Formation of the 1,4-Diazabutadien-2-yl Complex [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] through Methylation of a Manganese(−I) Isonitrilate

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Alkylation of [Mn(CNPh*)$_5$]$^-$ with CH$_3$I gives the 1,4-diazabutadien-2-yl complex [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] (**2**) in a 30% yield, as established by a single-crystal X-ray diffraction study. The same product can be obtained in poor yield when CH$_3$OSO$_2$CF$_3$ is used as the alkylating agent, and use of ethyl iodide gives the corresponding ethyl complex [Mn(CNPh*)$_4${C(=NPh*)C(CH$_2$CH$_3$)=N(Ph*)}] (**3**). It is proposed that the first step in the formation of **2** is alkylation at manganese: transient [Mn(CNPh*)$_5$CH$_3$] is then converted into an iminoacyl complex by isonitrile/alkyl insertion. Insertion of a second isonitrile into the metal−iminoacyl bond leads to the 1,4-diazabutadien-2-yl complex. The addition of free CNPh* to the reaction solution leads to only a modest increase in the yield of **2**, but the importance of exogenous isonitrile is supported by the formation of [Mn(CN^{t}Bu)(CNPh*)$_3${C(=NPh*)C(CH$_3$)=N(Ph*)}] (**4**), in which 1 equiv of CN^{t}Bu is coordinated to Mn, when CN^{t}Bu is added to a solution of **1**$^-$ before reaction with CH$_3$I.

Introduction

Recent reports from our laboratory on the chemistry of isonitrilates,[1] guided by the obvious analogy between isonitrilates and carbonylmetalates, have established close structural and reactivity parallels between these two classes of molecules. Structural parallels include those between the tetrahedral Co(−I) complex [Co(CNPh*)$_4$]$^-$ (Ph* = 2,6-(CH$_3$)$_2$C$_6$H$_4$)[2] and the isoelectronic carbonylmetalate [Co(CO)$_4$]$^-$ [3] and between the trigonal bipyramidal Mn(−I) complex [Mn(CNPh*)$_5$]$^-$ [4] and [Mn(CO)$_5$]$^-$;[5] reactivity parallels include the derivatization of both [Co(CNPh*)$_4$]$^-$ and [Mn(CNPh*)$_5$]$^-$ by electrophilic addition of Ph$_3$SnCl in a manner similar to that used by our group[6] and by Ellis[7] to characterize highly reactive carbonylmetalates and the use of both Ph$_3$SnCl addition and the formation of metallocycles from α,ω-dihaloalkanes to establish the existence of the Ru(−II) isonitrilates [Ru(CNR)$_4$]$^{2-}$ (R = Ph* and ^{t}Bu).[8]

More recently we have begun to examine areas in which the parallels between isonitrilates and carbonylmetalates do not hold. We now wish to report, as summarized in Scheme 1, examples in which the combination of the high nucleophilicity of an isonitrilate with the high propensity of isonitriles to undergo insertion reactions[9,10] results in alkylation-induced coupling of two isonitrile ligands to form a structurally characterized 1,4-diazabutadien-2-yl complex of manganese similar to those previously reported by Alexander as the products of PdO-catalyzed double isonitrile insertion into manganese−aryl bonds.[11]

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of nitrogen by means of standard Schlenk techniques or a Vacuum Atmospheres Dry-lab glovebox unless otherwise noted. Glassware was oven-dried or flamed under vacuum. Celite 545 (Fisher) was oven dried (24 h) prior to use. Tetrahydrofuran (THF) was first dried over sodium wire for at least 12 h and then distilled from molten potassium. Pentane was pretreated with 5% nitric acid/sulfuric acid and then potassium carbonate and distilled from calcium hydride. All solvents were freshly distilled and deoxygenated immediately prior to use. The following reagents were purchased from commercial sources: methyl iodide (Aldrich), *tert*-butyl isocyanide (Aldrich), ethyl iodide (Aldrich), and 2,6-dimethylphenyl isocyanide (Fluka).

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(1) Homoleptic isonitrile complexes of metals in negative oxidation states.

(2) (a) Warnock, G. F.; Cooper, N. J. *Organometallics* **1989**, *8*, 1826. (b) Leach, P. A.; Geib, S. J.; Corella, J. A.; Warnock, G. F.; Cooper, N. J. *J. Am. Chem. Soc.* **1994**, *116*, 8566.

(3) (a) Klüfers, P. *Z. Kristallogr.* **1984**, *167*, 253. (b) Schussler, D. P.; Robinson, W. R.; Edgell, W. F. *Inorg. Chem.* **1974**, *13*, 153.

(4) Utz, T. L.; Leach, P. A.; Geib, S. J.; Cooper, N. J. *Chem. Commun.* **1997**, 847.

(5) (a) Frenz, B. A.; Ibers, J. A. *Inorg. Chem.* **1972**, *11*, 1109. (b) Heberhold, M.; Wehrmann, F.; Neugebauer, D.; Huttner, G. *J. Organomet. Chem.* **1978**, *152*, 329. (c) Balbach, B.; Baral, S.; Biersack, H.; Herrmann, W. A.; Labinger, J. A.; Scheidt, W. R.; Timmers, F. J.; Ziegler, M. L. *Organometallics* **1992**, *11*, 35. (d) Ben Laarab, H.; Chaudret, B.; Dahan, F.; Devillers, J.; Poilblanc, R.; Sabo-Etienne, S. *New J. Chem.* **1990**, *14*, 321. (e) Petz, W.; Weller, F. *Z. Naturforsch.* **1991**, *B46*, 297.

