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The Synthesis, Structure, and Reactivity of Phenyl Tris(3-*tert*-butylpyrazolyl)borato Iron Methyl, [PhTp$^{Bu^t}$]FeMe: Isolation of a Four-Coordinate Monovalent Iron Carbonyl Complex, [PhTp$^{Bu^t}$]FeCO

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The organometallic chemistry of iron is dominated by cyclopentadienyl derivatives which satisfy the 18-electron rule.[1] As frequently cited analogues of cyclopentadienyl, tris(pyrazolyl)hydroborato ligands[2] form a variety of complexes that have counterparts in the classic cyclopentadienyl−iron system; for example, [Tp]$_2$Fe is an analogue of ferrocene, Cp$_2$Fe, while [Tp]Fe(CO)$_2$X derivatives are analogues of CpFe(CO)$_2$X. In this paper, we demonstrate that the sterically demanding phenyl tris(3-*tert*-butylpyrazolyl)borato ligand enables isolation of iron complexes which have no counterparts in the cyclopentadienyl−iron system, such as low-electron-count, four-coordinate methyl and carbonyl derivatives.

Trofimenko's tris(pyrazolyl)hydroborato ligand system, [Tp$^{RR'}$], has been used extensively in synthesizing and studying the reactivity of four-coordinate alkyl derivatives of the pre- and post-transition metals, e.g., [Tp$^{RR'}$]MR (M = Be, Mg, Zn, Cd).[2b] By comparison, however, [Tp$^{RR'}$] ligands have not yet been widely employed for studying four-coordinate alkyl complexes of the transition metals. For this reason, we have started to explore the organometallic chemistry of iron supported by such ligands. In this regard, [Tp$^{Bu^t}$]FeCl, the first four-coordinate tris(pyrazolyl)hydroborato iron complex,[3] which we previously reported, has the potential for being a useful precursor for the synthesis of organometallic derivatives. The possibility of ligand degradation via reaction at the B−H bond, however, prompted us to investigate the modified ligand [PhTp$^{Bu^t}$][4] in which the hydride substituent is replaced by phenyl. Indeed, this modified ligand allows facile isolation of the iron methyl complex [PhTp$^{Bu^t}$]FeMe via reaction of [PhTp$^{Bu^t}$]FeCl with either Me$_2$Mg or MeLi (Scheme 1). [PhTp$^{Bu^t}$]FeMe is a colorless paramagnetic complex, the methyl group of which is characterized by a signal at 1453 ppm in the ^{2}H NMR spectrum of the d_3-isotopomer at room temperature.[5] The molecular structure of [PhTp$^{Bu^t}$]FeMe has been determined by X-ray diffraction (Figure 1), and the Fe−CH$_3$ bond length of 2.079(3) Å is comparable to the mean value of 2.046 Å for structurally characterized iron methyl complexes in the Cambridge Structural Database.[6] As a 14-electron four-coordinate complex belonging to the classification [FeL$_2$X$_2$],[7] [PhTp$^{Bu^t}$]FeMe provides a marked contrast with other structurally characterized iron methyl complexes which typically belong to the 18-electron class [FeL$_4$X$_2$], as exemplified by [Cp^R]Fe(CO)(L)Me[1] and *cis*-(dmpm)$_2$FeMe$_2$.[8] The closely related allyl and benzyl complexes [Tp$^{Pr^i_2}$]FeR (R = CH$_2$CHCH$_2$, CH$_2$-*p*-Tol)[9,10] have also been recently reported.[11]

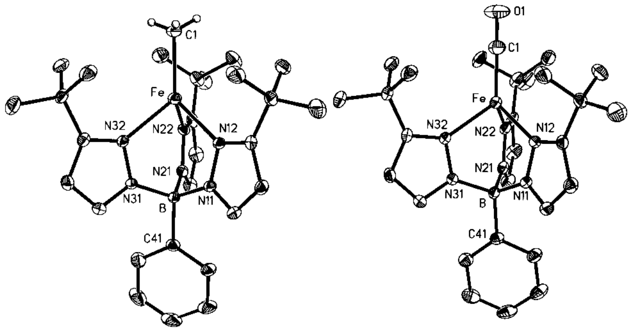
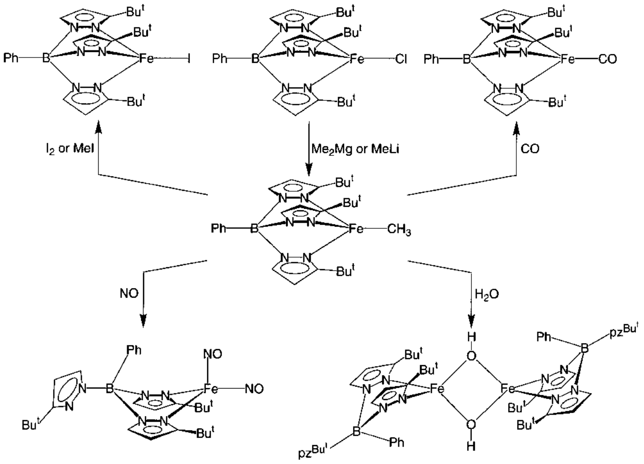


Figure 1. Molecular structures of [PhTp$^{Bu^t}$]FeCH$_3$ (left) and [PhTp$^{Bu^t}$]FeCO (right).

