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Mono- and Zerovalent Manganese Alkyl Complexes Supported by the α,α′-Diiminato Pyridine Ligand: Alkyl Stabilization at the Expense of Catalytic Performance

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Summary: The reaction of {[2,6-(i-Pr)$_2$PhN═C(Me)]$_2$-(C$_5$H$_3$N)}MnCl$_2$ with MeLi or Me$_3$SiCH$_2$Li afforded reduction toward rare examples of non-cyclopentadienyl and non-carbonyl Mn(I) and Mn(0) alkyl derivatives.

In the past few years, efforts to develop alternatives to group IV metallocene single-site olefin polymerization catalysts have resulted in major breakthroughs. In particular, the employment of the sterically hindered [2,6-(i-Pr)$_2$PhN═C(Me)]$_2$(C$_5$H$_3$N) ligand system, pioneered by the groups of Gibson,[1] Brookhart,[2] and Bennett,[3] has enabled the preparation of an unprecedented family of potent catalysts based on late transition metals. Theoretical work has suggested that the tremendous success of the Fe(II) and Co(II) catalysts[4,5] relies chiefly on the complex electronic configuration capable of maintaining a low-energy ethylene insertion barrier while providing a relatively high activation energy for the β-H transfer and β-H elimination termination steps.[6]

Our investigation on the trivalent vanadium complex of this particular ligand[7] has outlined a surprising involvement of the ligand in the catalytic performance of the alkylating agents. This unusual reactivity pattern provides both activation of the vanadium metal via alkylation on the pyridine ring and at the same time a two-electron reduction pathway toward rare monovalent vanadium alkyls.

To expand our understanding of the unique behavior of this important ligand system, we have now investigated the behavior of the Mn derivative. Given the high activity of the V and Fe derivatives, a Mn(II) diiminopyridinate complex may also be expected to be another potent catalyst. However, we anticipated some uncertainties regarding how the high-spin d^5 electronic configuration of Mn(II) might affect the stability of the Mn−C bond and the other critical steps of the catalytic cycle. It is worth noting that divalent Mn alkyl complexes are stable species, and a substantial number of homoleptic derivatives have been reported in the literature.[8] Herein we describe our findings.

The reaction of MnCl$_2$(THF)$_2$ with [2,6-(i-Pr)$_2$PhN═C(Me)]$_2$(C$_5$H$_3$N) in toluene is a straightforward complexation reaction affording {2,6-bis[2,6-(i-Pr)$_2$PhN═C(Me)]$_2$(C$_5$H$_3$ N)}MnCl$_2$ (**1**), which was crystallized from methylene chloride.[9] The coordination geometry of manganese[10] is identical to that of the Fe and Co "supercatalysts"[4,5] with the same distorted square py-

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[8] See for example: (a) Andersen, R. A.; Berg, D. J.; Fernholt, L.; Faegri, K. Jr., Green, J. C.; Haaland, A., Lappert, M. F.; Leung, W. P.; Rypdal, K. *Acta Chem. Scand., Ser. A* **1988**, *A42* (8−9), 554. (b) Cahiez, G.; Alami, M. *Tetrahedron Lett.* **1986**, *27*, 569. (c) Kauffmann, T.; Bisling, M. *Tetrahedron Lett.* **1984**, *25*, 293. (d) Leleu, J. *Cah. Notes Doc.* **1977**, *88*, 361. (e) Tamura, M.; Kochi, J. *J. Organomet. Chem.* **1971**, *29*, 111.

