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# Dicarbonyl(isocyanide)(arene)manganese Cations, Preparation and Nucleophilic Addition Reactions. Molecular Structure of $[(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2(CNCH_3)][O_3SCF_3]$

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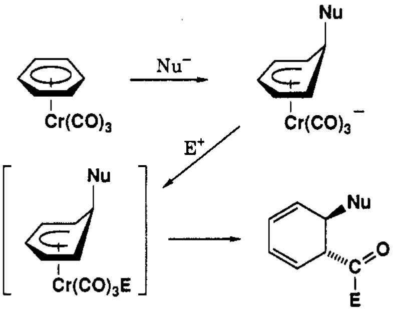
A variety of organic and inorganic electrophiles add to $[(\eta^6\text{-arene})Mn(CO)_2(CN)]$ to form isonitrile complexes. The cationic isonitrile complexes are sufficiently activated to undergo nucleophilic addition to the arene ligand by hydride and carbanion donors, producing cyclohexadienyl complexes. The latter reaction competes with electrophile abstraction by the incoming nucleophile. Both $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(\text{thiocyanate})]$ linkage isomers have been prepared and also undergo electrophile addition. A crystal structure of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNMe)]OTf$ (OTf = $O_3SCF_3$) is reported: space group $P2_1/c$, $a = 9.8758(14)$, $b = 7.6812(12)$, $c = 25.497(3)$ Å, $\beta = 96.549(10)°$, $V = 1921.6(4)$ Å$^3$, $Z = 4$, $D_{calc} = 1.602$ mg m$^{-3}$, $R = 0.0297$ and w$R = 0.0377$ on 3013 reflections with $F > 2.0\ \sigma(F)$.

## Introduction

Scheme I



Unsaturated hydrocarbons are generally resistant to nucleophilic attack. However several investigators have demonstrated remarkable electrophilic activation of such hydrocarbons upon coordination to metal centers. Systems which have received attention include $[(\eta^6\text{-arene})Cr(CO)_3]$,[1,2] $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$,[3] $[(\eta^6\text{-arene})_2Fe]^{2+}$,[4] $[(\eta^6\text{-arene})Mn(CO)_3]^+$,[5–8] $[(\eta^5\text{-dienyl})Mn(CO)_2(NO)]^+$,[6,9] and others. Kundig and co-workers[2] have shown that nucleophilic addition to (arene)chromium complexes occurs at the arene ring and this further activates the ring toward electrophilic attack (Scheme I). The latter occurs initially at the metal. However no one has yet demonstrated the reverse process, that is, activation of a metal $\pi$-hydrocarbon complex toward nucleophilic attack by means of initial electrophile addition. There are several examples of the production of neutral complexes from anionic ones[10,11] and of cationic complexes from neutral ones[12–15] by the addition of cationic electrophiles to coordinated cyanide. Attack occurs at the nitrogen lone pair, affording the well-known $\pi$-acceptor isonitrile (isocyanide) ligand.[16] It seemed likely that this robust ligand would not be especially subject to simple removal of the added electrophile by an incoming nucleophile. The system chosen for the study was $[(\eta^6\text{-arene})Mn(CO)_2(CN)]$. The synthesis of this complex has previously been dem-

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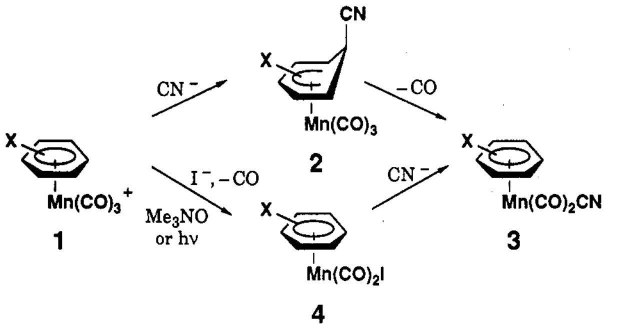
**Scheme II**



onstrated[17,18] and the addition of certain Lewis acids to the cyanide ligand has also been noted.[13-15]

## Results and Discussion

**Synthesis of (Arene)manganese(I) Cyanide Complexes (3).** Preparation of [($\eta^6$-arene)Mn(CO)$_2$(CN)], **3** (arene = hexamethylbenzene, **A**; mesitylene, **B**; benzene, **C**), from the tricarbonyl cation may be pursued by either of the routes shown in Scheme II.[17,18] The upper route was considered advantageous in avoiding possible contamination of the product with the halide complex **4**. Cyanide, as the tetraethylammonium salt in CH$_3$OH, readily attacks **1** at the arene ring, providing the cyanocyclohexadienyl complex **2**. Migratory replacement of a carbonyl by cyanide probably occurs by initial regeneration of **1**. Hence it occurs more readily in polar solvents. The degree of arene methylation plays an important role as well. Heating **1A** in CH$_3$OH with KCN yields **3A**. Contrary to Mawby's results,[17] when **1B** or **1C** was treated in this manner, species **2B** and **2C** were found to be the final products. Complex **3B** was prepared in moderate yield by heating **1B** in KCN/H$_2$O for 1 h. The yield was somewhat lower for **3C**.

Like the cyanide anion, thiocyanate anion (SCN$^-$) has previously been shown to add to the ring in **1C**.[19] The mode of attachment (through nitrogen or sulfur) was not determined in the previous study. When **1A** was treated with thiocyanate in refluxing methanol as part of the current study, carbonyl replacement was observed. Two products were isolated by chromatography: an orange and a red solid, being formed in about 5:1 ratio. Infrared, $^1$H-NMR, and elemental analysis indicated that the composition of the two products was identical, showing them to probably be linkage isomers. The assignment of thiocyanate linkage isomers is not a trivial matter.[20] Oftentimes the CN stretching frequency lies at higher wavenumbers for S-bound complexes. However this rule is fraught with exceptions, especially for octahedral complexes. Moreover the two products showed only a 5 cm$^{-1}$ difference in the position of this band. A preferable criterion is the position of the (predominantly) CS stretching band. N-Bound isomers exhibit this band near 820 cm$^{-1}$, while S-bound species show a band at about 700 cm$^{-1}$. In Nujol mull, the major (orange) isomer gave a band at 808 cm$^{-1}$, indicating that it is probably N-bound. Both isomers and the cyanide complex **3A** (examined for comparison) showed a series of bands between 730–530 cm$^{-1}$, making identification of the CS stretch for the S-bound isomer uncertain.

