acetophenone to benzyl alcohol in 93% in yield in 1 h at room temperature[6] whereas, even under much more forcing conditions, acetophenone was not reduced by $NaBH_2(CN)_2$ or $n\text{-}Bu_4NBH_2(CN)_2$. Likewise, $NaBH_3CN$ in hexamethylphosphoramide readily reduces alkyl halides to the corresponding alkane[7] but no evidence could be found for the reduction of heptyl iodide under much more forcing conditions.

We conclude that the reducing ability of $BH_2(CN)_2^-$ is appreciably less than that of H_3BCN^-, and experiments to exploit the difference and its reducing ability toward other functional groups are in progress.

Acknowledgment. The experimental assistance of Mark Scheitlin is gratefully acknowledged. We thank the Army Research Office for support of this work.

Note Added in Proof. Alternate preparations of $BH_2(CN)_2^-$ have now been published: $LiBH_2(CN)_2$ (Gyori, B.; Emri, J.; Feher, I. *J. Organomet. Chem.* **1983**, *225*, 17) and $NaBH_2(CN)_2$ (Emri, J.; Gyori, B. *J. Chem. Soc., Chem. Commun.* **1983**, 1303).

Registry No. $NaBH_2(CN)_2$, 88503-36-0; $C_6H_5NH_2\cdot BH_2CN$, 66632-44-8; $n\text{-}Bu_4NBH_2(CN)_2$, 91128-60-8; $Et_4NBH_2(CN)_2$, 91128-61-9; $C_7H_{15}I$, 4282-40-0; acetophenone, 98-86-2.

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First Observation of Resolvable Coupling between Manganese-55 and Carbon-13

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During our studies of the electron-transfer reaction[1,2]

$$(RNC)_6Mn^+ + (RNC)_6Mn^{2+} \rightleftarrows (RNC)_6Mn^{2+} + (RNC)_6Mn^+$$

(where R = methyl, ethyl, isopropyl, *tert*-butyl, cyclohexyl, and benzyl) we encountered discrepancies in the literature regarding the spectroscopic and electrochemical properties of these complexes. We, therefore began a thorough characterization of the physical properties of them.[2] We report here $^1J(^{55}Mn-^{13}C)$ for R = methyl, ethyl, isopropyl, *tert*-butyl, and cyclohexyl in $(RNC)_6MnBF_4$. This is the first direct observation of resolvable coupling between ^{55}Mn and ^{13}C.

The observation of the ^{13}C NMR signal of a carbon atom bonded directly to a metal atom with a large quadrupole moment is usually difficult because the electric field gradients of the quadrupolar nucleus provide an efficient relaxation mechanism for it and thus a broadened ^{13}C signal.[3,4] Due to the low natural abundance of ^{13}C, this broadened signal is often unobservable. Several researchers have performed NMR experiments at lower temperatures in order to cause a shorter T_1 for the quadrupolar nucleus and thus "thermally decouple" the ^{13}C spin from the quadrupolar nucleus.[5,6] This gives sharpened ^{13}C signals, but the spin–spin coupling information is lost. For the case of symmetric complexes such as the octahedral $(RNC)_6MnBF_4$ series,[7] the electric field gradients are averaged out to nearly zero. This removes the major relaxation mechanism, and better resolved spectra result. The reason $^{55}Mn-^{13}C$ coupling constants are previously unreported is primarily the lack of diamagnetic, symmetric, organometallic complexes of manganese. A ^{55}Mn NMR study on $Mn(CO)_6^+$ has been reported, but the authors did not report any resolvable coupling of ^{13}C to ^{55}Mn.[8] The only previously reported coupling constant of a nucleus bonded to ^{55}Mn is for ^{17}O in MnO_4^-.[9,10] A further problem, at least for the isocyanide series, is that the coupling is not observable as satellites in the ^{55}Mn spectrum. This occurs because the center of the satellites is isotopically shifted 36 Hz upfield, which causes the downfield satellite to become hidden under the large singlet. The ^{55}Mn spectrum thus appears as a large peak with a smaller peak slightly upfield. For wider lines, the small peak is a shoulder on the larger one.