(6) Leong, V. S.; Cooper, N. J. *Organometallics* **1987**, *6*, 2000 and references therein.

(7) Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1.

(8) Corella, J. A.; Thompson, R. L.; Cooper, N. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 83.

(9) (a) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21. (b) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193. (c) Singleton, E.; Oosthuizen, M. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

(10) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

(11) Motz, P. L.; Alexander, J. J.; Ho, D. H. *Organometallics* **1989**, *8*, 2589.

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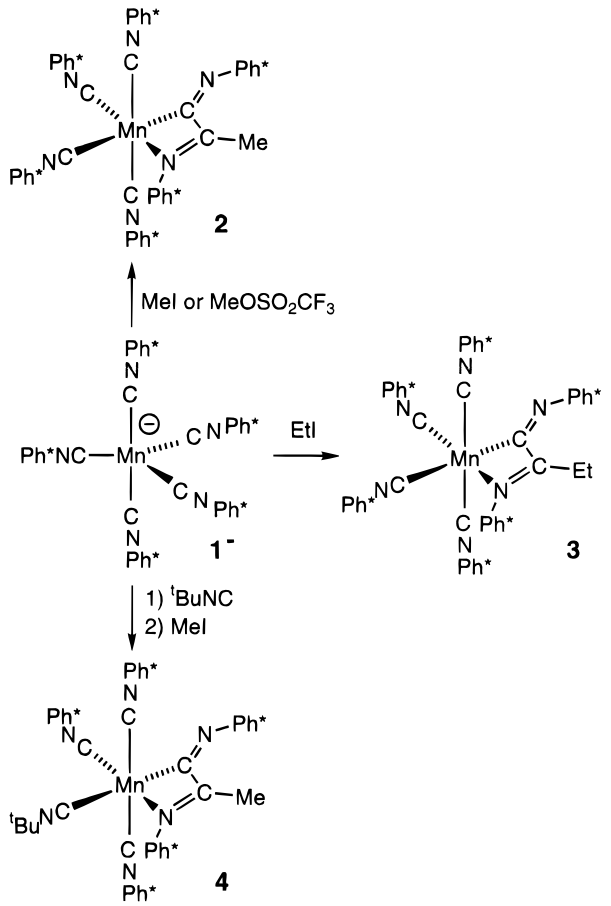
Scheme 1



Infrared spectra were recorded on a Perkin Elmer 783 grating spectrophotometer with polystyrene as an external standard. Solutions were loaded via small-bore steel cannula into 0.1-mm NaCl cells (Teflon seals) fitted with 5-mm septa. Nujol mulls were prepared under an inert atmosphere in a drybox and were loaded onto NaCl plates unless otherwise noted. All NMR spectra were recorded on a Bruker AF 300 spectrometer (^{1}H, 300.13 MHz). Deuterated solvents were purchased from Aldrich. Microanalyses were carried out by Atlantic Microlab, Inc., Norcross, GA. Samples of [K(18-C-6)][Mn(CNPh*)$_5$] were prepared as reported previously[4] and stored under nitrogen at −30 °C before use.

Preparation of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] (2) from CH$_3$I. To a blood red solution of [K(18-C-6)][Mn(CNPh*)$_5$] (0.10 g, 0.10 mmol) in 10 mL of THF was added neat CH_3I (7 μL, 0.16 mmol). The solution immediately underwent a color change to cherry red. After the solution had stirred for 1 h, the solvent was removed under reduced pressure without warming to give a red residue. The product was extracted with pentane, and concentration of the pentane solution followed by cooling to −78 °C yielded 0.025 g of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] (0.029 mmol, 30%) as red crystals. IR (Nujol, ν_{CN}): 2010 (w), 1955 (s) cm^{-1}. ^{1}H NMR (dichloromethane-d_2): δ 7.12−6.75 (m, 15 H, CN(CH$_3$)$_2$C$_6$H$_3$), 6.61 (d, 2 H, CN(CH$_3$)$_2$C$_6$H$_3$), 6.20 (t, 1 H, CN(CH$_3$)$_2$C$_6$H$_3$), 2.41 (s, 12 H, mutually *trans* CN(C*H*$_3$)$_2$C$_6$H$_3$), 2.37 (s, 6 H, CN(C*H*$_3$)$_2$C$_6$H$_3$), 2.34 (s, 6 H, CN(C*H*$_3$)$_2$C$_6$H$_3$), 1.97 (or 1.91) (s, 6 H, C{=N(C*H*$_3$)$_2$C$_6$H$_3$}C(CH$_3$)=N{(CH$_3$)$_2$C$_6$H$_3$}), 1.91 (or 1.97) (s, 6 H, C{=N(CH$_3$)$_2$C$_6$H$_3$}C(CH$_3$)=N{(C*H*$_3$)$_2$C$_6$H$_3$}), 1.84 (s, 3 H, C*H*$_3$). ^{13}C NMR (dichloromethane-d_2): δ 222.22 (s, 1 C, *C*N(CH$_3$)$_2$C$_6$H$_3$), 203.89 (s, 1 C, *C*N(CH$_3$)$_2$C$_6$H$_3$), 197.81 (s, 1 C, *C*N(CH$_3$)$_2$C$_6$H$_3$), 195.71 (s, 1 C, *C*N(CH$_3$)$_2$C$_6$H$_3$), 187.19 (or 154.5) (s, 1 C, *C*{=N(CH$_3$)$_2$C$_6$H$_3$}C(CH$_3$)=N{(CH$_3$)$_2$C$_6$H$_3$}), 154.5 (or 187.19) (s, 1 C, C{=N(CH$_3$)$_2$C$_6$H$_3$}*C*(CH$_3$)=N{(CH$_3$)$_2$C$_6$H$_3$}), 150.0−120.0 (m, 36 C, CN(CH$_3$)$_2$*C*$_6$H$_3$), 27−10 (m, 13 C, CN(*C*H$_3$)$_2$C$_6$H$_3$ and *C*H$_3$). Anal. Calcd for C$_{55}$H$_{57}$MnN$_6$: C, 77.1; H, 6.8; N, 9.8. Found: C, 76.5; H, 6.9; N, 9.3.