**Synthesis of (Arene)manganese(I) Isonitrile Complexes (5).** Complexes **3** were readily converted to isonitrile cations, [($\eta^6$-arene)Mn(CO)$_2$(CNE)]$^+$ (**5**) by reaction with electrophiles at ambient temperature in CH$_2$Cl$_2$. Yields were typically high and the products were precipitated from solution as yellow, crystalline solids by the addition of diethyl ether. Strong electrophiles, such as alkyl triflates, were ideal electrophiles for this reaction. Methyl sulfate was also effective. On the other hand, alkyl and acyl chlorides, methyl tosylate, tropylium, diazonium salts, and acetic anhydride were unreactive toward **3**. Acyl chlorides have previously been used to acylate anionic cyanide complexes.[11] As a further confirmation of its identity, **5** was also prepared from the solvent complex via reaction 1. Its spectral characteristics were comparable

$$[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(THF)]PF_6 + CNCMe_3 \rightarrow [(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNCMe_3)]PF_6 \quad (1)$$

to those of the electrophile adducts (see Table I).

The trityl cation was found to be a very effective alkylating agent despite its rather weak electrophilicity. Mawby[13] reported this transformation but indicated the product to be very unstable in solution. In fact the product has now been found to be air-stable indefinitely in the solid state and for several hours in solution. However, in contrast to the methyl or ethyl isonitrile products, the trityl cation may be removed by the addition of excess triethylamine. Mawby also reported protonation of the cyano complexes by aqueous acid.[13] He was unable to isolate **5**, E = H, upon reaction with aqueous HBF$_4$. He instead obtained the neutral Lewis acid–base complex [($\eta^6$-arene)Mn(CO)$_2$(CNBF$_3$)]. These complexes have now been prepared and isolated by direct reaction of **3A** with fluoroboric acid or boron trifluoride etherate in CH$_2$Cl$_2$. Like trityl, BF$_3$ and H$^+$ are removed by NEt$_3$. Very recently Eyman and co-workers[14,15] have also prepared complex **5A** for E = AlMe$_3$, BH$_3$, BEt$_3$, and CPh$_3^+$.

In the presence of even weak electrophiles, **3A** shows shifting of infrared bands, indicating the formation of Lewis acid–base complexes. This phenomenon has previously been recognized for anionic metal cyanide complexes,[21] as well as neutral metal carbonyls[22] and nitrosyls.[23] Spectral data for several nonisolable Lewis acid complexes of **3A** are included in Table I. There is little difference in carbonyl stretching frequency between the various complexes. On the other hand, the CN stretch is informative. Strong electrophiles, such as carbocations, provide values >2140 cm$^{-1}$. Relatively poor Lewis acidity is demonstrated by non-transition metal electrophiles, such as Ag$^+$, AlCl$_3$, and Li$^+$, the product CN stretches occurring at <2120 cm$^{-1}$. The product complexes were not suc-

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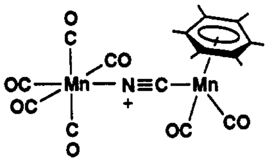
**Table I. IR Spectral Data for $[(\eta^6\text{-arene})Mn(CO)_2(CNE)]^{+,0}$ Complexes 5**

| arene | E | $\nu_{CO}$ (cm$^{-1}$)[a] | $\nu_{CN}$ (cm$^{-1}$)[b] |
|---|---|---|---|
| $C_6Me_6$ | $H^+$ | 2001, 1956 | 2167 |
| $C_6Me_6$ | $Me^+$ | 2010, 1966 | 2193 |
| $C_6Me_6$ | $Et^+$ | 2010, 1966 | 2178 |
| $C_6Me_6$ | $CPh_3^+$ | 2009, 1969 | 2146 |
| $C_6Me_6$ | $CMe_3^+$ [c] | 2008, 1963 | 2160 |
| $C_6Me_6$ | $Cu(NCMe)^+$ | 1992, 1945 | 2123 |
| $C_6Me_6$ | $Cu(PPh_3)_3^+$ | 1988, 1942 | 2107 |
| $C_6Me_6$ | $Cu(P(OPh)_3)_3^+$ | 1988, 1940 | 2117 |
| $C_6Me_6$ | $BF_3$ | 2001, 1956 | 2166 |
| $C_6Me_6$ | $Mn(CO)_5^+$ [d] | 1992, 1946[e] | 2120 |
| $C_6Me_6$ | $CpFe(CO)_2^+$ [d] | 1991, 1945[f] | 2119 |
| $C_6Me_6$ | $Li^+$ [d] | 1981, 1930[g] | 2112[g] |
| $C_6Me_6$ | $AlCl_3$[d] | 2003, 1961 | 2111 |
| mesitylene | $H^+$ | 2015, 1971 | 2174 |
| mesitylene | $Me^+$ | 2019, 1977 | 2204 |
| mesitylene | $Et^+$ | 2021, 1978 | 2186 |
| mesitylene | $CPh_3^+$ | 2020, 1981 | 2155 |
| mesitylene | $Cu(NCMe)^+$ | 2006, 1961 | 2128 |
| mesitylene | $Cu(PPh_3)_3^+$ | 2001, 1957 | 2113 |
| $C_6H_6$ | $H^+$ | 2030, 1990 | 2182 |
| $C_6H_6$ | $Me^+$ | 2031, 1990 | 2218 |
| $C_6H_6$ | $Et^+$ | 2035, 1996 | 2206 |
| $C_6H_6$ | $CPh_3^+$ | 2036, 1998 | 2167 |
| $C_6H_6$ | $Cu(NCMe)^+$ | 2021, 1979 | 2137 |
| $C_6H_6$ | $Cu(PPh_3)_3^+$ | 2015, 1971 | 2120 |