[9] Complex 1: A solution of 2,6-bis[1-(2,6-diisopropylphenylimino)-ethyl]pyridine (2.0 g, 4.1 mmol) in toluene (100 mL) was treated with MnCl$_2$(THF)$_2$ (1.1 g, 4.1 mmol). The mixture was refluxed overnight, upon which the yellow suspension changed to an orange solution. The solution was evaporated to dryness, yielding an orange residue, which was then dissolved in 20 mL of methylene chloride. The orange solution was filtered and layered with hexane, yielding orange crystals of **1** over a period of 2 weeks (1.8 g, 2.9 mmol, yield 71%). IR (Nujol mull, cm^{-1}): 3055(m), 2906(s), 1570(m), 1458(s), 1379(s), 1321(m), 1302(w), 1255(m), 1236 (m), 1146(w), 1103(m), 1078 (w), 995(w), 960(w), 868(w), 824(m), 800(w), 769(s), 723(m), 688(w). Anal. Calcd (found) for C$_{33}$H$_{43}$Cl$_2$N$_3$Mn: C 65.24 (63.91), H 7.13 (6.96), N 6.92 (6.64). $\mu_{\mathrm{eff}} = 5.74\ \mu_{\mathrm{BM}}$. Complex 2: A suspension of **1** (1.5 g, 2.5 mmol) in freshly distilled diethyl ether (100 mL) was treated with 2 equiv of MeLi (3.5 mL of 1.4 M solution in diethyl ether, 5.0 mmol). The mixture was stirred for 2 days, upon which the color changed from orange to maroon. The solution was filtered and the solvent was reduced to 15 mL to crystallize for 4 days, upon which burgundy crystals of **2** suitable for single-crystal X-ray analysis were obtained (0.7 g, 1.3 mmol, yield 52%). IR (Nujol mull, cm^{-1}): 3058(w), 2923(s), 2854(w), 1586(s), 1462(s), 1378(s), 1319(w), 1255(m), 1236(m), 1145(w), 1104(m), 1091 (m), 997(w), 950 (m), 854(m), 822(w), 798(w), 772(m), 756(m), 724(m), 694(m), 502 (m). Anal. Calcd (found) for C$_{34}$H$_{46}$N$_3$Mn: C 74.02 (74.18), H 8.40 (8.72), N 7.62 (7.41). $\mu_{\mathrm{eff}} = 4.82\ \mu_{\mathrm{BM}}$. Complex 3: Solid LiCH$_2$Si(CH$_3$)$_3$ (0.3 g; 3.4 mmol) was added to an orange suspension of **1** (1.0 g; 1.7 mmol) in toluene (80 mL) at room temperature. A fast reaction was observed in which the solution changed in color from orange to dark brown. The solution was stirred for additional 4 h, and the solvent was removed under vacuum. The resulting brown solid was dissolved in freshly distilled diethyl ether (80 mL) and centrifuged to eliminate a small amount of pale-colored solid, and the volume was further reduced to 50 mL. A dark blue-black solid precipitated upon standing overnight at room temperature and was separated. The dark brown mother liquor was placed at 4 °C, in which yellow-brown crystals of **3** were isolated (0.6 g, 0.6 mmol, 35%). Anal. Calcd (found) for C$_{53}$H$_{94}$LiMn N$_3$O$_4$Si: 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). $\mu_{\mathrm{eff}} = 3.91\ \mu_{\mathrm{BM}}$.

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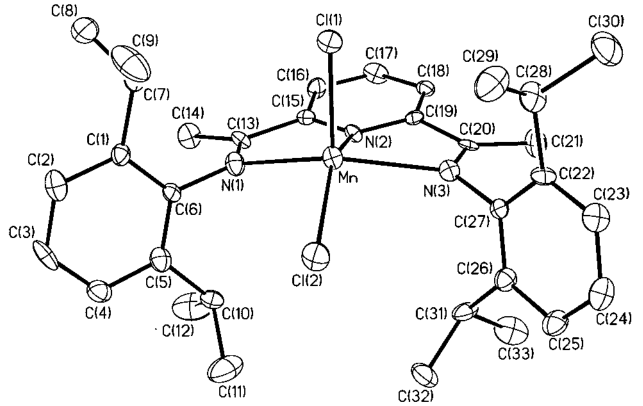

Figure 1. Thermal ellipsoid plot of **1**. Relevant bond distances and angles: Mn−Cl(1) = 2.350(3) Å, Mn−Cl(2) = 2.313(2) Å, Mn−N(1) = 2.333(5) Å, Mn−N(3) = 2.318(5) Å, Mn−N(2) = 2.201(5) Å, Cl(1)−Mn−Cl(2) = 119.68(9)°, Cl(1)−Mn−N(1) = 103.25(17)°, Cl(1)−Mn−N(2) = 98.93(17)°, Cl(1)−Mn−N(3) = 101.71(16)°, Cl(2)−Mn−N(2) = 141.36(18)°, N(1)−Mn−N(3) = 135.4(2)°, N(1)−Mn−N(2) = 69.71(19)°.

ramidal arrangement and with the coordination geometry defined by two chlorine atoms and the three nitrogen donor atoms of the tridentate ligand (Figure 1).