Scheme 1



The iron methyl group is highly reactive toward a variety of substrates, as illustrated in Scheme 1. For example, both I$_2$ (room temperature) and MeI (120 °C) react with [PhTp$^{Bu^t}$]FeMe to yield the iodide complex [PhTp$^{Bu^t}$]FeI. Much more interesting, however, is the reaction of [PhTp$^{Bu^t}$]FeMe with CO (120 °C) which yields the novel 15-electron four-coordinate monovalent iron carbonyl complex [PhTp$^{Bu^t}$]FeCO.[12] The latter complex has been structurally determined by X-ray diffraction (Figure 1) and is

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[1] See, for example: Kerber, R. C. In *Comprehensive Organometallic Chemistry II*.; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Volume 7, Chapter 2.

[2] For recent reviews, see: (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980. (b) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291−393.

[3] Gorrell, I. B.; Parkin, G. *Inorg. Chem.* **1990**, *29*, 2452−2456.

[4] Li[PhTp$^{Bu^t}$] is prepared via reaction of Li[BPhH$_3$] with Hpz$^{Bu^t}$, from which [PhTp$^{Bu^t}$]FeCl is obtained by metathesis with FeCl$_2$.

[5] The ^{2}H NMR chemical shift of the CD$_3$ group is highly temperature-dependent, moving to a value of 1213 ppm at 70 °C. For other uses of ^{2}H NMR in characterizing paramagnetic iron complexes, see: Stokes, S. L.; Davis, W. M.; Odom, A. L.; Cummins, C. C. *Organometallics* **1996**, *15*, 4521−4530.

[6] CSD Version 5.14. 3D Search and Research Using the Cambridge Structural Database, Allen, F. H.; Kennard, O. *Chemical Design Automation News* 1993, Vol. 8 (1), pp 1 and 31−37.

[7] For the use of this classification system for covalent compounds, see: Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127−148.

[8] Wong, W. K.; Chiu, K. W.; Wilkinson, G.; Howes, A. J.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1985**, *4*, 603−614.

[9] Akita, M.; Shirasawa, N.; Hikichi, S.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1998**, 973−974.

[10] 14-electron iron alkyls of the class [FeL$_2$X$_2$] also include the dialkyls (dippe)FeR$_2$ (R = CH$_2$SiMe$_3$, CH$_2$CMe$_3$, CH$_2$CMe$_2$Ph, CH$_2$Ph, CH$_2$Tol),[10a] and a variety of heteroatom substituted metallacycle derivatives.[10b,c] (a) Hermes, A. R.; Girolami, G. S. *Organometallics* **1987**, *6*, 763−768. (b) Leung, W.-P.; Lee, H. K.; Weng, L.-H.; Luo, B.-S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1996**, *15*, 1785−1792. (c) Hursthouse, M. B.; Izod, K. J.; Motevalli, M.; Thornton, P. *Polyhedron* **1996**, *15*, 133−145.

[11] Other examples of four-coordinate alkyl complexes of the *d*- and *f*-block elements supported by tris(pyrazolyl)hydroborato ligation include [Tp$^{Bu^t,Me}$]CrR (R = Et, Ph, CH$_2$SiMe$_3$)[11a] and [Tp$^{Bu^t,Me}$]YbCH(SiMe$_3$)$_2$.[11b] (a) Kersten, J. L.; Kucharczyk, R. R.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Chem. Eur. J.* **1997**, *3*, 1668−1674. (b) Hasinoff, L.; Takats, J.; Zhang, A. H.; Rogers, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 8833−8834.

[12] Related tris(pyrazolyl)hydroborato cobalt carbonyl complexes, [Tp^{Np}]CoCO, [Tp$^{Bu^t,Me}$]CoCO, and {[Tp$^{Bu^t,Me}$]Co(μ-CO)}$_2$Mg(THF)$_4$, have been reported. See: Detrich, J. L.; Konecny, R.; Vetter, W. M.; Doren, D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1996**, *118*, 1703−1712.