[a] In $CH_2Cl_2$, strong bands. [b] In $CH_2Cl_2$, moderate to weak bands. [c] Prepared using free isonitrile, see text. [d] Not isolated. [e] Others: 2073(s), 2069(s), 2041(w). [f] Others: 2074(s), 2028(s). [g] In $CH_3CN$.

cessfully isolated in these latter cases. Products with moderate stability were also realized by using transition metal-based electrophiles. Adducts of $[Mn(CO)_5]^+$ and $[CpFe(CO)_2]^+$ could not be isolated despite considerable effort. Their formulation as **6** and **7** was confirmed by the complete complement of expected carbonyl infrared bands.



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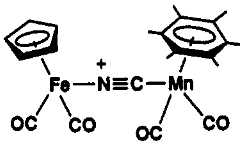


7

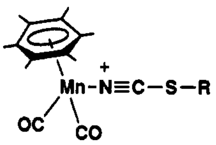
Reaction of **3A** with $[Cu(NCMe)_4]PF_6$ provided a readily isolated salt. Elemental analysis indicated a single equivalent of acetonitrile in the product; thus the correct formulation was $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(\mu\text{-}CN)Cu(NCMe)]PF_6$, **8**. The stability of **8** is much greater than expected based on its low CN stretching frequency (2123 cm$^{-1}$). The copper is not removed by triethylamine. Phosphines and phosphites are known to form stable Cu(I) complexes.[24] Therefore the presence of vacant coordination sites on the copper suggested the possibility of further elaboration of **8**. However, upon reaction with $PMe_3$, $P(^nBu)_3$, $P(OMe)_3$, $P(O^nBu)_3$, $Ph_2PCH_2CH_2PPh_2$, $CH_3C(CH_2PPh_2)_3$ or $P(CH_2CH_2CN)_3$, the copper was found to be removed, generating **3A** and presumably $[CuL_4]^+$. In contrast, $P(OPh)_3$ and $PPh_3$ were found to bind to the complex without causing rupture of the CN–Cu bond. This behavior may be understood in terms of the weaker nucleophilicity of these latter phosphorus ligands. Cyanide stretching frequencies for the copper–phosphorus complexes were found in the region which had previously indicated nonisolability, (2117 and 2107 cm$^{-1}$, respectively). Nevertheless both were isolated and the $PPh_3$ complex was fully characterized. Elemental analysis and $^1$H-NMR indicated 3 equiv of $PPh_3$ and therefore tetrahedral four-coordinate Cu(I), i.e. $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(\mu\text{-}CN)Cu(PPh_3)_3]PF_6$.

**Table II. IR Spectral Data for $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(NCSE)]^+$ and $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(SCNE)]^+$ Complexes**

| NCSE or SCNE | $\nu_{CO}$ (cm$^{-1}$)[a] | $\nu_{CN}$ (cm$^{-1}$)[b] |
|---|---|---|
| NCSH | 2007, 1961 | not obsd |
| NCSMe | 2007, 1961 | not obsd |
| NCSEt | 2006, 1961 | not obsd[c] |
| $NCSCPh_3$ | 2005, 1961 | not obsd |
| SCNH | 1989, 1942 | 2187 |
| SCNMe | 1991, 1944 | 2229 |
| $SCNCPh_3$ | 1992, 1947 | 2183 |

[a] In $CH_2Cl_2$, strong bands. [b] In $CH_2Cl_2$, moderate to weak bands. [c] $^1$H-NMR ($CD_2Cl_2$): 3.11 (s, 2 H, $CH_2$), 2.29 (s, 18 H, $C_6Me_6$), 1.46 (s, 3 H, Me).

As indicated in Table II, spectral studies showed that both manganese thiocyanate isomers were also subject to electrophilic attack. Alkylthiocyanato **9** and alkyl isothiocyanato **10** complexes were produced in quantitative yields as judged by infrared spectroscopy. Due to low yields during the preparation of the neutral manganese thiocyanate isomers, this chemistry was pursued no further.



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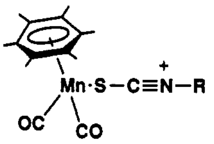

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**Crystallographic Studies.** A representative example of **5**, $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNMe)]OTf$, was subjected to single crystal X-ray diffraction analysis. Solution of the monoclinic structure was accomplished by direct methods. Crystallographic data are listed in Table III, fractional non-hydrogen atom coordinates in Table IV and selected bond lengths and angles in Table V. An ORTEP drawing of the cation is provided in Figure 1. The general configuration of the ion is that of a piano stool, with staggering of the ring carbons with respect to the tripod ligands. The carbonyl ligands are approximately linear. The structure may be advantageously compared to the previously reported $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2Cl]$,[18] $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(SCHNEt_2)]BF_4$,[14] and the unpublished $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(NCMe)]PF_6$.[25] The isonitrile ligand is essentially linear, with Mn–C(1)–N = 176.6(2)° and C(1)–N–C(4) = 178.2(2)°. Likewise the coordinated acetonitrile had been found to be linear. The C–N distance (typically 1.16 Å in the absence of metal coordination) is essentially unaffected by bonding to the metal. The methyl isonitrile complex shows a C–N distance of 1.146(3) Å, while the acetonitrile complex showed a value of 1.153(10) Å.