Preparation of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] from CH$_3$OSO$_2$CF$_3$. This reaction was carried out in a manner similar to that described above, except that 11 μL of a 0.01 mol L^{-1} solution of $CH_3OSO_2CF_3$ in THF (0.10 mmol, 1 equiv) was added to the solution of [K(18-C-6)][Mn(CNPh*)$_5$] in place of CH_3I. After recrystallization from pentane, this gave a 0.005 g yield (0.006 mmol, 6%) of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] (IR, ^{1}H NMR).

Preparation of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] in the Presence of Free CNPh*. This reaction was carried out in a manner similar to that described above, except that 0.023 g (0.18 mmol, 1.8 equiv) of CNPh* was added to the solution of [K(18-C-6)][Mn(CNPh*)$_5$] before the addition of CH_3I. After recrystallization from pentane, this gave a 0.027 g yield (0.032 mmol, 32%) of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] (IR, ^{1}H NMR).

Preparation of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_2$CH$_3$)=N(Ph*)}] (3). To a blood red solution of [K(18-C-6)][Mn(CNPh*)$_5$] (0.10 g, 0.10 mmol) in 10 mL of THF was added neat CH_3CH_2I (9 μL, 0.11 mmol). The solution immediately underwent a color change to cherry red and was allowed to stir for 30 min. The solvent was removed under reduced pressure at low temperature (<0 °C) to give a red residue, and the product was extracted with pentane. Concentration of the pentane solution under reduced pressure and reduction of the temperature to −78 °C gave 0.020 g of red crystals of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_2$CH$_3$)=N(Ph*)}] (0.023 mmol, 23%). IR (THF, ν_{CN}): 2057 (m), 1963 (s) cm^{-1}. ^{1}H NMR (dichloromethane-d_2): δ 7.04−6.72 (m, 15 H, CN(CH$_3$)$_2$C$_6$H$_3$), 6.62 (d, 2 H, CN(CH$_3$)$_2$C$_6$H$_3$), 6.19 (t, 1 H, CN(CH$_3$)$_2$C$_6$H$_3$), 2.42 (s, 12 H, CN(C*H*$_3$)$_2$C$_6$H$_3$), 2.40 (s, 6 H, CN(C*H*$_3$)$_2$C$_6$H$_3$), 2.38 (s, 6 H, CN(C*H*$_3$)$_2$C$_6$H$_3$), 2.22 (q, 2 H, C*H*$_2$CH$_3$), 1.94 (or 1.89) (s, 6 H, C{=N(C*H*$_3$)$_2$C$_6$H$_3$}C(CH$_2$CH$_3$)=C{N(CH$_3$)$_2$C$_6$H$_3$}), 1.89 (or 1.94) (s, 6 H, C{=N(CH$_3$)$_2$C$_6$H$_3$}C(CH$_2$CH$_3$)=C{N(C*H*$_3$)$_2$C$_6$H$_3$}), 1.17 (t, 2 H, CH$_2$C*H*$_3$). Anal. Calcd for C$_{56}$H$_{59}$MnN$_6$: C, 77.2; H, 6.8; N, 9.7. Found: C, 77.3; H, 7.0; N, 9.6.

Preparation of [Mn(CN^{t}Bu)(CNPh*)$_3${C(=NPh*)C(CH$_3$)=N(Ph*)}] (4). To a blood red solution of [K(18-C-6)][Mn(CNPh*)$_5$] (0.20 g, 0.20 mmol) in 10 mL of THF was added neat *tert*-butyl isocyanide (23 μL, 0.20 mmol). A neat aliquot of CH_3I (15 μL, 0.24 mmol) was added to the THF solution, immediately giving a cherry red colored solution. After the solution had stirred for 30 min, the THF was removed under reduced pressure and the residue extracted into pentane. Concentration of the pentane solution under reduced pressure, followed by recrystallization at −78°C, yielded 0.025 g of [Mn(CN^{t}Bu)(CNPh*)$_3${C(=NPh*)C(CH$_3$)=N(Ph*)}] (0.031 mmol, 16%) as a red solid. IR (THF, ν_{CN}): 2055 (s), 1950 (m, br) cm^{-1}. ^{1}H NMR (dichloromethane-d_2): δ 7.04−6.55 (m, 14 H, CN(CH$_3$)$_2$C$_6$H$_3$), 6.23 (t, 1 H, CN(CH$_3$)$_2$C$_6$H$_3$), 2.40 (m, 18 H, CN(C*H*$_3$)$_2$C$_6$H$_3$), 2.05 (or 1.96) (s, 6 H, C{=N(C*H*$_3$)$_2$C$_6$H$_3$}C(CH$_3$)=C{N(CH$_3$)$_2$C$_6$H$_3$}), 1.96 (or 2.05) (s, 6 H, C{=N(CH$_3$)$_2$C$_6$H$_3$}C(CH$_3$)=C{N(C*H*$_3$)$_2$C$_6$H$_3$}), 1.78 (s, 3 H, C*H*$_3$), 1.51 (s, 9 H, CNC(C*H*$_3$)$_3$). Anal. Calcd for C$_{51}$H$_{57}$MnN$_6$: C, 75.7; H, 7.1; N, 10.4. Found: C, 75.0; H, 7.4; N, 9.4.