Complex **1** shares with the Fe(II) and Co(II) bis(imino)pyridine analogues the same geometry and the high-spin electronic configuration. Thus, it is at least surprising that **1** *does not* exhibit ethylene polymerization activity upon activation with methylalumoxane (Mn:Al 1:1000) or other cocatalysts and under standard reaction conditions (1 atm of ethylene at room temperature). The high-spin d^5 electronic configuration (μ_{eff} = 5.74 μ_{BM}) of manganese is obviously responsible for the lack of activity by either preventing alkylation of the manganese center by the Al or, more likely, causing instability of the Mn-alkyl function. In an attempt to probe this second possibility, complex **1** was treated in separate experiments with MeLi with different stoichiometric ratios. The reaction with 2 equiv of MeLi afforded the monovalent {2,6-bis[2,6-(i-Pr)$_2$PhN=C(Me)]$_2$(C$_5$H$_3$N)}-MnCH$_3$ (**2**) derivative (Figure 2).[9] The complex was obtained in reasonable yield and displays the same d^6 high-spin electronic configuration observed for the Fe(II) complex. The same reaction with 4 equiv of MeLi afforded instead a quantitative deposition of a very bright mirror of metallic manganese.

Complex **2** has a distorted square planar geometry[10] with the central Mn atom surrounded by three coordinating nitrogen atoms from the bis(imino)pyridine ligand and one methyl group (Figure 2) and with the methyl group substantially deviating from the plane defined by the metal and the three ligand donor atoms.

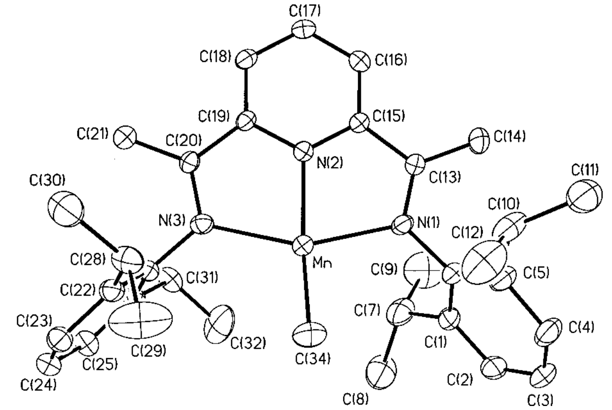

Figure 2. Thermal ellipsoid plot of **2**. Relevant bond distances and angles: Mn−C(34) = 2.086(7) Å, Mn−N(1) = 2.175(3) Å, Mn−N(2) = 2.039 Å, Mn−N(3) = 2.160(3) Å, C(34)−Mn−N(1) = 104.8(2)°, C(34)−Mn−N(2) = 163.3(3)°, C(34)−Mn−N(3) = 110.6(2), N(1)−Mn−N(3) = 143.09(13)°, N(1)−Mn−N(2) = 74.18(12)°, N(2)−Mn−N(3) = 74.96(12)°.

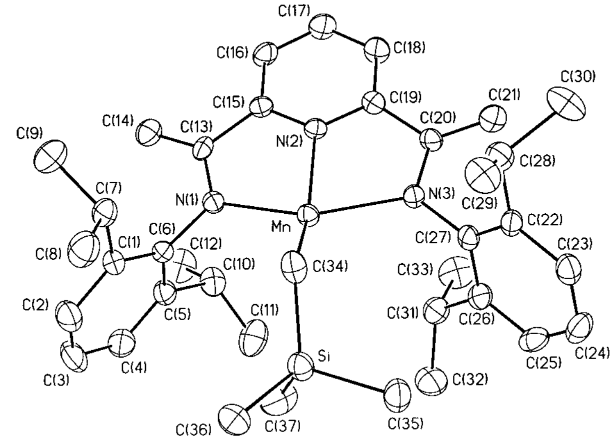

Figure 3. Thermal ellipsoid plot of **3**. Relevant bond distances and angles: Mn−C(34) = 2.147(6) Å, Mn(N(1) = 2.138(4) Å, Mn−N(2) = 2.185(4) Å, Mn−N(3) = 2.160(4) Å, C(34)−Mn−N(1) = 109.6(2)°, C(34−Mn−N(2) = 151.5(2)°, C(34)−Mn−N(3) = 109.0(2)°, N(1)−Mn−N(3) = 141.86(17)°, N(1)−Mn−N(2) = 72.94(17)°, N(2)−Mn−N(3) = 73.08(17)°.