The isonitrile, nitrile, thioformamide, and chloride complexes exhibit varying degrees of trans influence upon the arene ring–metal bonds. All four of these ligands are significantly poorer $\pi$-acceptors than carbonyl. This is evident from the CO stretching frequencies for $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2X]^{+,0}$, which are compared in Table VI. (Higher stretching frequencies indicate greater electron withdrawing power of X.) As a result, Mn–C distances

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**Table III. Crystallographic Data for $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNMe)]OTf$**

| empirical formula | $C_{17}H_{21}F_3MnNO_5S$ |
|---|---|
| color; habit | yellow rectangular prism |
| crystal size (mm) | 1.0 × 0.53 × 0.28 |
| space group | $P2_1/c$, monoclinic |
| unit cell dimensions | $a = 9.8758(14)$ Å<br>$b = 7.6812(12)$ Å<br>$c = 25.497(3)$ Å<br>$\beta = 96.549(10)°$ |
| volume | 1921.6(4) Å$^3$ |
| $Z$ | 4 |
| formula weight | 463.3 |
| density (calcd) | 1.602 mg/m$^3$ |
| absorption coefficient | 0.853 mm$^{-1}$ |
| $F(000)$ | 952 |
| diffractometer used | Siemens R3m/V |
| radiation | Mo K$\alpha$ ($\lambda = 0.710\ 73$ Å) |
| temperature (K) | 238 |
| monochromator | highly oriented graphite crystal |
| $2\theta$ range | 4.0–50° |
| scan type | omega |
| scan speed | variable, 4.00–29.30°/min in $\omega$ |
| scan range ($\omega$) | 1.00° |
| background measurement | stationary crystal and stationary counter at beginning and end of scan, each for 12.5% of total scan time |
| standard reflections | 3 measured every 100 reflections |
| index ranges | $0 \le h \le 11, 0 \le k \le 9, -30 \le l \le 30$ |
| reflections collected | 3597 |
| independent reflections | 3384 ($R_{int} = 0.95\%$) |
| observed reflections | 3013 ($F > 2.0\sigma(F)$) |
| absorption correction | face-indexed numerical |
| min/max transmission | 0.6449/0.7992 |
| refinement method | full-matrix least-squares |
| quantity minimized | $\sum w(F_o - F_c)^2$ |
| hydrogen atoms | riding model, fixed isotropic $U$ |
| weighting scheme | $w^{-1} = \sigma^2(F)\ 0.0002F^2$ |
| number of parameters refined | 276 |
| final $R$ indices (obsd data) | $R = 0.0297$, $wR = 0.0377$ |
| goodness-of-fit | 1.57 |
| largest and mean $\Delta/\sigma$ | 0.214, 0.008 |
| data-to-parameter ratio | 10.9:1 |
| largest difference peak/hole | 0.75/–0.27 e Å$^{-3}$ |

are shortened for those ring carbons trans to ligand X. In the case of X = CNMe, the trans Mn–C(6) and Mn–C(7) were 2.172(3) and 2.196(2) Å, while the other metal–ring carbon bonds were in the range of 2.200–2.216 Å. This also resulted in a slight displacement of the metal atom from the ring centroid toward carbons C(6) and C(7). In the case of the chloro complex, a slight folding of the ring also resulted. This effect was less profound for the acetonitrile and methyl isonitrile cations. For the latter, least-squares plane calculation showed C(6) and C(9) to be out of plane toward the metal atom by 0.019(3) and 0.015(2) Å.

**Table IV. Atomic Coordinates (× 10$^4$) and Isotropic Temperature Factors $U^a$ (Å$^2$ × 10$^3$) for $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNMe)]OTf$**

| atom | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| Mn | 4330(1) | 140(1) | 1126(1) | 22(1) |
| S | 8837(1) | 3143(1) | 1169(1) | 33(1) |
| F(1) | 9809(2) | 4888(2) | 2010(1) | 67(1) |
| F(2) | 11310(2) | 3433(3) | 1653(1) | 69(1) |
| F(3) | 9918(2) | 2123(2) | 2101(1) | 69(1) |
| O(1) | 6184(2) | 1112(2) | 352(1) | 44(1) |
| O(2) | 4470(2) | 3682(2) | 1563(1) | 40(1) |
| O(3) | 9125(2) | 4613(3) | 854(1) | 55(1) |
| O(4) | 7541(2) | 3181(3) | 1373(1) | 52(1) |
| O(5) | 9223(2) | 1490(2) | 971(1) | 49(1) |
| N | 1978(2) | 1367(3) | 336(1) | 33(1) |
| C(1) | 2840(2) | 861(3) | 636(1) | 28(1) |
| C(2) | 5464(2) | 745(3) | 654(1) | 28(1) |
| C(3) | 4421(2) | 2309(3) | 1386(1) | 28(1) |
| C(4) | 929(3) | 2018(4) | –50(1) | 43(1) |
| C(5) | 3884(2) | –806(3) | 1903(1) | 27(1) |
| C(6) | 5328(2) | –804(3) | 1875(1) | 26(1) |
| C(7) | 5860(2) | –1739(3) | 1468(1) | 26(1) |
| C(8) | 4966(2) | –2611(3) | 1072(1) | 27(1) |
| C(9) | 3546(2) | –2555(3) | 1089(1) | 29(1) |
| C(10) | 3001(2) | –1661(3) | 1514(1) | 28(1) |
| C(11) | 3303(3) | 108(3) | 2355(1) | 42(1) |
| C(12) | 6291(3) | 168(3) | 2277(1) | 40(1) |
| C(13) | 7389(2) | –1843(3) | 1459(1) | 41(1) |
| C(14) | 5573(3) | –3591(3) | 641(1) | 43(1) |
| C(15) | 2592(3) | –3486(3) | 677(1) | 46(1) |
| C(16) | 1479(3) | –1656(4) | 1541(1) | 48(1) |
| C(17) | 10024(3) | 3417(3) | 1764(1) | 42(1) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