X-ray Diffraction Study of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}]. Crystals of **2** suitable for crystallographic analysis were grown by slow diffusive mixing of pentane into a concentrated toluene solution of the product at −30 °C over

Table 1. Summary of Crystal Data, Data Collection, and Refinement Parameters for [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}]

Crystal Data	
formula	$C_{55}H_{57}MnN_6 \cdot 0.5C_5H_{12}$
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	12.586(12)
b, Å	14.341(10)
c, Å	16.047(12)
α, deg	68.08(5)
β, deg	69.53(7)
γ, deg	76.14(7)
V, Å^3	2497(3)
Z	2
ρ (calcd), g cm^{-3}	1.188
Data Collection	
μ, cm^{-1}	3.07
temp, °C	−65(2)
cryst dimens, mm	0.21 × 0.22 × 0.32
radiation	Mo Kα (λ = 0.710 73 Å), graphite-monochromated
diffractometer	Siemens P3
scan speed, deg min^{-1}	variable, 3−20
2θ scan range, deg	3.82 < 2θ < 45
scan technique	ω
data collected	$+h, \pm k, \pm l$
weighting factor, g	0.100
unique data	6537
standard reflns	3/197
Agreement Factors	
$R(F)$, % (based on 6537 data, $F_o > 4\sigma(F_o)$)	5.95
w$R(F^2)$, % (all data)	18.02
GOF (on F^2)	1.053
max peak, e Å^{-3}	0.440, −0.351
data/parameter	11.27
Δ/σ	0.001

a period of weeks. The crystals rapidly powdered when removed from the mother liquor, presumably as a consequence of loss of a volatile pentane of solvation from the crystal lattice (see below), but a suitable crystal was eventually mounted by coating it in Fluorolube and rapidly cooling the crystal to ca. −65 °C in a stream of cold N_2.

Axial photographs confirmed the crystal quality, and systematic absences did not reveal any crystal symmetry higher than triclinic. The centrosymmetric space group $P\bar{1}$ was chosen on the basis of E-values and confirmed by the successful solution and refinement of the structure. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with 18° ≤ 2θ ≤ 25°. Diffraction data were collected on a Siemens P3 diffractometer. Data collection parameters and other crystallographic data are summarized in Table 1. A semi-empirical absorption correction was applied to the diffraction data using the program XEMP. No decay was observed in three standard reflections during the data collection.

The structure was solved using the direct methods program TREF, which located the Mn atom. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and were refined anisotropically. The crystal contained a pentane molecule disordered about an inversion center. The molecule was modeled in two orientations, each with $^1/_2$ occupancy. Idealized atomic positions were calculated for all hydrogen atoms except those anticipated for pentane (d(C−H) = 0.96 Å, $U = 1.2U$ of the attached carbon atom). The final difference Fourier syntheses showed only a diffuse background (maximum contour 0.45 e/Å^3). Inspections of F_o vs F_c values and trends based upon sin θ, Miller indeces, and parity groups failed to reveal any systematic errors in the X-ray data. Atomic coordinates for **2** are listed in the Supporting Information, and selected bond lengths and angles are given in Table 2. All of the computer programs used in the data collection and refinement are contained in the Siemens program packages P3 and SHELXTL PLUS.[12]

Table 2. Selected Bond Lengths (Å) and Angles (deg) within [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}]