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characterized by an Fe−CO bond length of 1.789(3) Å[13] and a ν(CO) stretching frequency of 1907 cm^{-1} [ν(^{13}CO) = 1863 cm^{-1}]. [PhTp$^{\mathrm{Bu^t}}$]FeCO is of interest not only because its cyclopentadienyl counterpart [CpFeCO] is unstable and has not been isolated,[14] but also because analogous complexes have not yet been isolated using other [Tp$^{\mathrm{RR'}}$] ligands; specifically, only 18-electron six-coordinate iron carbonyl complexes, illustrated by [Tp]Fe(CO)$_2$[C(O)Me],[15] [Tp]Fe(CO)[η^2-CF$_2$C(O)N$^{\mathrm{Pr^i_2}}$],[16] and [Tp$^{\mathrm{Pr^i_2}}$]Fe(CO)$_2$[C(O)CH$_2$-*p*-Tol],[9] have previously been structurally authenticated.[17] Moreover, [PhTp$^{\mathrm{Bu^t}}$]FeCO is of interest since Fe(I) is a most uncommon valence state for iron.[18] Undoubtedly, the ability to isolate the four-coordinate 15-electron carbonyl complex [PhTp$^{\mathrm{Bu^t}}$]FeCO is a consequence of the steric protection provided by the bulky *tert*-butyl substituents.[19]

In addition to the above reactions in which the [PhTp$^{\mathrm{Bu^t}}$] ligand retains tridentate coordination, there is also a class of reactions which is characterized by the formation of products in which the [PhTp$^{\mathrm{Bu^t}}$] ligand adopts a bidentate coordination mode. For example, rather than yield a terminal hydroxide derivative, [PhTp$^{\mathrm{Bu^t}}$]FeMe reacts with H$_2$O to give a dinuclear complex {[η^2-PhTp$^{\mathrm{Bu^t}}$]Fe(μ-OH)}$_2$ in which one of the pyrazolyl donors of each ligand is displaced as a result of the hydroxide bridges. The molecular structure of {[η^2-PhTp$^{\mathrm{Bu^t}}$]Fe(μ-OH)}$_2$[20] is of interest since it is unlike those of other tris(pyrazolyl)borato iron hydroxide complexes, namely the four-coordinate terminal hydroxide complex [Tp$^{\mathrm{Bu^t,Pr^i}}$]FeOH[21] and the dinuclear five-coordinate bridging hydroxide complex {[Tp$^{\mathrm{Pr^i_2}}$]Fe(μ-OH)}$_2$[22] which retain tridentate coordination of the [Tp$^{\mathrm{Pr^i_2}}$] ligand. Correspondingly, the average Fe−OH bond length in {[η^2-PhTp$^{\mathrm{Bu^t}}$]Fe(μ-OH)}$_2$ [1.98(1) Å] is intermediate between those in [Tp$^{\mathrm{Bu^t,Pr^i}}$]FeOH [1.830(8) Å][21] and {[Tp$^{\mathrm{Pr^i_2}}$]Fe(μ-OH)}$_2$ [2.03(1) Å].[22]

A further example of a reaction of [PhTp$^{\mathrm{Bu^t}}$]FeMe which involves a tridentate-to-bidentate conversion of the [PhTp$^{\mathrm{Bu^t}}$] ligand is that with NO to give the 17-electron dinitrosyl complex [η^2-PhTp$^{\mathrm{Bu^t}}$]Fe(NO)$_2$ (Scheme 1).[23] The molecular structure of [η^2-PhTp$^{\mathrm{Bu^t}}$]Fe(NO)$_2$ has been determined by X-ray diffraction,[24] and the Fe−NO bond lengths of 1.688(3) Å and 1.694(3) Å are comparable to the mean value of 1.663 Å for iron nitrosyl complexes listed in the Cambridge Structural Database.[6] [η^2-PhTp$^{\mathrm{Bu^t}}$]Fe(NO)$_2$ is also characterized by ν(NO) absorptions at 1811 and 1728 cm^{-1} in the IR spectrum.

In summary, the four-coordinate iron methyl complex [PhTp$^{\mathrm{Bu^t}}$]FeMe, synthesized by reaction of [PhTp$^{\mathrm{Bu^t}}$]FeCl with Me$_2$Mg, is a versatile precursor to an array of tris(pyrazolyl)borato derivatives, including the novel monovalent iron carbonyl complex [PhTp$^{\mathrm{Bu^t}}$]FeCO.

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Supporting Information Available: Experimental and crystallographic data for all new complexes (53 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[13] For comparison, the mean Fe−CO bond length for complexes in the Cambridge Structural Database is 1.778 Å. See ref 6.

[14] In this regard, photolysis of [CpFe(CO)(μ-CO)]$_2$ in a 3-methylpentane matrix yields the transient dimer [CpFe(CO)]$_2$, which exists in a triplet form with terminal carbonyl ligands, and the more stable singlet with bridging carbonyl ligands. See: (a) Vitale, M.; Archer, M. E.; Bursten, B. E. *J. Chem. Soc., Chem. Commun.* **1998**, 179−180. (b) Kvietok, F. A.; Bursten, B. E. *J. Am. Chem. Soc.* **1994**, *116*, 9807−9808.