A structural study was also undertaken for $[(\eta^6\text{-}C_6H_6)Mn(CO)_2(CNCPh_3)]PF_6$. The monoclinc $P2_1/c$ cell parameters were $a = 11.006(2)$, $b = 26.601(4)$, $c = 19.639(3)$ Å, $\beta = 94.278(12)°$, $V = 5731.7(16)$ Å$^3$. The asymmetric unit for this structure was found to contain two pairs of ions and a solvent molecule ($CH_2Cl_2$). Extensive orientational disorder was evident in both $PF_6^-$ ions. Some degree of disorder was found in one of the phenyl rings as well. Modeling of the disordered regions improved the quality of the solution; however, $R$ could not be brought below 0.10. Nevertheless the general features of the complex were apparent. Like the methyl isonitrile structure discussed above, the general configuration was that of a staggered piano stool with linear isonitrile and carbonyls. Not surprisingly, space-filling projection of this structure revealed significant blockage on one side of the arene ring, due to the bulk of the trityl isonitrile ligand.

**Addition of Nucleophiles to (Arene)manganese(I) Isonitrile Complexes (5).** Cationic complexes **5** undergo attack by anionic nucleophiles. In this regard they behave analogously to other $[(\eta^6\text{-arene})Mn(CO)_2L]^+$ species, L = CO, $PR_3$, or olefin.[5–9,17,19,26] A variety of possible outcomes of attack upon **5** may be envisioned. These are summarized in Scheme III. Ligand attack at the arene ring, a carbonyl, or the isonitrile would give rise to cyclohexadienyl (**11**), acyl (**12**), or iminoacyl (**13**) products. Attack at the metal center would provide a ligand substitution product, such as **14**. In the case of certain highly electrophilic organometallics, such as $[(\eta^6\text{-arene})_2Fe]^{2+}$, and **1**, some nucleophiles are known to react via electron transfer.[4,27] The 19-electron radicals which result are extremely reactive and have been found to dimerize or to react with chlorinated solvents. Two further possibilities exist. The nucleophile may react by abstracting the added electrophile, regenerating **3**. Finally the nucleophile may behave as a Bronsted base, removing a proton from the hexamethylbenzene ligand. This would provide cyclohexadienyl **16**. Eyman[15] has recently synthesized **16**, E = $CPh_3$, $BEt_3^-$, $BH_3^-$ through the use of strong bases, e.g. KH.[28]

Several anionic nucleophiles were used to test the reactivity of **5**. Trityl isonitrile complexes were chosen for this work as a result of their preparative convenience (single-pot reaction from **3**, see Experimental Section).

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**Table V. Selected Bond Lengths and Angles in $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNMe)]OTf$**