Mn−C(3)	1.802(5)	N(2)−C(2)	1.264(5)
Mn−C(5)	1.847(5)	N(2)−C(26)	1.409(6)
Mn−C(4)	1.849(5)	N(3)−C(3)	1.174(5)
Mn−C(6)	1.861(5)	N(3)−C(36)	1.371(6)
Mn−C(2)	2.020(4)	C(4)−N(4)	1.179(5)
Mn−N(1)	2.104(4)	N(4)−C(46)	1.386(6)
Mn−C(1)	2.564(5)	C(5)−N(5)	1.168(6)
C(1)−N(1)	1.272(5)	N(5)−C(56)	1.373(6)
C(1)−C(2)	1.468(6)	C(6)−N(6)	1.155(5)
C(1)−C(7)	1.484(6)	N(6)−C(66)	1.381(6)
N(1)−C(16)	1.414(6)		
C(3)−Mn−C(2)	99.5(2)	C(16)−N(1)−Mn	137.7(3)
C(5)−Mn−C(2)	161.0(2)	C(2)−N(2)−C(26)	119.6(3)
C(4)−Mn−C(2)	96.8(2)	N(2)−C(2)−C(1)	118.7(4)
C(6)−Mn−C(2)	86.0(2)	N(2)−C(2)−Mn	148.0(3)
C(3)−Mn−N(1)	163.6(2)	C(1)−C(2)−Mn	93.3(3)
C(5)−Mn−N(1)	97.1(2)	C(3)−N(3)−C(36)	169.1(4)
C(4)−Mn−N(1)	93.7(2)	N(3)−C(3)−Mn	175.8(4)
C(6)−Mn−N(1)	91.7(2)	N(4)−C(4)−Mn	170.8(4)
C(2)−Mn−N(1)	64.4(2)	C(4)−N(4)−C(46)	157.9(4)
N(1)−C(1)−C(2)	106.5(3)	N(5)−C(5)−Mn	175.8(4)
N(1)−C(1)−C(7)	126.7(4)	C(5)−N(5)−C(56)	175.6(5)
C(2)−C(1)−C(7)	126.7(4)	N(6)−C(6)−Mn	178.7(4)
C(1)−N(1)−C(16)	126.1(4)	C(6)−N(6)−C(66)	172.9(4)

Results and Discussion

Alkylation of [Mn(CNPh*)$_5$]$^-$ was examined by addition of 1 equiv of CH_3I to a blood red THF solution of [K(18-C-6)][Mn(CNPh*)$_5$] ([K(18-C-6)]**1**), prepared as previously reported by naphthalenide reduction of [Mn(CNPh*)$_5$Cl] at −78 °C.[4] This resulted in an immediate color change from blood red to cherry red, together with a shift in the IR bands assigned to the isonitrile ligands from 1920 and 1710 cm^{-1} to 2010 and 1955 cm^{-1}. This large shift is consistent with the formation of a product in which the isonitrile ligands are coordinated to a neutral metal center, and it was possible to isolate a nonpolar product which could be recrystallized from pentane. This material is not completely stable at ambient temperatures, and cherry red THF solutions acquire a greenish hue when left at room temperature for more than 30 min. It was, however, immediately clear from inspection of ^{1}H NMR spectra that this was not the simple methyl adduct [Mn(CNPh*)$_5$CH$_3$] which would be the product of an S_N2 addition of CH_3I to **1**$^-$, as expected if the reaction had paralleled the addition of CH_3I to [Mn(CO)$_5$]$^-$ to form [Mn(CO)$_5$CH$_3$].[13]

Structural Characterization of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] (2). Growing X-ray quality crystals of the methylation product was difficult, partly because of the limited stability of the material in solution at room temperature, but it was eventually determined that suitable crystals of a pentane solvate could be grown by slow diffusive mixing of pentane into a concentrated toluene solution of the product at −30 °C. A single-crystal diffraction study of the red blocks obtained in this way was carried out as described in the

(12) Sheldrick, G. M. *SHELXTL User's Manual, Issue 5.1*; Siemens: Madison, WI, 1994.

(13) (a) Clossen, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598. (b) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417.

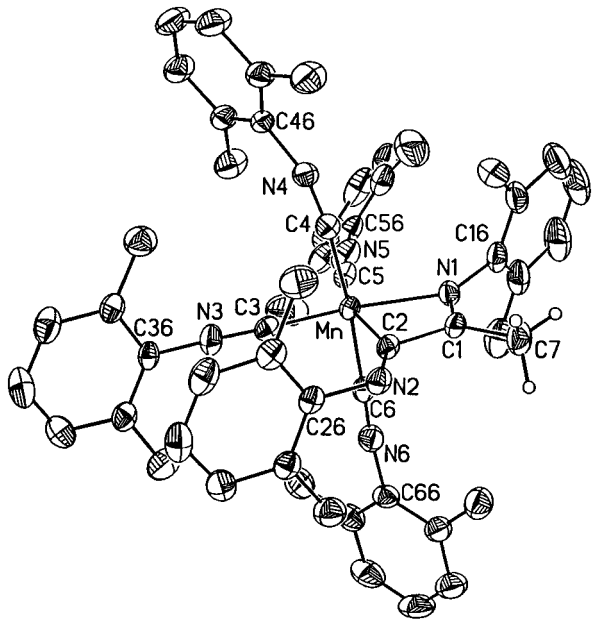


Figure 1. Molecular structure of [Mn(CNPh*)$_4${C(=N-Ph*)C(CH$_3$)=N(Ph*)}] (35% probability ellipsoids).

Experimental Section and established that the product is the 1,4-diazabutadien-2-yl complex [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] (**2**) with the molecular structure shown in Figure 1.

