]$_2$(4-$PhCH_2C_5H_3N$)Cr-(CH_2Ph)}$_2$·(toluene) (4). A suspension of CH_2Cl_2-free **3** (213 mg, 0.33 mmol) in toluene (5 mL) at −36 °C was treated with an Et_2O solution of $C_6H_5CH_2MgCl$ (0.51 M, 2 mL, 1.0 mmol). The color changed immediately from green to reddish-brown and then gradually to dark green. The mixture was stirred at ambient temperature for 4 h and then filtered and extracted with toluene (20 mL × 3) to remove the white precipitate of $MgCl_2$. The dark green extracts were concentrated to the volume of ca. 5 mL, from which dark green crystals of **4** (54 mg, 0.035 mmol, 21%). were obtained by slow addition of hexane (5 mL) for a period of 2 days. Anal. Calcd (Found) for $C_{101}H_{122}N_6Cr_2$: C 79.59-(79.51), H 8.07(7.97), N 5.51(5.48). IR (NaCl, Nujol mull, cm^{-1}) 3062 (m), 3022 (m), 1591 (s), 1515 (m), 1489 (m), 1439 (s), 1334 (w), 1320 (w), 1306(s), 1276 (s), 1253 (w), 1242 (w), 1224 (m), 1206 (m, sh), 1175 (m), 1149 (s), 1117 (w), 1094 (m), 1056 (w), 1029 (w), 1004 (w), 977 (s), 959 (m), 934 (w), 900 (w), 877 (w), 862 (m), 853 (w), 820 (w), 800 (s), 778 (m), 767 (m), 762 (s), 739 (m), 726 (w), 711(w), 698 (s). $\mu_{eff} = 4.75\mu_{BM}$.

Preparation of Cr($C_{33}H_{43}N_3$){ClAl(CH_3)$_3$}$_2$·(toluene) (5). A suspension of CH_2Cl_2-free **3** (652 mg, 1.02 mmol) in cold (0 °C) toluene (30 mL) was treated with a heptane solution of $Al(CH_3)_3$ (2.0 M, 5 mL, 10 mmol) over a period of 30 min, affording a dark-green homogeneous solution. The solution gradually changed the color to dark-brown, and separated crystalline **5** (623 mg, 0.741 mmol, 73%) was obtained upon standing at room temperature. Anal. Calcd for $C_{46}H_{69}N_3Al_2Cl_2Cr$: C 65.70 (65.58), H 8.27(8.19), N 5.00(4.93). IR (NaCl, Nujol mull, cm^{-1}) 3078 (w), 3062 (w), 2361 (m), 2343 (m), 1573 (s), 1320 (w), 1270 (s), 1211 (m), 1172 (s), 1103 (w), 1058 (w), 1033 (w), 982 (w), 936 (w), 842 (w), 813 (m), 802 (m), 795 (m), 776 (m), 756 (w), 734 (s), 698 (s), 678 (s). $\mu_{eff} = 4.83\mu_{BM}$.

X-ray Crystallography: Structural Determination of 2, 3, 4, and 5. These compounds consistently yielded crystals that diffract weakly, and the results presented are the best of several trials. The data crystals were selected, mounted on thin, glass fibers using paraffin oil and cooled to the data collection temperature for **2**, **3**, and **4** and in a Lindemann capillary for **5**. Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω-scans at 0°, 90°, and 180° in ϕ. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[18]

Systematic absences in the diffraction data sets and unit-cell parameters were consistent with $P2_1/c$ (no.13) for **2**, $P1$ (no. 1) and P-1 (no. 2) for **3**, $C2/c$ (no. 15) and Cc (no. 9) for **4**, and $Pnma$ (no. 62) and $Pn2_1a$ [$Pna2_1$ (no. 33)] for **5**. Solution in the centrosymmetric space groups yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2.

The compound molecule was located on a 2-fold axis in **4**, on a mirror plane in **5**, and at an inversion center in **2**. Cocrystallized toluene solvent molecules were located each on a 2-fold axis in **4** and on a mirror plate in **5**. Three symmetry-unique but chemically equivalent compound molecules were located in the asymmetric unit of **3** cocrystallized with four symmetry-unique molecules of methylene chloride solvent. All non-hydrogen atoms, except those of the solvent molecule in **5**, which were refined isotropically with idealized geometry, were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library

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Table 1. Crystal Data and Structure Analysis Results

	2	**3**	**4**	**5**
formula	$C_{74}H_{106}N_6Si_2Mn_2$	$C_{34.3}H_{45.67}Cl_{5.67}N_3Cr$	$C_{101}H_{12}N_6Cr_2$	$C_{46}H_{69}Al_2Cl_2CrN_3$
MW	1245.71	753.29	1524.05	840.90
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	*P*2(1)/*c*	*P*2(1)/*n*	*C*2/*c*	Pnma
a (Å)	17.479(3)	18.124(2)	23.5634(10)	17.968(2)
b (Å)	12.0607(19)	16.440(1)	18.8452(7)	14.715(1)
c (Å)	18.368(3)	37.861(3)	21.9494(8)	19.712(2)
β (deg)	110.800(3)	95.932(2)	111.4240(10)	
V (Å^3)	3619.9(10)	11220(2)	9073.3(6)	5211.9(8)
Z	2	12	4	4
radiation (Kα Mo)	0.710 73	0.710 73	0.710 73	0.710 72
T (K)	203	203	203	293
D_{calcd} (g cm^{-3})	1.143	1.338	1.116	1.072
μ_{calcd} (cm^{-1})	0.425	0.738	0.287	0.386
F_{000}	1340	4716	3272	1800
R	0.0818	0.0702	0.0677	0.0868
R_w2 [a]	0.1541	0.2064	0.1765	0.2663
GoF	1.088	1.022	1.044	1.049

[a] $R = \Sigma_o - F_c/\Sigma F_o R_w = [(\Sigma(F_o - F_c)^2 / \Sigma_w F_o^2)]^{1/2}$.