| | Bond Lengths (Å) | | |
|---|---|---|---|
| Mn–C(1) | 1.901(2) | O(1)–C(2) | 1.141(3) |
| Mn–C(2) | 1.796(2) | O(2)–C(3) | 1.146(3) |
| Mn–C(3) | 1.791(2) | N–C(1) | 1.146(3) |
| Mn–C(5) | 2.200(2) | N–C(4) | 1.435(3) |
| Mn–C(6) | 2.172(2) | C(5)–C(6) | 1.435(3) |
| Mn–C(7) | 2.196(2) | C(5)–C(10) | 1.406(3) |
| Mn–C(8) | 2.213(2) | C(5)–C(11) | 1.518(3) |
| Mn–C(9) | 2.209(2) | C(6)–C(7) | 1.413(3) |
| Mn–C(10) | 2.216(2) | C(6)–C(12) | 1.512(3) |
| S–O(3) | 1.433(2) | C(7)–C(8) | 1.429(3) |
| S–O(4) | 1.435(2) | C(7)–C(13) | 1.515(3) |
| S–O(5) | 1.434(2) | C(8)–C(9) | 1.409(3) |
| S–C(17) | 1.821(3) | C(8)–C(14) | 1.513(3) |
| F(1)–C(17) | 1.320(3) | C(9)–C(10) | 1.439(3) |
| F(2)–C(17) | 1.333(3) | C(9)–C(15) | 1.508(3) |
| F(3)–C(17) | 1.325(3) | C(10)–C(16) | 1.512(3) |
| | Bond Angles (deg) | | |
| C(1)–Mn–C(2) | 88.8(1) | Mn–C(2)–O(1) | 179.3(2) |
| C(1)–Mn–C(3) | 88.5(1) | Mn–C(3)–O(2) | 178.4(2) |
| C(2)–Mn–C(3) | 89.9(1) | Mn–C(5)–C(6) | 69.8(1) |
| C(1)–Mn–C(5) | 117.9(1) | Mn–C(5)–C(10) | 72.1(1) |
| C(2)–Mn–C(5) | 153.2(1) | C(6)–C(5)–C(10) | 120.4(2) |
| C(3)–Mn–C(5) | 88.9(1) | Mn–C(5)–C(11) | 131.5(2) |
| C(1)–Mn–C(6) | 156.2(1) | C(6)–C(5)–C(11) | 120.0(2) |
| C(2)–Mn–C(6) | 114.9(1) | C(10)–C(5)–C(11) | 119.6(2) |
| C(3)–Mn–C(6) | 89.3(1) | Mn–C(6)–C(5) | 71.9(1) |
| C(5)–Mn–C(6) | 38.3(1) | Mn–C(6)–C(7) | 72.1(1) |
| C(1)–Mn–C(7) | 153.9(1) | C(5)–C(6)–C(7) | 119.4(2) |
| C(2)–Mn–C(7) | 89.0(1) | Mn–C(6)–C(12) | 128.1(2) |
| C(3)–Mn–C(7) | 117.5(1) | C(5)–C(6)–C(12) | 121.3(2) |
| C(5)–Mn–C(7) | 68.0(1) | C(7)–C(6)–C(12) | 119.3(2) |
| C(6)–Mn–C(7) | 37.7(1) | Mn–C(7)–C(6) | 70.2(1) |
| C(1)–Mn–C(8) | 116.2(1) | Mn–C(7)–C(8) | 71.7(1) |
| C(2)–Mn–C(8) | 90.2(1) | C(6)–C(7)–C(8) | 120.3(2) |
| C(3)–Mn–C(8) | 155.3(1) | Mn–C(7)–C(13) | 132.1(2) |
| C(5)–Mn–C(8) | 80.1(1) | C(6)–C(7)–C(13) | 119.5(2) |
| C(6)–Mn–C(8) | 68.4(1) | C(8)–C(7)–C(13) | 120.1(2) |
| C(7)–Mn–C(8) | 37.8(1) | Mn–C(8)–C(7) | 70.5(1) |
| C(1)–Mn–C(9) | 90.2(1) | Mn–C(8)–C(9) | 71.3(1) |
| C(2)–Mn–C(9) | 117.1(1) | C(7)–C(8)–C(9) | 120.2(2) |
| C(3)–Mn–C(9) | 152.9(1) | Mn–C(8)–C(14) | 131.2(2) |
| C(5)–Mn–C(9) | 67.9(1) | C(7)–C(8)–C(14) | 118.8(2) |
| C(6)–Mn–C(9) | 81.2(1) | C(9)–C(8)–C(14) | 121.0(2) |
| C(7)–Mn–C(9) | 67.9(1) | Mn–C(9)–C(8) | 71.6(1) |
| C(8)–Mn–C(9) | 37.1(1) | Mn–C(9)–C(10) | 71.3(1) |
| C(1)–Mn–C(10) | 91.2(1) | C(8)–C(9)–C(10) | 119.7(2) |
| C(2)–Mn–C(10) | 155.1(1) | Mn–C(9)–C(15) | 131.5(2) |
| C(3)–Mn–C(10) | 115.0(1) | C(8)–C(9)–C(15) | 120.6(2) |
| C(5)–Mn–C(10) | 37.1(1) | C(10)–C(9)–C(15) | 119.6(2) |
| C(6)–Mn–C(10) | 68.4(1) | Mn–C(10)–C(5) | 70.8(1) |
| C(7)–Mn–C(10) | 80.1(1) | Mn–C(10)–C(9) | 70.7(1) |
| C(8)–Mn–C(10) | 67.6(1) | C(5)–C(10)–C(9) | 119.9(2) |
| C(9)–Mn–C(10) | 37.9(1) | Mn–C(10)–C(16) | 131.4(2) |
| O(3)–S–O(4) | 115.4(1) | C(5)–C(10)–C(16) | 120.4(2) |
| O(3)–S–O(5) | 115.0(1) | C(9)–C(10)–C(16) | 119.6(2) |
| O(4)–S–O(5) | 115.4(1) | S–C(17)–F(1) | 111.7(2) |
| O(3)–S–C(17) | 103.1(1) | S–C(17)–F(2) | 111.2(2) |
| O(4)–S–C(17) | 102.3(1) | F(1)–C(17)–F(2) | 107.6(2) |
| O(5)–S–C(17) | 103.0(1) | S–C(17)–F(3) | 111.2(2) |
| C(1)–N–C(4) | 178.2(2) | F(1)–C(17)–F(3) | 107.8(2) |
| Mn–C(1)–N | 176.6(2) | F(2)–C(17)–F(3) | 107.0(2) |

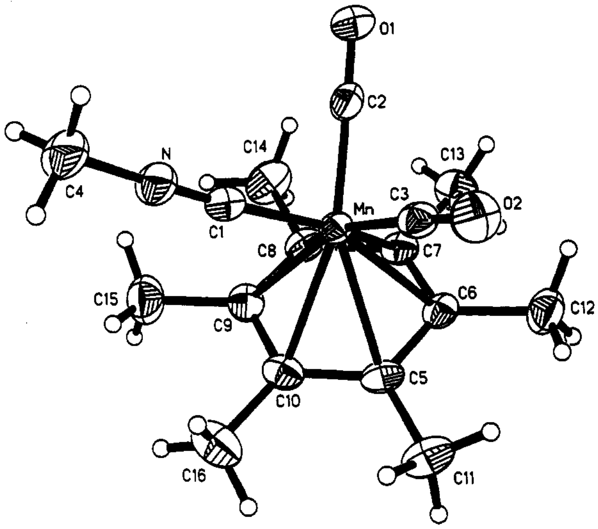

**Figure 1.** ORTEP drawing of the cation in $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNMe)]OTf$ with the thermal ellipsoids at the 50% probability level.

**Table VI. IR Spectral Data for $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2X]^{0,+}$ Complexes**[a]

| X | $\nu_{CO}$ (cm$^{-1}$)[b] | reference |
|---|---|---|
| CO | 2060, 2001(br) | this work |
| $C_2H_4$ | 2012, 1971 | 26 |
| CNMe | 2010, 1966 | this work |
| NCMe | 2001, 1954 | 25 |
| THF | 1992, 1942 | 26 |
| $CN^-$ | 1980, 1930 | this work |
| $SCHNEt_2$ | 1975, 1932[c] | 14 |
| $P(^nBu)_3$ | 1978, 1930 | 25 |
| $Cl^-$ | 1974, 1922 | 18 |
| $H^-$ | 1945, 1890 | 18 |

[a] Complex cationic when X is neutral. [b] In $CH_2Cl_2$. [c] In THF.