The manganese center in **2** has a distorted octahedral environment in which four coordination sites are occupied by terminal CNPh* ligands and the remaining sites are occupied by a 1,4-diazabutadien-2-yl unit formed by electrophilically induced coupling of two isonitriles and coordinated to the metal through C(2) and a donor bond from N(1). Three other examples of complexes containing 1,4-diazabutadien-2-yl ligands have been structurally characterized; the most closely related example is the Mn complex [Mn(CO)$_4${C(=N-*p*-tolyl)C(CH$_2$C$_6$H$_4$-*p*-X)=N(p-tolyl)}] (X = Cl, OMe) reported by Alexander and co-workers as the product of PdO-catalyzed double isonitrile insertion into a manganese−aryl bond,[11] and the earliest example is the iron complex [Fe(dppe)(CNPh)(I){C(=NPh)C(Me)=N(Ph)} prepared by Riera et al. by addition of MeI to [Fe(dppe)(CNPh)$_3$].[14] Filippou et al. have reported the formation of a molybdenum complex [Mo(η^5-C$_5$Me$_5$)(CO)$_2${C(=NR)C(Me)=N(Et)}] (X = Me, Et) containing the same functional group,[15] and Stone's group has observed the formation of this functional group by alkylation of [Fe(CN^{t}Bu)$_5$] to give [Fe(CN^{t}Bu)$_3$(I){C(=N^{t}Bu)C(CH$_3$)=N(CH$_3$)}], but did not characterize the species crystallographically.[16]

The metric parameters for the 1,4-diazabutadien-2-yl unit in **2** are consistent with this formulation. The C(1)−N(1) and C(2)−N(2) bond lengths of 1.273(5) and 1.266(5) Å, for example, are close to the C(sp^2)=N(2) average of 1.279 Å in the C*ar*−C=N−C# group, as cited in a statistical study,[17] and the C(1)−C(2) bond length of 1.468(6) Å is similar to the average value of 1.455 Å for conjugated C(sp^2)−C(sp^2) bonds.[17] The bond lengths of the 1,4-diazabutadien-2-yl ligand in **2** are also similar to those in those seen in earlier examples of this functional group. Alexander, for example, has reported[11] C=N bond lengths of 1.287(4) and 1.274(4) Å (for the in-ring and out-of-ring bonds, respectively) and a C−C bond length of 1.490(5) Å in [Mn(CO)$_4${C(=N-*p*-tolyl)C(CH$_2$C$_6$H$_4$-*p*-OMe)=N(*p*-tolyl)}], in good agreement with the corresponding bond lengths in **2**.

The sp^2 geometries of C(1), N(1), and C(2) would lead one to expect a planar geometry for the 1,4-diazabutadien-2-yl ligand, and indeed none of the constituent atoms are more than 0.03 Å out of the least-squares plane containing Mn, C(1), C(2), C(7), and N(1).

The Mn−C bond distances involving the terminal isonitrile ligands average 1.840 Å; this is somewhat shorter than the average values of 1.869 Å we have observed for the related Mn(0) isonitrile complex [Mn(CNPh*)$_5$SnPh$_3$],[18] but this difference is probably not chemically significant given the wide range from 1.802(5) to 1.861(5) Å covered by the Mn−C bond lengths in **2**. The average C≡N bond length of 1.169 Å in **2** is identical to that in [Mn(CNPh*)$_5$SnPh$_3$], but values again cover a wide range from 1.156(5) to 1.180(5) Å.

The C−N−C angles of the terminal isonitrile ligands cover a range of values from 157.9(4)° to 175.6(5)°. One of these angles is significantly outside the range from 170° to 180° considered typical of "linear" isonitrile ligands,[9b] but it is generally accepted that the variability in bend angles in typical isonitrile complexes reflects softness in the corresponding potential energy surfaces.[19] The variations in C−N−C angles in **2** are, therefore, probably a consequence of varying steric congestion, and the ligands can be best regarded as "electronically" linear. Thus, the most bent isonitrile ligand is that of the C(4) isonitrile, with a C(4)−N(4)−C(46) angle of 157.9 (4)°, and there is a close approach between the aryl group of this ligand and the disordered pentane of solvation.

NMR Spectra of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] (2). The molecular structure of **2** in Figure 1 provides a straightforward explanation for the initially surprising complexity of its NMR spectra, which contains six distinct resonances in the region from δ 2.8 to 1.8 assignable to methyl groups derived from the isonitrile ligands or the added methyl iodide. The peak at δ 1.84 can be straightforwardly assigned to the C(7) methyl group on the basis of its intensity, leaving resonances at δ 2.42, 2.37, 2.34, 1.97, and 1.91 with intensities corresponding to 4, 2, 2, 2, and 2 methyl groups, respectively. The distinct groupings of the chemical shifts suggests that the two higher field resonances can be assigned to the isonitrile-derived

(14) Riera, V.; Ruiz, J.; Jeannin, Y.; Philoche-Levisalles, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1591.
(15) Filippou, A. C.; Grünleitner, W.; Völkl, C.; Kiprof, P. *J. Organomet. Chem.* **1991**, *413*, 181.
(16) Bassett, J.-M.; Green, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1779.
(17) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* **1987**, S1.
(18) Utz, T. L.; Geib, S. J.; Cooper, N. J. Manuscript in preparation.
(19) (a) Kubiak, C. P. Personal communication. (b) Hoffmann, R. Personal communication.

methyl groups in the 1,4-diazabutadien-2-yl ligand, leaving those between δ 2.5 and 2.3 to be assigned to the terminal isonitrile ligands (c.f. δ 2.42 and 2.16 for the methyl groups of the *trans* and *cis* isonitrile ligands, respectively, in [Mn(CNPh*)$_5$SnPh$_3$]*).[18]

These assignments imply that two of the terminal isonitrile ligands in **2** are chemically equivalent, and this is consistent with the assignment of the resonance at δ 2.42 to the C(6) and C(4) isonitriles perpendicular to the 1,4-diazabutadien-2-yl plane. Assignments for the ^{13}C NMR spectra follow a similar argument.