Table 2. Selected Bond Distances and Angles[a]

2		**3**		**4**		**5**	
Mn−C(35)	2.097(9)	Cr−Cl(1)	2.295(2)	Cr−C(41)	2.153(4)	Cl(1)−Cr	2.3435(9)
Mn−N(1)	2.301(6)	Cr−Cl(2)	2.350(2)	Cr−N(1)	2.114(3)	Cl(2)−Cr	2.5415(8)
Mn−N(2)	2.073(6)	Cr−Cl(3)	2.273(2)	Cr−N(2)	2.051(3)	N(1)−Cr	2.1428(16)
Mn−N(3)	2.226(6)	Cr−N(1)	2.156(6)	Cr−N(3)	2.105(3)	N(2)−Cr	2.000(2)
N(1)−C(14)	1.317(9)	Cr−N(2)	1.996(5)	C(13)−N(1)	1.313(4)	Cl(1)−Al(1)	2.3482(16)
C(14)−C(13)	1.491(11)	Cr−N(3)	2.161(6)	C(13)−C(14)	1.517(5)	Cl(2)−Al(2)	2.3130(12)
C(14)−C(15)	1.474(11)	N(3)−C(20)	1.291(8)	C(16)−C(18a)	1.563(5)	N(1)−C(13)	1.295(3)
N(2)−C(15)	1.362(9)	C(20)−C(21)	1.500(10)	C(18)−C(16a)	1.563(5)	C(13)−C(14)	1.510(3)
N(2)−C(19)	1.367(9)	Cl(1)−Cr−N(2)	171.59(17)	C(17)−C(34)	1.523(6)	Al(1)−C(19)	1.969(6)
C(19)−C(20)	1.450(11)	Cl(2)−Cr−Cl(3)	176.38(8)	C(15)−C(16)	1.516(5)	Al(2)−C(20)	2.026(3)
C(20)−N(3)	1.344(9)	N(1)−Cr−N(3)	152.1(2)	C(41)−Cr−N(2)	169.23(16)	Cl(1)−Cr−N(1)	100.45(4)
C(21)−C(21a)	1.562(15)	Cl(1)−Cr−N(1)	100.35(15)	C(41)−Cr−N(1)	103.06(13)	Cl(1)−Cr−N(2)	159.23(6)
C(35)−Mn−N(2)	151.0(3)	Cl(1)−Cr−N(3)	107.24(16)	N(1)−Cr−N(3)	153.09(11)	Cl(1)−Cr−N(1a)	100.45(4)
N(3)−Mn−N(1)	140.3(3)	Cl(2)−Cr−N(1)	92.74(15)	C(41)−Cr−N(3)	103.84(13)	Cl(1)−Cr−Cl(2)	103.37(3)
C(35)−Mn−N(1)	108.1(3)	Cl(2)−Cr−N(3)	95.08(16)	N(1)−Cr−N(2)	76.65(10)	N(1)−Cr−N(1a)	151.63(8)
N(3)−Mn−C(35)	111.4(3)	Cl(2)−Cr−N(2)	82.20(16)	C(17)−C(34)−C(40)	113.8(3)	Cr−Cl(1)−Al(1)	148.08(5)
C(20)−C(21)−C(21a)	111.2(8)			Cr−C(41)−C(47)	119.2(3)	Cr−Cl(2)−Al(2)	124.96(4)
						Cl(2)−Cr−N(1)	96.79(4)
						Cl(2)−Cr−N(2)	97.40(6)
						Cl(2)−Cr−N(1a)	96.79(4)

[a] Distances are given in angstroms; angles are given in degrees.

with the latest used version being v.6.12 (Sheldrick, G. M. Bruker AXS; Madison, WI, 2001). Crystallographic data and relevant bond distances and angles are reported in Tables 1 and 2.

Calculations. Geometry optimizations of the minima of the reaction path were performed with the GAMESS−UK package[19] using the UB3LYP hybrid density functional[20] with split-valence basis sets: LANL2DZ (small core pseudopotential) on Mn/Cr[21] and 3-21G(*) for all other atoms.[22] Geometries were optimized without constraints.

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Supporting Information Available: Complete crystallographic data (CIF) for complexes **2**, **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) GAMESS-UK is a package of ab initio programs written by M. F. Guest, J. H. van Lenthe, J. Kendrick, K. Schoffel, and P. Sherwood, with contributions from R. D. Amos, R. J. Buenker, H. J. J. van Dam, M. Dupuis, N. C. Handy, I. H. Hillier, P. J. Knowles, V. Bonacic-Koutecky, W. von Niessen, R. J. Harrison, A. P. Rendell, V. R. Saunders, A. J. Stone, D. J. Tozer, and A. H. de Vries. The package is derived from the original GAMESS code due to M. Dupuis, D. Spangler and J. Wendoloski, NRCC Software Catalog, Vol. 1, Program QG01 (GAMESS), 1980.

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