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Multinuclear NMR Studies of $Mn(CNR)_6^{+,2+}$: R = Methyl, Ethyl, Isopropyl, *tert*-Butyl, Cyclohexyl, Benzyl, Phenyl, *p*-Tolyl, and *p*-Anisyl

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Multinuclear NMR results are presented for the hexakis(isocyanide)manganese(I) and -manganese(II) complexes of methyl, ethyl, isopropyl, *tert*-butyl, cyclohexyl, benzyl, phenyl, *p*-tolyl, and *p*-anisyl isocyanide. The data include the ^1H, ^{13}C, ^{14}N, and ^{55}Mn NMR data on all of the complexes. All spectra were run in acetonitrile, and the ^{55}Mn data are also given as a function of temperature, -35 to +45 °C, and solvent. The low-spin Mn(II) complexes give sharp lines for the ligand atoms. The observed chemical shifts and line widths compared to those of the diamagnetic Mn(I) complexes and the free ligands are discussed. Data are also presented on the apparent EPR signal, which is attributed to decomposition, and the solution and solid-state magnetic susceptibilities.

Introduction

The manganese(I, II) hexakis(isocyanide) complexes form an appealing series of compounds for the study of spectroscopic and other physical properties since rather subtle changes can be made in the ligands without changing the electronic structure drastically. The series is especially appropriate for investigating NMR properties since the complexes are a diamagnetic–paramagnetic pair with the same octahedral structures and the $^{55}Mn(I)$ and all the ligand atoms can be observed directly. This allows a comparison to be made with currently available NMR theories of chemical shifts and line widths, including an experimental method for separating the shift induced by coordination to the diamagnetic center from the effect of the paramagnetic center.

This paper presents NMR (^1H, ^{13}C, ^{14}N, ^{55}Mn), EPR, and magnetic susceptibility results on Mn^I and $Mn^{II}(CNR)_6$ complexes where R is methyl, ethyl, isopropyl, *tert*-butyl, cyclohexyl, benzyl, and phenyl, and just NMR data are presented for the *p*-tolyl and *p*-anisyl isocyanide complexes. All of the complexes will be identified in the rest of the text by the R group. A second paper presents infrared, Raman, and ultraviolet spectroscopic data, cyclic voltammetry, and molecular orbital calculations as well as a general discussion of the bonding trends.[1] Other work from our laboratory on these complexes has pursued their electron self-exchange reactivity.[2]

Data in the literature on these complexes include some ^1H[3,4] and ^{14}N[5] NMR data and EPR measurements.[3,4] Of these data, we have been unable to reproduce the EPR and ^1H NMR results for the Mn(II) complexes.

Experimental Section

The manganese isocyanide complexes were prepared as previously described.[2] Acetonitrile-d_3 was purchased from Aldrich and Bio-Rad and used with no further purification. Acetonitrile, dimethyl sulfoxide, ethanol, acetone, chloroform, and bromobenzene were purified as previously described.[2]

All NMR measurements were obtained on a Nicolet NT200WB instrument. The experimental parameters are listed in the footnotes to the tables. The data were taken at ambient temperature (18 °C) unless otherwise indicated. The instrument was locked on the ^2H signal of the solvent for the proton and ^{13}C measurements while the ^{55}Mn and ^{14}N data were collected in proteated solvents and not locked. This resulted in no additional error since the ^{55}Mn and ^{14}N lines are relatively broad, and the data were collected in a few minutes per spectrum. The ^{13}C spectra were obtained proton decoupled except for some run nondecoupled for assignment purposes. The ^{13}C spectra of the paramagnetic complexes were obtained at -40 °C due to the instability at room temperature of the alkyl complexes. All chemical shifts are reported such that increasing positive values are to lower field.

The EPR spectra were recorded with a Varian E9 spectrometer operating in the X-band with a field modulation of 100 kHz, 100-mW microwave power, and a modulation amplitude of 5 G. Calibration of the frequency and the magnetic field was checked with diphenylpicrylhydrazyl (DPPH) in KCl. To calibrate the instrument for the decomposition studies, several solutions of $Mn(ClO_4)_2\cdot 6H_2O$ (G. Frederick Smith Chemical Co.) in acetonitrile were made. The total Mn^{2+} concentration in these solutions was then checked spectrophotometrically after converting the manganese to permanganate. The EPR spectra were recorded for several 0.01-10 mM solutions at several gain settings, and the intensity of the largest peak was measured to give a calibration curve of intensity/instrument gain vs. the Mn^{2+} concentration. Care was required in adjusting the sample capillary position so that spectra could be reproduced accurately. For the spectra of the Mn isocyanide complexes, fresh solutions of carefully recrystallized complex were used. Temperatures to -160 °C were controlled with a gas-flow temperature controller. Liquid-N_2 temperatures were obtained with a small Dewar placed in the microwave cavity.

Solution-state magnetic susceptibilities were measured by the Evans method[6] on a JEOL MH100 NMR instrument at ambient temperature. Concentric sample tubes (Wilmad) were used with a 0.15 M diamagnetic sample in the central tube and a similar concentration of the paramagnetic sample in the outer tube. The solvent was a 10% solution of tetramethylsilane (Me_4Si) in acetonitrile or acetone. The Me_4Si peak was used to calculate the chemical shift due to the paramagnetism. Shifts of 60-90 Hz were observed. Values are corrected for the differences between the solution and solvent densities. Care was taken to minimize the time between mixing the sample and the measurement to avoid decomposition of the complex.

Solid-state magnetic susceptibilities were measured by the Faraday method at room temperature. Calibration was achieved by using $HgCo(SCN)_4$ as the standard (16.44×10^{-6} emu/g),[7] and diamagnetic corrections to the Mn(II) complex paramagnetism were obtained by measuring the gram-susceptibility of the corresponding diamagnetic complex and adding -0.42×10^{-6} emu/g to this value to account for the additional BF_4^- anion in the paramagnetic complex.[8]

Results

The ^{55}Mn spectra had an excellent signal-to-noise ratio and consisted of a single Lorentzian peak with a smaller peak upfield about 1.9 ppm. This small peak was well resolved in the spectra of the methyl and ethyl complexes and had an area about 4% of the larger peak. This resonance became less resolved as the size of the complex increased and was not observed at all in the spectra of the *p*-tolyl or the *p*-anisyl complexes. Figure 1 is the room-temperature ^{55}Mn NMR spectrum of $Mn(CNCH_3)_6BF_4$ in acetonitrile.