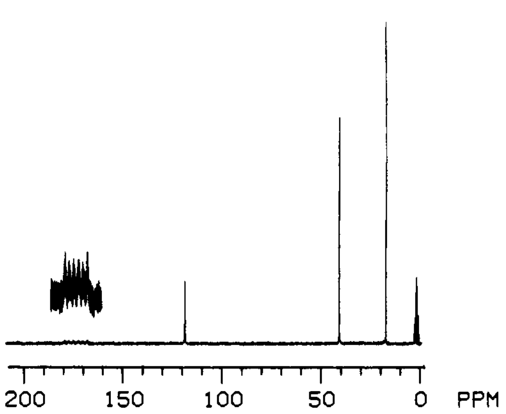

Figure 1. ^{13}C NMR spectrum for saturated $(CH_3CH_2NC)_6MnBF_4$ in CD_3CN at 50 °C. NMR experimental conditions are found in the footnotes to Table I. The septet at 1.2 ppm and the peak at 118 ppm are due to CD_3CN. The peaks at 16 and 40 ppm are due to CH_3 and CH_2, respectively. The insert above the 175 ppm region is the multiplet enlarged 10 times to show the fine structure due to the $^{55}Mn-^{13}C$ coupling. All shifts were measured relative to CD_3CN, which was taken to be 1.2 ppm downfield from Me_4Si.

The ^{13}C NMR spectra of $(RNC)_6MnBF_4$ (R = methyl, ethyl, isopropyl, *tert*-butyl, cyclohexyl, and benzyl) were collected at room temperature in CD_3CN, and six peaks were resolved for the isocyano carbon in all cases except for the benzyl isocyanide complex, which showed a broad absorption with no resolvable splitting. The resolution of the splitting became poorer as the R group increased in size from methyl to cyclohexyl. An additional spectrum of the ethyl isocyanide complex obtained at 50 °C gave better resolution, and the total width of the multiplet was equal to that of the spectrum taken at room temperature.

Figure 1 shows the ^{13}C NMR spectrum of $(CH_3CH_2NC)_6MnBF_4$ in CD_3CN at 50 °C. The insert shows the isocyano carbon region of the spectrum enlarged 10 times to exhibit the fine structure. Since ^{55}Mn has a spin of $^5/_2$, six lines are observed in the ^{13}C NMR spectrum for the carbon bonded to the manganese. They have different intensities and widths but the same area. It has been shown,[12] for the NMR spectrum of a nucleus of spin $^1/_2$ bonded to a nucleus of spin $^5/_2$, that six lines of equal intensity will be observed only if the spin–

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Table I. $^{13}C^{a}$ and $^{55}Mn^{b}$ Data for $(RNC)_6MnBF_4$ in CD_3CN at Room Temperature

R	$^1J(^{55}Mn-^{13}C)$, Hz	multiplet width,^{c} Hz	^{55}Mn NMR line width,^{d} Hz
methyl	121	581	28.9
ethyl	119	577	33.4
isopropyl	118	561	36.7
tert-butyl	113	540	40.7
cyclohexyl	111	523	42.9

^{a} ^{13}C data were obtained with a Nicolet NT200WB instrument on saturated solutions at 50.31 MHz with a 6-μs pulse width and a 750-ms postacquisition delay. Typically, 20 000–30 000 scans were collected in double precision in a 64K block size. ^{b} ^{55}Mn data were obtained with the Nicolet instrument at 49.52 MHz with a 20-μs pulse width and 500-ms post-acquisition delay in a 16K block size on 0.02 M solutions. Typically, 2000–10 000 scans were obtained. ^{c} Separation between the outer two peaks of the six-peak multiplet. ^{d} Widths are at half-height, obtained by fitting the frequency domain data to a Lorentzian line shape by using a least-squares minimizing program available on the Nicolet instrument.

lattice relaxation time (T_1) of the quadrupolar nucleus is long compared to the inverse of the coupling constant (J). When T_1 is comparable to $1/J$, the line shape becomes more complex. Suzuki and Kubo[12] have calculated a series of NMR line shapes for such a case as a function of T_1 and J. The general trend is that as T_1 decreases, the total width of the multiplet decreases and the lines acquire different widths. This narrowing continues until the individual components of the multiplet become unresolvable and a broad absorbance results. When T_1 is much shorter than $1/J$, the signal becomes a sharp singlet. The $(RNC)_6MnBF_4$ system seems to be in the intermediate region bordering on the long T_1 side.