The reduction of the metal center is not particularly surprising given that Mn(II) complexes are used as radical initiators for radical polymerization processes.[11] Thus, it is tempting to propose a methyl radical elimination mechanism for reducing the manganese metal center to the +1 state. However, a very similar reaction conducted with Me$_3$SiCH$_2$Li afforded instead the *zero-valent* [{[2,6-(i-Pr)$_2$PhN=C(Me)]$_2$(C$_5$H$_3$N)}Mn(CH$_2$SiMe$_3$)]-[Li(OEt$_2$)$_4$] (**3**).[9] This species displays a magnetic moment consistent with the presence of three unpaired electrons on a tetracoordinated high-spin d^7 zerovalent manganese [μ_{eff} = 3.91 μ_{B}]. The coordination geometry is remarkably similar to **2** (Figure 3)[10] and, besides the presence of the Me$_3$SiCH$_2$ group replacing the methyl and of a Li(ether)$_4$ cation in the lattice, is the same

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(10) Crystal data. **1:** C$_{33}$H$_{43}$Cl$_2$MnN$_3$, M_{w} = 607.54, triclinic, $P\bar{1}$, a = 8.741(2) Å, b = 9.793(2) Å, c = 20.843(5) Å, α = 82.333(4)°, β = 88.424(5)°, γ = 65.987(4)°, V = 1614.5(7) Å^3, Z = 2, T = 203 K, F_{000} = 642, R = 0.0564, wR2 = 0.1463, GoF = 1.039. **2:** C$_{33}$H$_{46}$MnN$_3$, M_{w} = 927.28, monoclinic, $P2(1)/n$, a = 14.159(3) Å, b = 8.775(2) Å, c = 25.300(5) Å, β = 94.784(4)°, V = 3132.4(10) Å^3, Z = 4, T = 203 K, F_{000} = 1184, R = 0.0618, wR2 = 0.1582, GoF = 1.043. **3:** C$_{53}$H$_{94}$N$_3$-MnLiSiO$_4$, M_{w} = 927.28, monoclinic, $P2(1)/c$, a = 19.039(3) Å, b = 15.776(3) Å, c = 18.905(3) Å, β = 90.810(4)°, V = 5677.7(16) Å^3, Z = 4, T = 203 K, F_{000} = 2028, R = 0.0615, wR2 = 0.1415, GoF = 1.024.

(11) See for example: (a) Sherigara, B. S.; Rai, S. K.; Shivakumar, K. *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.* **2001**, *40A(1)*, 46. (b) Danilovtseva, E. N.; Annenkov, V. V.; Skushnikova, A. I.; Svyatkina, L. I. *J. Appl. Polym. Sci.* **2000**, *78*, 101. (c) Anisimov, Y. N.; Kolodyazhnyi, A. V.; Grekhova, O. B. *Russ. J. Gen. Chem.* **1999**, *69*, 1784. (d) Rai, S. K.; Shivakumar, K.; Sherigara, B. S. *Eur. J. Polym.* **2000**, *36*, 1339. (e) Sherigara, B. S.; Rai, S. K.; Shivakumar, K. *J. Indian Counc. Chem.* **1999**, *16*, 29. (f) Jocheska, N.; Petrov, G.; Janevski, A.; Sebenik, A. *Eur. Polym. J.* **1996**, *32*, 209. (g) Cakmak, I. *Angew. Makromol. Chem.* **1995**, *224*, 49. (h) Sumi, K.; Kimura, M.; Nakamura, I. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1243.

distorted square planar. The Mn atom is coplanar with the three nitrogen donor atoms and has the alkyl group significantly deviating from planarity. The Mn−C bond distance is longer than in **2**, as could be expected given the difference in oxidation state.

The transformation of **1** to **3** is a two-electron process and can hardly be explained in terms of Mn−C bond homolytic cleavage given the fact that one alkyl residue remains attached to the metal. The reaction can be more easily rationalized in terms of the same mechanism responsible for the previously reported reduction of the trivalent vanadium derivative, and that implies alkylation/dealkylation of the pyridine ring.[7] However, this obviously does not apply to **2**, whose formation is only a one-electron process. In any event, the fact that reduction was independently observed with both vanadium and manganese strongly suggests that perhaps a similar reduction may occur also in the case of Fe and Co derivatives where, however, the low-valent alkyl are not necessarily catalytically inactive.[12] Should this point be confirmed, it will open new interesting perspectives for further research.

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Supporting Information Available: Complete listing of structural parameters and crystal data for the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) While this work was in progress, a reduction of the Co derivative affording a zerovalent dinitrogen complex was reported: (a) Gibson, V. C.; Humphries, M.; Tellmann, K.; Wass, D.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 2252. (b) Kooistra, T. M.; Knijnenburg, Q.; Smits, J. M. M.; Horton, A. D.; Budzelaar, P. H. M.; Gal, A. W. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 4719.