Over the range -35 to +45 °C in acetonitrile, the ^{55}Mn chemical shift increased linearly with temperature. For all the complexes, except methyl and ethyl, the line width decreased monotonically with temperature. The magnitude of the line width change was 290 Hz for cyclohexyl and only 9 Hz for isopropyl over a similar temperature range. The line width increased slightly with temperature for methyl and ethyl. Figure 2 shows the temperature

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[1] Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1985**, *24*, 1803.
[2] Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 1338. Nielson, R. M.; Wherland, S. *J. Am. Chem. Soc.* **1985**, *107*, 1505.
[3] Fantucci, P.; Naldini, L.; Cariati, F.; Valenti, V. *J. Organomet. Chem.* **1974**, *64*, 109.
[4] Matteson, D. S.; Bailey, R. J. *J. Am. Chem. Soc.* **1969**, *91*, 1975.
[5] Becker, W.; Beck, W.; Rieck, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1970**, *25B*, 1332.
[6] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
[7] Figgis, B. N.; Nyholm, R. S. *J. Chem. Soc.* **1958**, 4190.
[8] Angelici, R. J. "Synthesis and Technique in Inorganic Chemistry"; McGraw-Hill: New York, 1972; p 465.

0020-1669/85/1324-3458$01.50/0

Table I. ^{55}Mn NMR Data[a] for MnL_6BF_4

L	solvent[b]	δ[c]	$\nu_{1/2}$, Hz[d]	dδ/dT, ppm/°C	$\Delta\nu_{1/2}$, Hz[e]	ΔT, °C
$CNCH_3$	CH_3CN	−1292.3	29.1	0.707	−7.1	−35 to +25
$CNCH_2CH_3$	CH_3CN	−1309.6	31.3	0.570	−4.7	−35 to +30
$CNCH(CH_3)_2$	CH_3CN	−1335.4	37.2	0.510	9.4	−35 to +30
$CNC(CH_3)_3$	CH_3CN	−1359.9	40.9	0.443	22.0	−35 to +30
CNC_6H_{11}	CH_3CN	−1362.8	42.9	0.629	289.7	−35 to +26
	$(CH_3)_2SO$	−1367.1	110.9	0.688	38.8	+15 to +30
	C_2H_5OH	−1380.2	41.9	0.674	153.8	−35 to +26
	$(CH_3)_2CO$	−1371.2	40.8	0.655	125.2	−35 to +26
	C_6H_5Br	−1373.1	75.8	0.676	361.5	−30 to +26
	$CHCl_3$	−1374.7	67.8	0.628	164.0	−25 to +26
$CNCH_2C_6H_5$	CH_3CN	−1361.5	35.7	0.528	9.6	+15 to +45
CNC_6H_5	CH_3CN	−1381.9	42.3	0.704	58.0	−35 to +30
$CNC_6H_4CH_3$	CH_3CN	−1362.0	85.1			
$CNC_6H_4OCH_3$	CH_3CN	−1348.1	89.4			

[a] NMR parameters: 49.52-MHz spectrometer frequency, 20-μs pulse width, 500-ms postacquisition delay, 16K block size, 0.02 M solutions in 12-mm sample tubes, 2000–10000 scans. [b] Gutmann acceptor numbers: CH_3CN, 19.3; $(CH_3)_2SO$, 19.3; C_2H_5OH, 37.1; $(CH_3)_2CO$, 12.5; $CHCl_3$, 23.1 (Gutmann, V. *Chimia* **1977**, *31*, 1). [c] Referenced relative to 0.02 M $KMnO_4$(aq) external standard. Increasing positive values are to lower field. [d] Line width at half-height at 18 °C. [e] Line width change over the temperature range ΔT.

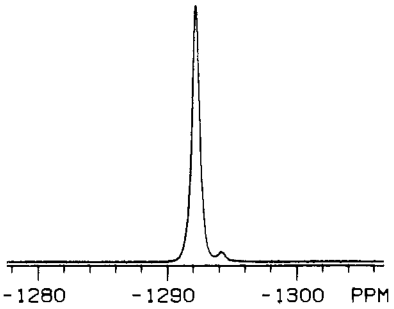

Figure 1. ^{55}Mn NMR spectrum of $Mn(CNCH_3)_6BF_4$ in acetonitrile at room temperature. Conditions: spectrometer frequency, 49.52 MHz; pulse width, 20 μs; postacquisition delay time, 500 ms; block size, 16 K; 0.02 M solution in a 12-mm sample tube; 3500 pulses; temperature, 18 °C.

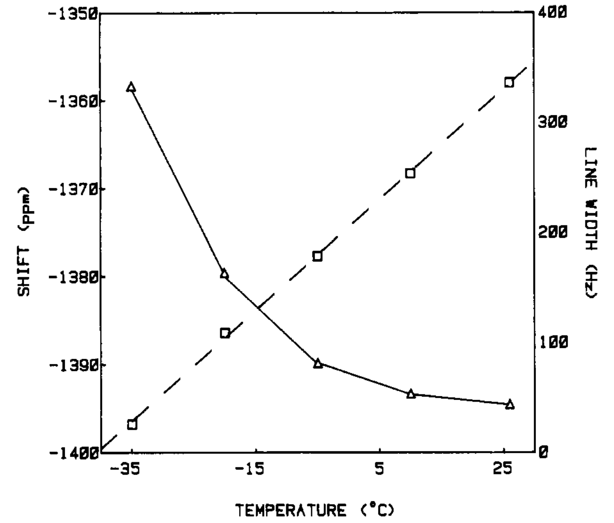

Figure 2. Plots of the ^{55}Mn chemical shift (□) and line width (△) vs. temperature for $Mn(CNC_6H_{11})_6BF_4$ in acetonitrile.

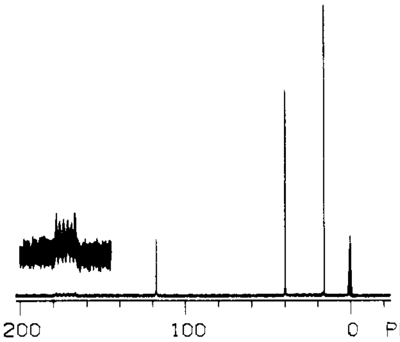

Figure 3. ^{13}C spectrum of $Mn(CNC_2H_5)_6BF_4$ in acetonitrile-d_3 at room temperature. The enlarged region shows the scalar coupling to ^{55}Mn. Conditions: spectrometer frequency, 50.31 MHz; pulse width, 6 μs; postacquisition delay time, 750 ms; block size, 64K; saturated solution in a 12-mm sample tube; 26000 scans; temperature, 18 °C.

dependence of the shift and line width for $Mn(CNC_6H_{11})_6BF_4$ in acetonitrile.