[15] Cotton, F. A.; Frenz, B. A.; Shaver, A. *Inorg. Chim. Acta* **1973**, *7*, 161−169.

[16] Anderson, S.; Hill, A. F.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 266−267.

[17] [Tp]Fe(CO)(PMe$_3$)[C(O)Me] has also been reported, but not structurally characterized. See: Bellachioma, G.; Cardaci, G.; Gramlich, V.; Macchioni, A., Pieroni, F.; Venanzi, L. M. *J. Chem. Soc., Dalton Trans.* **1998**, 947−951.

[18] Several 17-electron monovalent carbonyl complexes, e.g., [(R$_2$C)$_x$Fe(CO)$_y$(PR$'_3$)$_z$]$^+$ ($x + y + z = 5$; R$_2$C = [MeNCH$_2$CH$_2$N(Me)]C), [C$_6$H$_4$(AsMe$_2$)$_2$]Fe(CO)$_2$I, and [Fe(CO)$_3$(PR$_3$)$_2$]$^+$ have been described in the literature, but none have been structurally authenticated by X-ray diffraction. See: Lappert, M. F.; MacQuitty, J. J.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1981**, 1583−1592 and references therein.

[19] Four-coordinate iron carbonyl complexes typically adopt 18-electron configurations, e.g., (Ph$_3$P)Fe(CO)(NO)$_2$, [Fe(CO)$_3$(NO)]$^-$, and [Fe(CO)$_4$]$^{2-}$. See, for example: Albano, V. G.; Araneo, A.; Bellon, P. L.; Ciani, G.; Manassero, M. *J. Organomet. Chem.* **1974**, *67*, 413−422.

[20] Selected metrical data for {[η^2-PhTp$^{\mathrm{Bu^t}}$]Fe(μ-OH)}$_2$: d(Fe−OH) = 1.978(4) Å and 1.974(10) Å; d(Fe···Fe) = 3.075 Å; Fe−O−Fe′ 102.2(3)°; O−Fe−O 77.8(3)°.

[21] Hikichi, S.; Ogihara, T.; Fujisawa, K.; Kitajima, N.; Akita, M.; Moro-oka Y. *Inorg. Chem.* **1997**, *36*, 4539−4547.

[22] Kitajima, N.; Tamura, N.; Tanaka, M.; Moro-oka, Y. *Inorg. Chem.* **1992**, *31*, 3342−3343.

[23] Four coordinate 17-electron iron nitrosyl compounds of the class [Fe(NO)$_2$LX] are relatively common, e.g., (Ph$_3$P)XFe(NO)$_2$ (X = Cl, Br, I). See, for example: Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992.

[24] [PhTp$^{\mathrm{Bu^t}}$]FeMe is monoclinic, $P2_1/n$ (No. 14), a = 10.4777(5) Å, b = 17.4872(8) Å, c = 16.1405(7) Å, β = 93.293(1)°, V = 2952.5(2) Å^3, Z = 4, and T = 203 K. [PhTp$^{\mathrm{Bu^t}}$]FeCO is monoclinic, $P2_1/n$ (No. 14), a = 9.9106(6) Å, b = 17.982(1) Å, c = 16.348(1) Å, β = 92.956(1)°, V = 2905.5(3) Å^3, Z = 4, and T = 203 K. [PhTp$^{\mathrm{Bu^t}}$]FeCl·(C$_7$H$_8$) is triclinic, $P\bar{1}$ (No. 2), a = 11.4672(6) Å, b = 15.3337(8) Å, c = 21.457(1) Å, α = 71.618(1), β = 82.672(1)°, γ = 82.957(1)°, V = 3537.4(3) Å^3, Z = 4, and T = 203 K. [PhTp$^{\mathrm{Bu^t}}$]FeI is monoclinic, $P2_1/n$ (No. 14), a = 9.8183(4) Å, b = 18.8196(8) Å, c = 15.8495(7) Å, β = 91.542(1)°, V = 2927.6(2) Å^3, Z = 4, and T = 203 K. [η^2-PhTp$^{\mathrm{Bu^t}}$]Fe(NO)$_2$ is monoclinic, $P2_1/n$ (No. 14), a = 10.6522(5) Å, b = 12.1150(5) Å, c = 24.059(1) Å, β = 102.237(1)°, V = 3034.3(2) Å^3, Z = 4, and T = 203 K. {[η^2-PhTp$^{\mathrm{Bu^t}}$]Fe(μ-OH)}$_2$·(C$_5$H$_{12}$) is monoclinic, $P2/n$ (No. 13), a = 12.0432(6) Å, b = 11.5356(6) Å, c = 22.709(1) Å, β = 95.659(1)°, V = 3139.5(3) Å^3, Z = 2, and T = 203 K.