When T_1 is long compared to $1/J$, $^1J(^{55}Mn-^{13}C)$ can be obtained from measuring the peak separation within the multiplet. When T_1 is in the intermediate range described above, the coupling constant is best obtained by comparing the experimental spectra to computer-simulated spectra calculated with varying T_1 and J.[12,13,14] Such a procedure requires a better signal-to-noise ratio than we have been able to obtain. Our estimate of $^1J(^{55}Mn-^{13}C)$ comes from the separation of the center two peaks of the multiplet. The values obtained in this manner will be close to the actual values.

Table I shows that the width of the ^{55}Mn line increases with increasing size of the R group. Assuming that the system is in the "extreme narrowing" region (i.e. $T_1 = T_2$), then as R increases in size, T_1 of Mn decreases. This leads to a decrease in the width of the ^{13}C multiplet with increasing R group size, as observed here and predicted for such a case by Suzuki and Kubo.[12] The decrease in T_1 for ^{55}Mn with increasing size of the R group probably originates in increased deviations from octahedral symmetry due to collisions and intramolecular motions in the larger, more flexible complexes. This distortion produces electric field gradients and hence increases the relaxation rate due to quadrupolar interactions. The decrease in T_1 with the larger molecules can also be explained by the fact that T_1 is inversely proportional to the correlation time, which in turn is proportional to the volume of the molecule. Larger molecules with larger volumes increase the correlation time and decrease T_1.[15]

The coupling constant values reported here should be of interest to both experimentalists and theoreticians. There are reports of ^{13}C NMR studies on organometallic complexes of manganese where the authors failed to observe the NMR peak due to the carbon bonded to manganese.[16] Our results show that the signal is observable and characteristic, at least in symmetric complexes. Theoretical calculations of coupling constants continue to be of interest. The experimental values reported here (Table I) should provide a test of these theories. Mann[17] calculated $^1J(^{55}Mn-^{13}C)$ for $Mn(CO)_6^+$ using a very simplified theory and obtained a value of 110 Hz. This value compares well with those reported in this work.

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Registry No. $(RNC)_6MnBF_4$ (R = methyl), 91281-18-4; $(CH_3CH_2NC)_6MnBF_4$, 91281-19-5; $(RNC)_6MnBF_4$ (R = isopropyl), 91281-21-9; $(RNC)_6MnBF_4$ (R = *tert*-butyl), 91281-22-0; $(RNC)_6MnBF_4$ (R = cyclohexyl), 89463-46-7; ^{13}C, 14762-74-4.

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Copper(I) and Copper(II) Complexes of 3-Methoxy-1,5-dithiacyclooctane. Evidence of a Long-Range Electrostatic Interaction in the Copper(I) Complex Giving an "Apparent" Five-Coordinated Complex

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The eight-membered mesocyclic dithioether 1,5-dithiacyclooctane (1,5-DTCO) rapidly reduces $Cu(ClO_4)_2$ to $Cu(1,5\text{-DTCO})_2ClO_4$ such that no Cu(II) complexes have been isolated.[1] Substitution of a hydroxyl group at the three-position of the ring (3-hydroxy-1,5-dithiacyclooctane, 3-OH-1,5-DTCO) gives a ligand that completely inhibits the reduction of Cu(II).[1] However, when the three-position is substituted by a methoxyl group (3-methoxy-1,5-dithiacyclooctane, 3-OMe-1,5-DTCO), both Cu(I) and Cu(II) complexes can be isolated and characterized. This tridentate ligand is one of few ligands that give cationic complexes with both Cu(I) and Cu(II) in which no additional ligands (solvent or anions) are involved in coordination. The structure of the Cu(I) complex is unusual in that one of the methoxyl oxygen atoms is situated in a potential energy well that imparts an "apparent" five-coordinated trigonal-bipyramidal geometry to Cu(I).

Experimental Section

Preparation of Compounds. Reagents. The following reagents were obtained from the indicated sources: 3-hydroxy-1,5-dithiacyclooctane (1,5-dithiacyclooctan-3-ol) from Aldrich Chemical Co., Milwaukee, WI; $Cu(ClO_4)_2\cdot 6H_2O$ from G. Frederick Smith Chemical Co., Columbus, OH.

3-Methoxy-1,5-dithiacyclooctane. A reflux condenser, an addition funnel, and a nitrogen inlet were placed on a 300-mL, three-necked, mortonized, round-bottom flask. A 50% dispersion of sodium hydride in oil (4.80 g, 100 mmol) was washed with pentane to give a gray powder. A magnetic stir bar, tetrahydrofuran (60 mL), and the washed

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