^{55}Mn NMR spectra were also obtained for the cyclohexyl complex in $(CH_3)_2SO$, C_2H_5OH, $(CH_3)_2CO$, C_6H_5Br, and $CHCl_3$ at various temperatures. The chemical shift again increased linearly with temperature, and the slopes were quite similar. The line widths decreased with temperature in the same manner as observed in acetonitrile, with the greatest effect, 360 Hz, being observed in C_6H_5Br. All the ^{55}Mn NMR data are summarized in Table I.

Table II summarizes the ^{13}C NMR data in acetonitrile-d_3 and gives the atom-numbering scheme. The ^{13}C resonances were observed for all carbons of both the diamagnetic Mn(I) complexes and the paramagnetic Mn(II) complexes, with the exception of the C^0 resonance for the paramagnetic *p*-tolyl and *p*-anisyl complexes. The resonances were assigned by reference to literature values for the free ligand.[9]

The spectra of the Mn(I) complexes consisted of sharp singlets for all the carbons except C^0, which was split into a sextet due to scalar coupling to the spin $^5/_2$ Mn nucleus.[10] For all the alkyl complexes, except benzyl, this multiplet was well resolved, and coupling constant information could be obtained. Figure 3 is the ^{13}C spectrum of $Mn(CNCH_2CH_3)_6BF_4$ in acetonitrile. No clear evidence for $^{14}N-^{13}C$ coupling was observed. Upon coordination to the manganese, the C^0 resonance of the alkyl complexes shifts 15–19 ppm (26 ppm for benzyl) downfield with respect to the free ligand. The shift increased in the order methyl < ethyl < cyclohexyl < isopropyl < *tert*-butyl < benzyl. The C^1 resonance also shifted downfield upon coordination but not nearly as much as C^0, and there was less difference between the ligands. These shifts were −2.7 ppm for benzyl and 3–5 ppm for the others. The shift due to coordination decreased with the number of bonds from the manganese, with the resonances for carbons far removed from the manganese unaffected. Coordination shifts for the aromatics are similar, except that the C^0 carbon was shifted somewhat less. The benzyl complex showed a pronounced oscillation in the sign of the coordination shift that was not observed in any other complexes.

The ^{13}C spectra of the paramagnetic complexes consisted of both broad and very sharp lines. The temperature dependence of the shift and integrated intensities of the proton nondecoupled spectra allowed for an unambiguous assignment of all resonances

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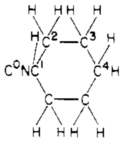
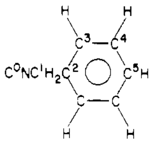
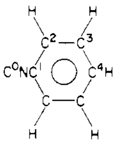
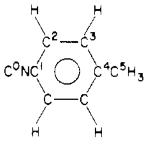
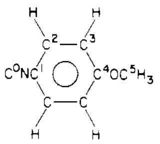
(9) Knol, D.; Koole, N. J.; deBie, M. J. A. *Org. Magn. Reson.* **1976**, *8*, 213.
(10) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 3265.

Table II. ^{13}C NMR Data[a] for MnL_6BF_4 and $MnL_6(BF_4)_2$ in CD_3CN

L	carbon no.	δ(Mn(I))[b]	coordn shift[c]	δ(Mn(II)) − δ(Mn(I))[d]
$C^0NC^1H_3$	0	171.2	15.5	−147.5
	1	30.4	4.7	−84.0
$C^0NC^1H_2C^2H_3$	0	172.0	16.6	−145.9
	1	40.0	3.6	−73.9
	2	16.4	1.3	75.4
$C^0NC^1H(C^2H_3)_2$	0	172.5	18.0	−144.6
	1	48.9	3.5	−62.9
	2	24.4	1.2	77.0
$C^0NC^1(C^2H_3)_3$	0	172.9	19.3	−143.0
	1	57.1	3.1	−53.1
	2	31.2	1.0	72.7
	0	173.0	17.0	−145.8
	1	54.6	3.1	−63.1
	2	33.5	0.7	71.8
	3	22.7	0.1	−1.4
	4	25.9	0.8	0.2
	0	173.7	26.3	−146.0
	1	48.7	−2.7	−78.7
	2	135.5	3.0	69.0
	3	127.3	−0.7	−1.8
	4	129.8	0.3	2.1
	5	129.0	0.0	1.3
	0	177.4	12.8	−138.1
	1	129.7	3.6	−146.9
	2	127.1	0.7	74.5
	3	130.7	0.9	−52.5
	4	129.6	0.2	74.2
	0	176.3	12.2	
	1	126.3	2.7	−144.5
	2	126.6	0.4	68.2
	3	130.7	0.5	−58.3
	4	139.7	0.1	85.7
	5	20.9	0.0	−33.9
	0	177.3	14.0	
	1	122.1	3.3	−144.5
	2	127.9	0.1	58.9
	3	115.3	0.3	−59.7
	4	159.9	0.0	76.3
	5	55.9	0.3	−4.9

[a] NMR parameters: 50.31-MHz spectrometer frequency, 6-μs pulse width, 750-ms postacquisition delay, 64K double-precision block size, 0.1 M to saturated solutions in 12-mm sample tubes, 20 000–30 000 scans. The temperature was 18 °C and −40 °C for the Mn(I) and Mn(II) samples, respectively. [b] Shift relative to internal Me_4Si. Increasing positive values are to lower field. [c] The coordination shift (ppm) is the Mn(I) complex shift minus the corresponding free-ligand value. Free-ligand values were obtained from ref 9 and were measured in Me_2SO. [d] This is the shift of the Mn(II) complex resonance referenced to the corresponding Mn(I) value.