The aryl region of both the ^{1}H and ^{13}C NMR spectra contain resonances of an intensity appropriate for the molecule as formulated, but the complex overlapping resonances could not be meaningfully assigned to individual aryl groups.

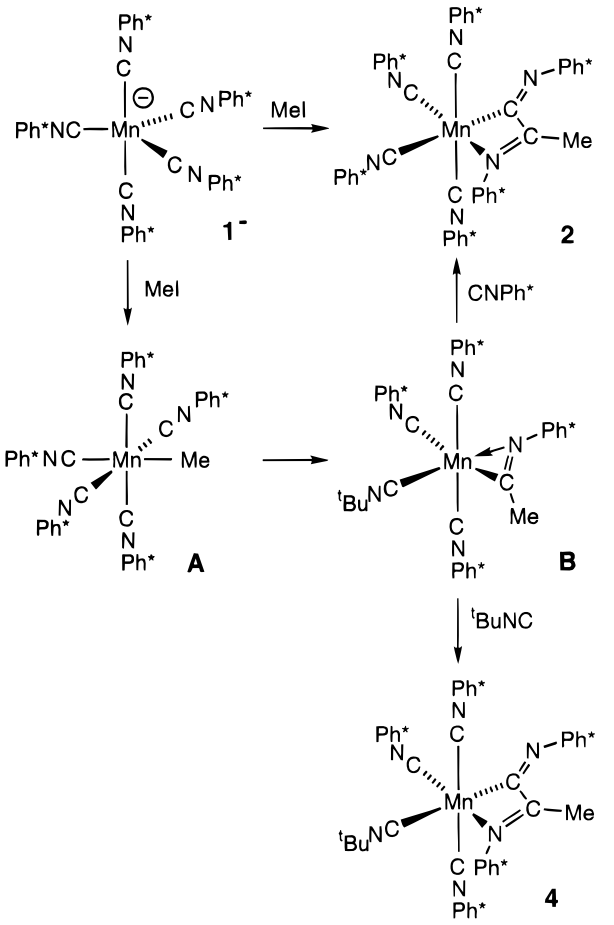
Generality of Alkylation-Induced Coupling of Isonitrile Ligands in [K(18-C-6)][Mn(CNPh*)$_5$]. We examined the use of sources of electrophilic alkyl groups other than methyl iodide to induce the coupling of isonitrile ligands in **1**$^-$ and have established that methyl iodide is not unique in its reactivity in this system. Methyl triflate, for example, will also react with **1**$^-$ to give **2**. The yield of the reaction is, however, disappointingly low, and methyl iodide remains the preferred reagent.

We have also established that the electrophilic coupling reaction can be carried out with higher alkyl groups. Reaction of **1**$^-$ with CH_3CH_2I in THF resulted in a color change from blood red to bright red, and we were able to isolate a 1,4-diazabutadien-2-yl complex analogous to **2**. IR and ^{1}H NMR spectra suggested the formulation of this complex as [Mn(CNPh*)$_4${C(=NPh*)C(CH$_2$CH$_3$)=N(Ph*)}] (**3**), as confirmed by combustion analysis.

Attempts to extend this chemistry to include the addition of more electrophilic alkyl halides such as $PhCH_2Br$ met with mixed success. The addition of 1 equiv of $PhCH_2Br$ to a THF solution of **1**$^-$ resulted in a color change from blood red to orange, and the resulting solution had an IR spectrum analogous to that of **2**. Crude ^{1}H NMR spectra were consistent with formulation of the product of this reaction as [Mn(CNPh*)$_4${C(=NPh*)C(CH$_2$Ph)=N(Ph*)}], but attempts to isolate pure samples were unsuccessful and precluded definitive characterization.

Mechanism of the Methylation-Induced Coupling of Isonitrile ligands in NMR Spectra of [Mn(CNPh*)$_4${C(=NPh*)C(CH$_3$)=N(Ph*)}] (2). The methylation-induced C−C coupling of the isonitrile ligands in **1**$^-$ to form a coordinated 1,4-diazabutadien-2-yl presents an interesting contrast with the extensive body of chemistry by Lippard[20] on electrophile-induced C−C coupling of isonitrile ligands in other low-valent complexes to form coordinated alkynes. In the isonitrilate system methylation occurs on one of the isonitrile carbons, while in the Lippard chemistry electrophiles add (in steps widely separated in the mechanistic sequence) to the nitrogen atoms of both of the isonitrile ligands incorporated in the coupled product so that the coupled product retains a higher degree of unsaturation at carbon.

Scheme 2



As in the case of other 1,4-diazabutadien-2-yl complexes, we propose that the ligand is formed (as shown in Scheme 2) by insertion of an isonitrile ligand into a metal−iminoacyl linkage, formed in situ by insertion of an isonitrile ligand into the Mn−alkyl bond of transient [Mn(CNPh*)$_5$CH$_3$] (**A**). The latter complex would be the isonitrile analog of [Mn(CO)$_5$CH$_3$], and the mild conditions under which **2** is formed suggests that isonitrile/alkyl insertion in **A** is more rapid than carbonyl/alkyl insertion in [Mn(CO)$_5$CH$_3$], the most extensively characterized substrate for migratory insertion.[21] Isonitrile/alkyl insertion reactions to form iminoacyl groups are well-established,[9,10] and formation of iminoacyl ligands is typically assisted by adoption of the η^2-iminoacyl coordination mode[10,22] so that an added donor ligand may not be required to drive the insertion.