Hydride donors $(^nBu)_4NBH_4$ and $LiBEt_3H$ were tested, along with carbanionic Grignard reagents and alkyl- and aryllithiums. Addition of these reagents at or below room temperature in $CH_2Cl_2$ invariably led to the appearance of the cyclohexadienyl product **11** and/or the cyanide complex **3**. These species were easily identified by infrared analysis. Careful examination of both IR and NMR data provided no evidence for species **12**, **13**, **14**, and **16**, nor any possible byproducts of **15** (except of course **11** through simple radical collapse). Several dienyls, **11**, were isolated and characterized. They were typically air-stable yellow solids or oils. In all cases, addition to the ring occurred in stereospecific exo fashion. In the case of $[(\eta^5\text{-}C_6H_7)Mn(CO)_2(CNCPh_3)]$, for example, a large $^1$H-NMR coupling of 12 Hz between the protons at 2.50 and 1.99 ppm is evident, indicating a geminal relation. These comprise the ring methylene unit ($H_{6\text{-exo}}$, $H_{6\text{-endo}}$, see **11** for numbering scheme). Decoupling experiments indicate that the resonance at 2.50 ppm is further coupled to $H_{1,5}$ with $J$ = ca. 6 Hz. This coupling pattern is typical of the $H_{6\text{-endo}}$ proton in a cyclohexadienyl. On the other hand, the resonance at 1.99 ppm ($H_{6\text{-exo}}$) showed no further couplings, as expected from the nearly 90° dihedral angle between $H_{6\text{-exo}}$ and $H_1$ or $H_5$.[29] When the complex was prepared using deuteride, rather than hydride, the resonance at 1.99 ppm was absent. Likewise when nucleophiles other than hydride were added, a resonance corresponding to $H_{6\text{-endo}}$ was always found, while $H_{6\text{-exo}}$ was not.

Conditions favoring the production of **11** over **3** were investigated. Isonitrile complexes, **5**, prepared from weak electrophiles (such as Cu(I) or $BF_3$) were almost always subject to regeneration of **3**, even when reacted with relatively weak uncharged nucleophiles. The more robust **5** prepared from alkyl triflates or $Ph_3CPF_6$ were less prone toward abstraction. The degree of ring methylation was also found to be a factor in determining whether addition or abstraction would predominate. Hexamethylbenzene and mesitylene complexes tended to undergo electrophile

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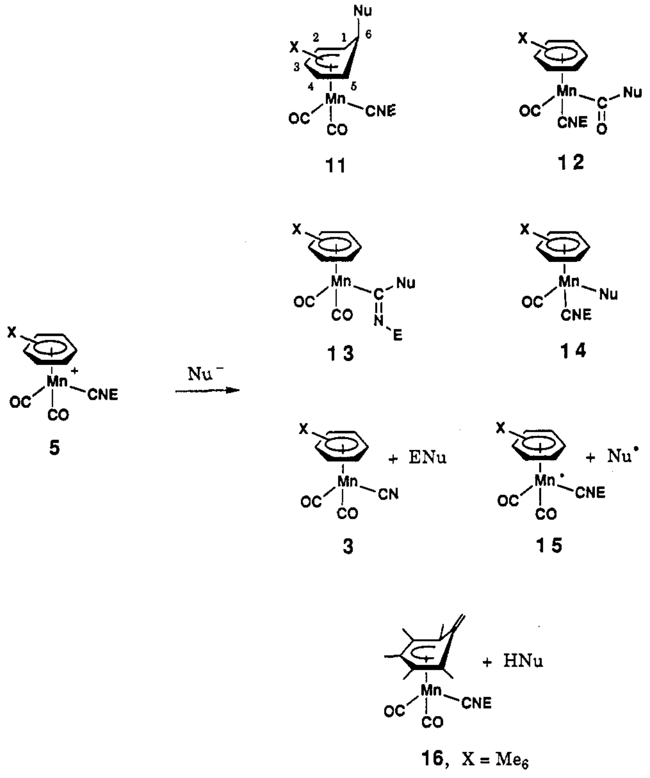
(29) Ittel, S. D.; Whitney, J. F.; Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1988**, *7*, 1323.

**Scheme III**



abstraction by carbanions, presumably due to steric blockage at the ring. Hydride, however, could be added to the ring by the use of $(^nBu)_4NBH_4$. Arene = benzene complexes were apt to give only **11**. Interestingly the strong hydride donor, $LiBEt_3H$ (superhydride), functioned as an electrophile abstracting agent in most cases, while borohydride was a hydride donor.

## Experimental Section

All reactions were carried out under dry nitrogen. Dichloromethane and acetonitrile were distilled from $CaH_2$. Methanol was predried over 4 Å molecular sieves and then distilled from $CaCl_2$. Hexane was stored over sodium ribbon. All solvents were outgassed before use. Pentacarbonylmanganese bromide,[30] $[(\eta^6\text{-arene})Mn(CO)_3]PF_6$,[31] $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(THF)]PF_6$,[26] and $[Cu(NCMe)_4]PF_6$[32] were prepared according to the literature. $[CpFe(CO)_2I]$ was purchased from Aldrich. Electrophiles: methyl triflate, ethyl triflate, trityl and tropylium hexafluorophosphates, benzoyl and acetyl chlorides, methyl sulfate, methyl tosylate, *p*-nitrophenyldiazonium tetrafluoroborate, boron trifluoride etherate, silver tetrafluoroborate, and aluminum chloride were purchased from Aldrich. Fluoroboric acid (54% in diethyl ether) was obtained from Fluka. Nucleophiles: triphenyl phosphite, triphenylphosphine (and other phosphines and phosphites), triethylamine, *tert*-butyl isocyanide, tetra-*n*-butylammonium borohydride, superhydride ($LiBEt_3H$, 1 M in THF), phenylmagnesium bromide (3 M in diethyl ether), methyllithium (1.5 M in diethyl ether), and other Grignards and lithiums were obtained from Aldrich. Potassium cyanide and potassium thiocyanate were purchased from Fisher and vacuum-dried before use.