Table III. ^{14}N NMR Data[a] for MnL_6BF_4 and $MNL_6(BF_4)_2$ in Acetone

L	Mn(I) δ[b]	Mn(I) $\nu_{1/2}$, Hz[c]	coordn shift[d]	δ(Mn(II)) − δ(Mn(I))[e]	$\nu_{1/2}$, Hz[c]
$CNCH_3$	−215.0	105.1	4.6	656.3	40.5
$CNCH_2CH_3$	−200.3	75.0	4.8	658.3	15.9
$CNCH(CH_3)_2$	−192.0	108.4	−2.3	663.4	21.1
$CNC(CH_3)_3$	−178.5	54.5	2.7	660.1	22.5
CNC_6H_{11}	−191.0	95.2	3.0	673.0	27.7
$CNCH_2C_6H_5$	−203.6	167.0	7.4	658.5	36.9
CHC_6H_5	−193.1	160.3	6.9	624.5	102.4
$CNC_6H_4CH_3$	−193.0	216.0			
$CNC_6H_4OCH_3$	−194.7	211.0	6.3		

[a] NMR parameters: 14.42-MHz spectrometer frequency, 120-μs pulse width, 500-ms postacquisition delay, 2K block size, 0.02 M solutions in 12-mm tubes, 10 000 scans, 18 °C. [b] Shift relative to saturated $NaNO_3$(aq) external standard. Increasing positive values are to lower field. [c] Line width at half-height. [d] The Mn(I) complex shift minus the corresponding free-ligand value. Free-ligand values were taken from: Witanowski, M.; Webb, G. A. "Nitrogen NMR"; Plenum Press: London, 1973; pp 200–1. [e] The Mn(II) complex shift referenced to the corresponding Mn(I) complex.

except for carbons C^2 and C^3 in cyclohexyl, phenyl, *p*-tolyl, and *p*-anisyl and carbons C^3 and C^4 in benzyl. The resonances were all found to have a temperature dependence proportional to the shift of the Mn(II) complex resonances from the Mn(I) complex resonances [δ(Mn(II)) − δ(Mn(I))].

Precise line width measurements were not obtained for the ^{13}C spectra due to the poor signal-to-noise ratios. The line widths were greater for the resonances shifted the greater amount, but there was no simple correlation between line width and shift. Line widths for the C^0 carbons were typically 1400–1500 Hz, and for the rest they were typically 150–200 Hz and showed signs of spin–spin coupling.

The spectra of all the alkyl complexes had similar behavior in the direction and magnitude of the δ(Mn(II)) − δ(Mn(I)) shift for each carbon. The C^0 resonance shifted upfield about 145 ppm and was the same magnitude for all the complexes. The C^1 resonance shifted upfield less, and there was a greater difference observed between the complexes. The C^2 resonance shifted downfield about 73 ± 4 ppm for all the complexes. For carbons farther removed from the manganese nucleus the shifts became greatly attenuated and alternated in sign. For the benzyl complex there was still a noticeable shift, 1.5 ppm, for the C^4 and C^5 carbons while for carbons a similar distance from the Mn nucleus in the cyclohexyl complex the shift was only 0.2 ppm.

The shifts for the aromatic complexes were different from those for the alkyl ligands in that no attenuation in shift was observed for carbons located past the CN bond. The shifts for the carbons of the R group alternated in sign, compared to that for the nearest carbon atom, even including those of the *p*-anisyl complex, which has an oxygen atom located between it and the ring.

Free *tert*-butyl isocyanide ligand was added to a solution of the Mn(II) *tert*-butyl complex to test for ligand substitution reactivity. No broadening or shifting of the ^{13}C peaks occurred. The ^{13}C spectra for both the diamagnetic and paramagnetic complexes are available as supplementary material.

Table III lists the results of the ^{14}N NMR measurements. The resonance was observed in all the diamagnetic and paramagnetic complexes as a single Lorentzian line. The Mn(I) alkyl spectra, in general, had small, downfield coordination shifts of 3–10 ppm and were shifted to slightly higher fields with increasing ligand bulk, while for the aromatic complexes these shifts were essentially constant. The line widths for the diamagnetic complexes ranged from 55 to 216 Hz for the *tert*-butyl and *p*-tolyl complexes, respectively. The spectra of the paramagnetic complexes consisted of single lines of width 16–100 Hz shifted downfield 650–675 ppm from the diamagnetic complex.

All proton NMR resonances were observed in both the Mn(I) and Mn(II) complexes, and the results are summarized in Table IV. The resonance lines of the Mn(I) complexes were split into multiplets due to ^{1}H–^{1}H spin–spin coupling just as in the free ligand, but the ^{14}N–^{1}H coupling, which is observed for the free ligand, was no longer apparent. Unambiguous assignments for all complexes, except for the protons H^2, H^3, H^4 in the cyclohexyl complex, were obtained on the basis of integrated intensities and by reference to ligand assignments.[11] Resonance assignments for the aromatic peaks were also based on the assumption that substitution at the para position on the aromatic ring will shift H^2 more than H^1 and on comparisons between the complexes. Coordination shifts of less than 2 ppm downfield were observed for all the diamagnetic complexes.

The ^{1}H spectra of the paramagnetic alkyl complexes had sharp signals in all cases with no apparent proton spin–spin coupling, except for the ring protons in benzyl, which showed coupling to the other protons in the ring. Shifts [δ(Mn(II)) − δ(Mn(I))] of

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(11) Malatesta, L.; Bonati, F. "Isocyanide Complexes of Metals"; Wiley-Interscience: London, 1969; p 18.

Table IV. ^1H NMR[a] Data for MnL_6BF_4 and $MnL_6(BF_4)_2$ in CD_3CN

L	proton no.[b]	δ(Mn(I))[c]	coordn shift[d]	δ(Mn(II)) − δ(Mn(I))[e]
$CNCH_3$	1	3.32	0.59	62.12
$CNCH_2CH_3$	1	3.61 q	0.22	62.80
	2	1.32 t	0.04	0.76
$CNCH(CH_3)_2$	1	3.92 s	0.05	59.15
	2	1.34 d	−0.11	1.41
$CNC(CH_3)_3$	2	1.43	0.26	2.00
CNC_6H_{11}	1	3.84	0.26	58.90
	2	1.48[f]	−2.1	g
	3	1.74[f]	−0.3	g
	4	1.74[f]	−2.0	g
$CNCH_2C_6H_5$	1	4.80	0.52	67.39
	3	7.30	0.27	0.28
	4	7.30	0.27	0.49
	5	7.30	0.27	0.14
CNC_6H_5	2	7.5 b	0.7	−10.28
	3	7.5 b	0.7	4.72
	4	7.5 b	0.7	−10.35
$CNC_6H_4CH_3$	2	7.36 d	0.20	−10.75
	3	7.26 d	0.10	4.49
	5	2.36	0.03	15.14
$CNC_6H_4OCH_3$	2	6.96 d	0.11	−10.88
	3	7.42 d	0.03	2.36
	5	3.81	0.00	3.37