Insertion of an added isonitrile into a metal−iminoacyl bond to give a 1,4-diazabutadien-2-yl complex has been directly observed by Filippou in the reaction of [Mo(η^5-C$_5$Me$_5$)(CO)$_2${η^2-C(=NEt)Me}] with alkyl isocyanides[15] and has been previously proposed by Alexander and co-workers to account for the formation of 1,4-diazabutadien-2-yl complexes following PdO-catalyzed substitution of *p*-tolyl isocyanide for carbonyl ligands in the benzylic manganese complexes [Mn(CO)$_5$CH$_2$C$_6$H$_5$-

(20) Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993**, *26*, 90.

(21) (a) Calderazzo, F.; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (b) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (c) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87.

(22) Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1977**, *99*, 6544.

p-X] (X = Cl, OMe).[11] It has also been inferred by Riera[14] and by Stone[16] to account for the formation of 1,4-diazabutadien-2-yl complexes following alkylation of low-valent isonitrile complexes of Fe, and a similar mechanistic proposal was put forward earlier by Adams to account for the reaction of $[Mo(\eta^5\text{-}C_5H_5)(CO)(CNMe)_2]^-$ with methyl iodide followed by 1 equiv of I^- to give $[Mo(\eta^5\text{-}C_5Me_5)(CO)(I)\{CNMe_2)C(CH_3)=N(Me)\}]$.[22] This was proposed to involve formation of a 1,4-diazabutadien-2-yl ligand by a sequence similar to that in Scheme 2, but in the molybdenum case a second equivalent of methyl iodide then alkylates the ligand on nitrogen to give the observed product. There is also a further reaction with excess methyl iodide in our system, but $[Mn(CNPh^*)_5I]$ is the only product that we have been able to isolate from this reaction to date.

Insertion of the second isonitrile ligand to form the 1,4-diazabutadien-2-yl ligand requires intermolecular redistribution of isonitrile ligands, and this led to an examination of the affect of added isonitrile on the course of the reaction. We were disappointed to discover that addition of 1 equiv of free CNPh* to a THF solution of $\mathbf{1}^-$ before the addition of CH_3I produced only a marginal improvement (from 30 to 32%) in the yield of **2**, but the importance of exogenous isonitrile was supported by an experiment in which 1 equiv of CN^tBu was added to the THF solution of $\mathbf{1}^-$ before alkylation with methyl iodide. This produced a product with spectroscopic characteristics similar to those of **2**: the presence of methyl resonances at δ 2.05 and 1.96 indicated the formation of a 1,4-diazabutadien-2-yl ligand by coupling of two CNPh* ligands induced by addition of the equivalent of CH_3I. The added methyl group gives rise to a signal of appropriate intensity at δ 1.78, while the singlet at δ 1.51 suggests that 1 (and only one) equiv of CN^tBu molecule had been incorporated into the product. This led to formulation of the product as $[Mn(CN^tBu)(CNPh^*)_3\{C(=NPh^*)C(CH_3)=N(Ph^*)\}]$ (**4**), as supported by combustion analysis. The appearance of a single ^{t}Bu resonance and a single resonance for the methyl groups of the terminal isonitrile ligands suggests that the three isonitrile ligands are rendered equivalent by a low-energy dynamic process, and the choice of isomer illustrated in Scheme 1 is arbitrary.

The proposal that **4** is formed by trapping an intermediate in the double insertion sequence was supported by a control experiment that eliminated the possibility that **4** had been formed by substitution of CN^tBu for a CNPh* ligand of **2**. This control involved ^{1}H NMR monitoring (5 min intervals) of a sample of **2** in THF-d_8 (0.023 mmol in 0.5 mL) to which 1 equiv of CN^tBu had been added. These conditions are similar in terms of the solvent and concentration to those under which **4** had been prepared, but after 30 min at room temperature about one-third of **2** had degraded without the formation of any **4.** Thermal degradation of **2** is consistent with earlier observations on the stability of **2**, and the failure to form **4** supports our suggestion that **4** is formed by addition of CN^tBu to the Mn center at some point in the double insertion sequence, most probably after formation of **B** by the first insertion reaction (Scheme 2).

Conclusion

The facility of isonitrile/alkyl insertion reactions in low-valent isonitrile complexes leads to the formation of the 1,4-diazabutadien-2-yl complex $[Mn(CNPh^*)_4\{C(=NPh^*)C(CH_3)=N(Ph^*)\}]$ when the Mn(−I) isonitrilate $[Mn(CNPh^*)_5]^-$ is alkylated with methyl iodide. This work and earlier reports of double isonitrile insertion sequences following the formation of low-valent isonitrile/alkyl complexes through alkylation reactions or through isonitrile substitution in carbonyl/alkyl precursors suggests that sequences of this type will be commonly observed as a consequence of the alkylation of isonitrilates.

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Supporting Information Available: Tables giving positional and thermal parameters and bond distances and angles for $[Mn(CNPh^*)_4\{C(=NPh^*)C(CH_3)=N(Ph^*)\}]$ (13 pages). Ordering information is given on any current masthead page.

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