[a] NMR parameters: 200.0-MHz spectrometer frequency, 3-μs pulse width, 500-ms postacquisition delay, 32K block size, 0.1 M solutions in 5-mm tubes, 256 scans, 18 °C. [b] Protons are numbered according to the carbon they are bonded to; see Table II. [c] Shift relative to internal Me_4Si. Positive shifts are to lower field; d = doublet, t = triplet, q = quartet, s = septet, b = broad. [d] The Mn(I) complex shift minus the corresponding free-ligand value. Free-ligand values were taken from ref 11. [e] The shift for the Mn(II) complex referenced to the corresponding Mn(I) complex. [f] These assignments are not conclusive. [g] Five peaks were obtained at 4.63, 3.29, 2.71, 1.62, and −0.09 ppm with intensities 2:2:2:2:2. No definite assignment could be made.

about 60 ppm were observed for protons bonded to the C^1 carbon for these complexes. These shifts are much larger than previously reported.[3] Much smaller shifts were observed for the other carbons. The spectra of the aromatic complexes had shifts of greater magnitude than the alkyls for a similar distance from the Mn center, and they alternated in sign. The ^1H NMR spectra are available as supplementary material.

Free methyl isocyanide ligand was added to a solution of the Mn(II) methyl complex. No broadening or shifting of the resonances occurred.

In contrast to earlier work,[3,4] we failed to observe an EPR signal for any of the Mn(II) isocyanide complexes when freshly prepared solutions of well-recrystallized samples were used. After about 5 min, a signal began to appear and increased in intensity with time for all the complexes. Figure 4 shows the EPR spectrum of the methyl complex solution taken at regular 10-min intervals. In all cases, the signal consisted of six peaks of unequal intensity with a *g* value of 2.043 and an *A* value of 93.7 G, comparable to the reported values. It was found that, except for that of the phenyl complex, the signal continued to grow for 10–24 h. This "aged" signal had the same *g* value, *A* value, and intensity as those of a similar concentration of $Mn(ClO_4)_2 \cdot 6H_2O$ in acetonitrile. The rate of signal intensity increase with time was taken as the decomposition rate of the Mn(II) isocyanide complexes. A calibration curve was constructed as described in the experimental section, and the decomposition rate of the complexes was determined. The results are given in Table V.

The EPR signal of the phenyl complex solution also increased with time but at a much lower rate. The signal intensity of the aged solution was not equal to that of a similar concentration of $Mn(ClO_4)_2$ in acetonitrile but did have the same *g* and *A* values as those of the perchlorate solution. The signal intensity of the aged solution indicated that about 5% of the solution was solvated Mn(II).

Examination of Table V reveals that, of the alkyls, the least stable complex is the methyl and the most stable is the benzyl.

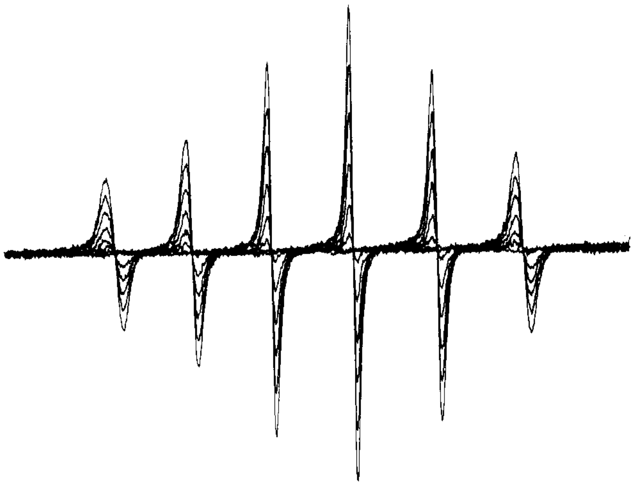

Figure 4. EPR spectrum of an acetonitrile solution of $Mn(CNCH_3)_6(BF_4)_2$ taken at 10-min intervals. Total scan range was 700 G. Conditions: Mn^{2+} concentration, 2.04 mM; field, 3900 G; scan time, 4 min; time constant, 1 s; modulation frequency, 100 kHz; modulation amplitude, 5 G; microwave power, 100 mW.

Table V. Magnetic Moment and Decomposition Rates for $MnL_6(BF_4)_2$ at 18 °C

L	μ_{eff}(293 K),[a] μ_B soln[b,c]	μ_{eff}(293 K),[a] μ_B solid	half-life, min
$CNCH_3$	2.29	2.07	100
$CNCH_2CH_3$	2.12	2.14	125
$CNCH(CH_3)_2$	2.05	2.16	182
$CNC(CH_3)_3$	2.07	2.22	281
CNC_6H_{11}	1.86	2.24	675
$CNCH_2C_6H_5$	1.62	2.08	765
CNC_6H_5	1.95	2.32	d

[a] $\mu_{eff}(293\ K) = 2.825(\chi_m T)^{1/2}$. [b] Accuracy of the method was checked by measuring the moments for $Fe(H_2O)_6^{3+}$ and $Fe(CN)_6^{3-}$. Values obtained (lit.): $Fe(H_2O)_6^{3+}$, 5.70 (5.92: Figgis, B. N.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 169); $Fe(CN)_6^{3-}$, 2.25 (2.25: Figgis, B. N.; Lewis, J. *Ibid.* **1964**, *6*, 172). [c] Acetonitrile was used for L = $CNCH_3$ and CNC_6H_5; acetone was used for the other complexes. [d] A value was not obtained since complex does not totally decompose to $Mn(CH_3CN)_6^{2+}$ as do the alkyl complexes.

Similar decomposition rates were obtained by measuring the line width increase of acetonitrile by ^1H NMR.

Several attempts were made to observe the EPR signal of the isocyanide complexes at reduced temperatures. No signal was observed in the temperature range obtainable with the gas-flow temperature controller (+25 to −160 °C). Another measurement at 77 K also produced no signal.

The room-temperature magnetic moments of the alkyl and phenyl isocyanide complexes are given in Table V, and range from 1.62 to 2.29 μ_B for solution and from 2.07 to 2.32 μ_B for solid samples. Differences exist between the solid and solution values that can be attributed to the inaccuracy of the solution-state values.

Discussion

Before we discuss the specific results, the experiments that considered the stability of the complexes should be emphasized. The Mn(I) complexes are quite stable in the solid state and in solution. The Mn(II) complexes, however, decompose appreciably in hours. The Mn(II) complexes do not exchange ligands rapidly, as indicated by the experiments with added *tert*-butyl isocyanide (^{13}C NMR) and with added methyl isocyanide (^1H NMR). Decomposition of the Mn(II) complexes to solvated Mn(II), as indicated by the nature of the EPR signal, can be rationalized by the fact that these complexes are 17-electron systems and thus do not satisfy the 18-electron rule. This makes them likely to be susceptible to reaction by an associative mechanism. The decomposition probably involves association of the complex with a solvent molecule, followed by loss of an isocyanide ligand. The complex could be labilized by the solvent ligand and could rapidly

Table VI. Calculated Correlation Coefficients[a] between the Chemical Shifts for the $Mn(CNR)_6BF_4$ Complexes

	^{55}Mn	$^{13}C^0$	^{14}N	$^{13}C^1$
^{55}Mn		0.978	0.906	0.984
$^{13}C^0$	0.183		0.927	0.989
^{14}N	0.779	0.474		0.962
$^{13}C^1$	0.987	0.022	0.870	

alkyls

aromatics

[a] The $|r|$ values for the alkyl complexes are listed in the upper part of the matrix, and the aromatic complexes are in the lower part.

be fully substituted by solvent. Such an associative mechanism would be impeded by bulkier ligands. This is consistent with the results in Table V, which show that decomposition rates decrease with ligand bulk.

The EPR spectra of the aged phenyl complex solutions never showed the peak intensity observed from a similar concentration of $Mn(ClO_4)_2$ in acetonitrile. Instead, the signal increased with time to a point of about 5% total decomposition and then stabilized for 1–2 days. This behavior can also be rationalized by use of the solvent association mechanism. When one of the solvent molecules displaces a ligand, the ligand is then free to reduce a remaining complex to the Mn(I) state. The reducing ability of free isocyanides has been noted before.[12] The small EPR signal is then due to some solvated Mn(II) that was produced by the same mechanism as for the alkyl complexes. This is supported by infrared spectral data that show the Mn(I) complex as one of the decomposition products.[3] This behavior is not observed with the alkyl complexes since they have lower reduction potentials.[13]

Several recent papers have considered the problem of separating the electronic and steric effects in the NMR chemical shifts of transition-metal complexes.[14,15] Poor correlations between the chemical shifts of the various nuclei have been attributed to concurrent changes in both the steric and electronic properties of the ligands. To our knowledge, only one paper has reported the shift correlations of a system when both the steric and electronic factors could be separated. In that system, Gray and co-workers reached the conclusion that "the degree of correlation between any two chemical shifts is a linear function of the similarity in their response to polar and resonance effects" when purely electronic and not steric effects were the cause of the chemical shift.[14] That particular study, and the majority of the studies concerning steric and electronic effects, involved complexes of the form $(CO)_5MoP(C_6H_5)_2X$ where X is one of a large number of groups with various electronic and steric properties. The manganese isocyanide complexes can be separated into two groups, which should permit the observed chemical shifts to be explained by either steric or electronic factors.

The manganese aromatic isocyanide complexes (excluding benzyl) should give predominantly electronic effects to the chemical shifts since the difference in the complexes is in the para position of the aromatic rings. The calculated correlation coefficients between the chemical shifts of the various nuclei for the aromatic complexes are given in Table VI. The correlations are poor except for ^{55}Mn vs. $^{13}C^1$, which has a correlation coefficient of 0.987. Even this value is not particularly good since only three points are used in the calculation. Gray and co-workers fit their NMR data to a three parameter equation using inductive and resonance Taft constants to characterize the substituents. Such a procedure is not possible for the data available for the manganese isocyanides since the number of fit parameters is equal to the number of data points. However, the poor correlations of these limited data suggest that the results reported by Gray for the Mo complexes will not be observed in the manganese isocyanides.

The correlation coefficients calculated between the chemical shifts of the various alkyl isocyanide nuclei are given in Table VI. The correlations range from fair (0.906) to quite good (0.989) for five points. The chemical shifts of these complexes should be dependent primarily on the steric factors of the ligands since the electronic factors are essentially constant. No poor correlation was observed, and this indicates that the chemical shifts of all the nuclei are affected similarly by changes in the R group. These results indicate either that the isocyanides are not as sensitive to cone angle changes as the phosphines or that there is very good electronic communication between the atoms in these complexes.

Most trends in chemical shift data are explained by changes in the paramagnetic term in the total shielding tensor and neglect changes in the diamagnetic term.[16] This is considered justified when comparisons are being made between similar complexes. The magnitude of the paramagnetic term depends on three factors: (1) the radial extension of the relevant orbitals, which are related to electron density about the atom, (2) the magnitude of the energy separation between electronic ground and the lowest excited state, and (3) the π-bond order between the atoms of interest. Evans and Norton have expressed a need for caution in the interpretation of chemical shifts in transition-metal complexes using only one of these three interrelated factors in the paramagnetic term.[17] Realizing these problems, we make the following observations. It is common practice to explain chemical shift data for a series of similar complexes by changes in the bonding in the complexes. The manganese isocyanides are a good system for such a treatment since they are very similar in structure and electronic properties. In a discussion of the influence of metal–isocyanide bonding on the chemical shifts, the coordination shifts should be examined rather than the shift referenced to Me_4Si. The multinuclear NMR data, Tables I–III, indicate that an increase in the cone angle of the ligand results in an upfield shift in the ^{55}Mn resonances, a downfield shift in the $^{13}C^0$ coordination resonances, and a slight upfield shift in the ^{14}N coordination resonances. This indicates an increase in electron density about the manganese nucleus and a decrease about the C^0 nucleus and might suggest that back-bonding is decreasing with increased ligand bulk. Cyclic voltammetry, ab initio MO calculations, and force constant studies on the manganese isocyanide complexes indicate the opposite, that back-bonding increases with increased ligand bulk.[1] Similar trends have been observed in the multinuclear NMR spectra of metal carbonyls. Todd and co-workers offered an explanation for the trend in the shifts by assuming that back-bonding disrupts one of the π bonds in the carbonyl ligand and causes the oxygen to gain electron density.[18] In a valence-bond (VB) approach this represents a greater contribution of structure I over II with increased back-bonding.

$$\underset{\text{I}}{\mathrm{M{=}C{=}\ddot{O}:}}\qquad \underset{\text{II}}{\mathrm{\overset{-}{M}{-}C{\equiv}\overset{+}{O}:}}$$

It is not entirely clear from the above VB structures why electron density at carbon decreases with increased contribution of structure I, but MO calculations on $V(CO)_6^-$, and $Cr(CO)_6$ do support this.[19] The MO calculations also show an increase in electron density about oxygen with increased back-bonding. An analogous situation can be pictured for the man-

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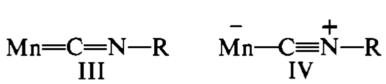
ganese isocyanide complexes where structure III will be favored over IV with increased back-bonding. No MO calculations are available for isocyanide complexes with varying degrees of back-bonding, but it is not unreasonable to assume that similar changes in the electron density about the carbon and nitrogen will be observed as in the carbonyl group of metal carbonyls. The NMR data therefore indicate that back-bonding increases with the bulk of the ligand, and this is confirmed from other measurements.[1]



$$\underset{\mathrm{III}}{\mathrm{Mn{=}C{=}N{-}R}} \qquad \underset{\mathrm{IV}}{\mathrm{Mn{-}\overset{-}{C}{\equiv}\overset{+}{N}{-}R}}$$

For the ^{55}Mn NMR, it has been shown that the small peak upfield from the large peak in Figure 1 is one of two satellites due to scalar coupling between ^{55}Mn and ^{13}C[10]. This coupling was also observed in the ^{13}C spectra as a six-peak multiplet. A coupling constant of 120 Hz was obtained.[10] Only one of the two satellites is visible because they are shifted upfield about 0.9 ppm, apparently due to the ^{13}C isotope effect. The satellite becomes less resolved for the bulkier complexes because the line width of the intense resonance increases while the separation between the satellite remains nearly the same.

Temperature dependences of the chemical shift have been observed for many transition-metal complexes.[20] Possible explanations given for these dependences include mechanisms by which an increase in temperature decreases the energy separation between the ground and the first excited state, thus resulting in a downfield shift.[21] This trend is observed for the manganese isocyanide system as Table I indicates. Such a temperature dependence should also be observable in the electronic spectrum of the complexes, and such is the case with many Co(III) complexes.[22] Unfortunately, these data are not available for the Mn(I) isocyanides.

Table I shows that there is a small chemical shift difference for the cyclohexyl complex in various solvents. A chemical shift difference of only −17 ppm was observed between acetonitrile and ethanol while for $Co(CN)_6^{3-}$ a shift of nearly −200 ppm was obtained between acetonitrile and methanol.[23] The effect of solvent on the chemical shift has no simple explanation. Hydrogen bonding, polarity of the solvent, and aromatic ring currents can all influence the shift. It appears, however, that the chemical shift increases in solvents with higher acceptor numbers. This would indicate that the solvent is penetrating between the ligands and interacting with the electrons available at the CN bond. The MO describing the back-bonding is the HOMO of the complex.[1] If electron density is shifted solely from the multiple-bond region to the solvent, the decrease in electron density could lead to increased back-bonding from manganese. This would stabilize the HOMO, increase the ligand field splitting energy, and shift the ^{55}Mn resonance to higher fields.[23] Smaller chemical shifts are observed in the isocyanide complexes than in $Co(CN)_6^{3-}$ probably because the Co complex is an anion and less sterically hindered, and thus interacts more strongly with the acceptor solvents.

A final consideration that should be made in treating the solvent effect is that the ion pairing of the Mn(I) complexes differs widely in the solvents studied. Conductivity experiments indicate that in Me_2SO and acetonitrile the complex is totally dissociated. In acetone and ethanol partial association is observed, and in chloroform and bromobenzene the complex is completely ion paired.[2] The results in Table I do not correlate with ion pairing.

The spin $^5/_2$ ^{55}Mn nucleus possesses a large electric quadrupole moment, and thus the nuclear relaxation mechanism is likely to involve quadrupolar relaxation. The expression for the line width, $\nu_{1/2}$, of the ^{55}Mn resonance line when this mechanism is predominant can be given by eq 1,[24] where $e^2qQ/\hbar$ is the quadrupole

$$\nu_{1/2} = 0.21\left(\frac{e^2qQ}{\hbar}\right)^2\left(1 + \frac{\eta'^2}{3}\right)\tau_c \qquad (1)$$

coupling constant, η' is the asymmetry parameter, and τ_c is the rotational correlation time given by eq 2, where η is the solution

$$\tau_c = \eta Vf/kT \qquad (2)$$

viscosity, V is the volume of the complex, and f is a microviscosity factor equal to $a/6a_s$, where a is the solute radius and a_s is the solvent radius. According to eq 1 and 2, the resonance line width is proportional to the complex volume and the viscosity of the solvent and inversely proportional to the temperature. Table I shows that the line widths of the alkyl complexes do increase roughly with size except for benzyl. However, Brown and coworkers[25] have shown for a series of manganese carbonyl complexes that the rotational correlation time is essentially independent of the shape and size of similar molecules and that differences in the ^{55}Mn line widths for similar complexes can be attributed to differing values of $e^2Qq/\hbar$. The octahedral manganese isocyanide complexes have six identical ligands and should have a zero electric field gradient (EFG) at the manganese nucleus due to the high symmetry of the molecule.[26] This would produce narrow NMR lines. Nonzero EFG's can be induced by vibrational and rotational distortions of the molecule.[27] Molecules with large, complex ligands will be likely to distort due to vibrational and rotational movements, and nonzero EFG's will result. Table I shows that larger line widths are observed for the complexes with more flexible ligands.

The complexes that have aromatic ligands should be much more rigid than those containing alkyl ligands, but the aromatics have larger line widths than the alkyls. Infrared, crystal structure, and other data indicate that greater back-bonding for the aromatic complexes lowers the symmetry by distorting the linearity of the ligand–Mn–ligand bonds.[1,28,29] This reduction in symmetry would result in nonzero EFG's and produce the observed wide lines.

The temperature dependences of the ^{55}Mn line widths are noteworthy. For the small methyl and ethyl complexes the line width increases with temperature while the opposite was observed for the other complexes. The increase in line width with temperature for the small complexes can be explained by assuming that spin–rotational (SR) relaxation is the dominant relaxation mechanism as opposed to quadrupolar relaxation. SR relaxation is the dominant relaxation mechanism for $Co(CN)_6^{3-}$ [30] and is the only mechanism that predicts an increase in line width with increasing temperature. The SR mechanism is more important for molecules of small size, and this is observed, since only the methyl and ethyl complex line widths increase with temperature.

The line width temperature dependences for the complexes other than methyl and ethyl are approximately that predicted from the $1/T$ dependence in eq 2 except for cyclohexyl. This complex has

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a much larger temperature dependence of the line width than eq 2 predicts. The origin of this large dependence is not known. The cyclohexyl rings in the ligands of the cyclohexyl complex can undergo conformational conversions and interconvert between chair and boat configurations. Studies on unsubstituted cyclohexane have shown that at 300 K the chair–boat interconversion occurs at a rate of 3800 s^{-1} and at 225 K the process occurs at 1.4 s^{-1}.[31] The rings of the manganese cyclohexyl isocyanide complex can be thought of as substituted cyclohexyl rings, and the rate mentioned above for chair–boat interconversion would be smaller. At lower temperatures, the interconversion process would be much slower than the ^{55}Mn spin–spin relaxation time, and the configuration of the ligand rings about the manganese would be a mixture of boat and chair forms; thus the symmetry of the complex would be lowered. At higher temperatures, the interconversion could occur at a rate faster than the ^{55}Mn spin–spin relaxation, and during the relaxation process, the ligands could have a configuration time averaged between chair and boat forms; then the symmetry of the complex would be greater at higher temperatures than at lower temperatures. The positioning of solvent molecules between the interligand spaces could have an effect on the chair–boat interconversion rate and account for the observed effect of solvent on the temperature dependence of the line width.

The line width for the cyclohexyl complex in the various solvents decreases in the order Me_2SO > bromobenzene > chloroform > acetonitrile > ethanol > acetone. The viscosities of the pure solvents decrease in the order Me_2SO > ethanol > bromobenzene > chloroform > acetonitrile > acetone. With the exception of that for ethanol, the qualitative prediction of eq 2 holds with respect to the viscosity.

A wide variety of line widths were obtained for the ^{13}C, ^{14}N, and ^{1}H resonances in the paramagnetic complexes. Line widths ranged from 1500 Hz for the C^0 carbon resonances to tenths of 1 Hz for protons far removed from the Mn(II) center. The line widths of the carbons that had highly shifted protons (>10 ppm) bonded directly to them or on a carbon one bond away showed evidence of spin–spin coupling since these lines were not Lorentzian in shape. This occurs because the highly shifted protons are not efficiently saturated by the proton decoupler, which covered the shift range +11 to –1 ppm.

The line widths of the ^{14}N resonances in the paramagnetic complexes are narrower than those of the diamagnetic complexes. A possible explanation for this is as follows. The line widths of the ^{14}N resonance in the Mn(I) complexes are 50–200 times wider than in the free ligand. This broadening could be due to scalar coupling to the ^{55}Mn nucleus as observed for the C^0 carbon. The paramagnetic complexes' ^{14}N line is narrower because the rapid relaxation of the Mn(II) nucleus (due to the unpaired electron) decouples the scalar interaction. The remaining line width is consistent with dipolar interaction with the unpaired electron on the Mn(II).[32]

The failure to observe an EPR signal for the Mn(II) isocyanides at room temperature is expected since the NMR signals of all the nuclei in the ligand are observable. In order for a room-temperature EPR signal to be observed, a long electron spin–lattice relaxation time (T_{1e}) must exist while the observation of an NMR signal for a paramagnetic complex requires a short T_{1e}.[33] For the low-spin Mn(II) hexacyanide complex, a temperature of 12 K was required to observe the EPR signal,[34] and it is expected that similar temperatures are required for the Mn(II) isocyanides.

The magnetic susceptibility results are consistent with a low-spin d^5 electron configuration with a $^2T_{2g}$ ground state in the solid and in solution for the Mn(II) complexes. We did not reproduce Matteson and Bailey's observation that the manganese(II) phenyl isocyanide complex was diamagnetic,[4] but we saw the expected paramagnetism in freshly prepared solutions of recrystallized material.

Conclusion

In conclusion, the NMR spectra of all the atoms for a series of manganese isocyanide complexes can be observed for both the diamagnetic and the paramagnetic forms. The diamagnetic spectra can be separated into two groups where the chemical shifts are influenced by steric or electronic effects in the ligands. It was found that the chemical shift correlations between the various nuclei were good for the complexes with predominantly steric effects and poor for the complexes where electronic effects should be important. This opposes prior observations for molybdenum phosphine complexes. The multinuclear NMR spectra exhibit a wide variety of line widths that are dependent upon solvent, temperature, and the R group of the ligand and can be rationalized by present NMR theory. The ^{55}Mn chemical shift also has a pronounced temperature dependence that is dependent on the R group of the ligand. The literature EPR and ^{1}H NMR data for the manganese isocyanide complexes could not be reproduced, and it is believed that these values are of decomposition products.

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Registry No. $Mn(CNCH_3)_6BF_4$, 91281-18-4; $Mn(CNCH_3)_6(BF_4)_2$, 95979-49-0; $Mn(CNCH_2CH_3)_6BF_4$, 91281-19-5; $Mn(CNCH_2CH_3)_6(BF_4)_2$, 95979-50-3; $Mn(CNCH(CH_3)_2)_6BF_4$, 91281-21-9; $Mn(CNCH(CH_3)_2)_6(BF_4)_2$, 97877-79-7; $Mn(CNC(CH_3)_3)_6BF_4$, 91281-22-0; $Mn(CNC(CH_3)_3)_6(BF_4)_2$, 97877-80-0; $Mn(CNC_6H_{11})_6BF_4$, 89463-46-7; $Mn(CNC_6H_{11})_6(BF_4)_2$, 89463-47-8; $Mn(CNCH_2C_6H_5)_6BF_4$, 95979-45-6; $Mn(CNCH_2C_6H_5)_6(BF_4)_2$, 95979-55-8; $Mn(CNC_6H_5)_6BF_4$, 95979-46-7; $Mn(CNC_6H_5)_6(BF_4)_2$, 95979-56-9; $Mn(CNC_6H_4CH_3)_6BF_4$, 95979-47-8; $Mn(CNC_6H_4CH_3)_6(BF_4)_2$, 95979-57-0; $Mn(CNC_6H_4OCH_3)_6BF_4$, 95979-48-9; $Mn(CNC_6H_4OCH_3)_6(BF_4)_2$, 95979-58-1.

Supplementary Material Available: Figures showing the ^{1}H and ^{13}C NMR spectra (9 pages). Ordering information is given on any current masthead page.

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