Infrared spectra were recorded on a Mattson Alpha Centauri FTIR and $^1H$- and $^{13}C$-NMR spectra were collected using Bruker WM250 and AM400 and GE QE-300 spectrometers. Microanalyses were carried out by Galbraith Laboratories, Knoxville, TN.

**Preparation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CN)]$ (3A).** $[(\eta^6\text{-}C_6Me_6)Mn(CO)_3]PF_6$ (1.05 g, 2.35 mmol) and KCN (0.450 g, 6.90 mmol) were refluxed for 2.5 h in 100 mL of $CH_3OH$. The solution became a brighter yellow and eventually clouded. After the solvent was removed in vacuo, the residue was washed with hexane and then flashed through a column of alumina in $CH_2Cl_2$ solvent. Evaporation of the solvent gave a bright yellow, crystalline solid (0.562 g, 1.88 mmol, 80% yield): IR ($CH_2Cl_2$): 2094(w), 1980(s), 1930(s) cm$^{-1}$; $^1H$-NMR ($CDCl_3$) 2.28 ppm.

**Preparation of $[(\eta^6\text{-Mesitylene})Mn(CO)_2(CN)]$ (3B).** $[(\eta^6\text{-Mesitylene})Mn(CO)_3]PF_6$ (0.160 g, 0.395 mmol) was suspended in 25 mL of $H_2O$ containing KCN (0.0257 g, 0.395 mmol). The suspension was heated and became homogeneous at reflux. After 0.5 h at 100 °C, it was cooled. The yellow solution was extracted repeatedly with $CH_2Cl_2$. After drying over $MgSO_4$, the $CH_2Cl_2$ layer was chromatographed through a column of alumina using 1:1 $CH_2Cl_2$/acetone. Evaporation left 0.0612 g (0.238 mmol) of cyano product, a 60% yield: IR ($CH_2Cl_2$) 2098(w), 1993(s), 1946(s) cm$^{-1}$; $^1H$-NMR ($CDCl_3$) 5.17 (s, 3 H, aryl), 2.32 (s, 9 H, Me) ppm.

**Preparation of $[(\eta^6\text{-}C_6H_6)Mn(CO)_2(CN)]$ (3C).** The procedure above was followed, except that the reaction solvent and temperature were 4:1 $H_2O/CH_3OH$ and 50 °C: 36% yield; IR ($CH_2Cl_2$) 2104(w), 2010(s), 1964(s) cm$^{-1}$; $^1H$-NMR ($CDCl_3$) 5.78 ppm.

**Preparation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(NCS)]$ and $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(SCN)]$.** $[(\eta^6\text{-}C_6Me_6)Mn(CO)_3]PF_6$ (1.07 g, 2.40 mmol) and KSCN (0.650 g, 6.68 mmol) were refluxed in 100 mL of $CH_3OH$ for 5.5 h. The color became red. The solution was cooled and evaporated in vacuo. Washing the residue with water removed the free thiocyanate as indicated by IR. Careful chromatography using $CH_2Cl_2$ on alumina yielded two bands. The first was orange and provided an orange solid, 0.145 g (0.438 mmol, 18% yield). This was identified as the Mn–NCS isomer: IR ($CH_2Cl_2$) 2113(m), 1987(s), 1935(s) cm$^{-1}$; (Nujol) 2103, 1967, 1916, 808, 730, 634, 594, 567, 533 cm$^{-1}$; $^1H$-NMR ($CDCl_3$) 2.26 ppm. The second band off the column was pink and provided a red solid, 0.0303 g (0.091 mmol, 4% yield). This was the Mn–SCN isomer: IR ($CH_2Cl_2$) 2107(w), 1978(s), 1930(s) cm$^{-1}$; (Nujol) 2098, 1966, 1919, 727, 636, 588, 564, 533 cm$^{-1}$; $^1H$-NMR ($CDCl_3$) 2.21 ppm.

**Preparation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNMe)]OTf$.** To a 50-mL $CH_2Cl_2$ solution containing 0.340 g (1.14 mmol) of **3A** was added excess (about 0.3 mL) $CH_3O_3SCF_3$ via syringe. Although no color change was evident, IR indicated immediate reaction. After a few minutes, the solution was concentrated to about 10 mL and was filtered. Addition of diethyl ether led to precipitation of yellow microcrystals (0.471 g, 1.02 mmol, 89% yield): $^1H$-NMR ($CD_2Cl_2$) 3.58 (s, 3 H, CNMe), 2.35 (s, 18 H, $C_6Me_6$) ppm. Anal. Calcd for $C_{17}H_{21}NSO_5F_3Mn$: C 44.1; H 4.58; N 3.02. Found: C 44.0; H 4.64; N 2.97. A similar procedure was used to prepare other isonitrile complexes, **5**, as well as complexes **9** and **10**. Infrared data for these species are found in Tables I and II.

**Preparation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNEt)]OTf$.** Prepared as above from **3A** and EtOTf: yield = 92%; $^1H$-NMR ($CD_2Cl_2$) 3.83 (q, $J$ = 7.2, 2 H, $CH_2$), 2.35 (s, 18 H, $C_6Me_6$), 1.43 (t, $J$ = 7.1, 3 H, Me) ppm. Anal. Calcd for $C_{18}H_{23}NSO_5F_3Mn$: C 45.3; H 4.87; N 2.93. Found: C 45.1; H 4.89; N 2.89.

**Preparation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNCPh_3)]PF_6$.** Prepared as above from **3A** and $Ph_3CPF_6$: yield = 82%; $^1H$-NMR ($CD_2Cl_2$) 7.2 (m, 15 H, Ph), 2.28 (s, 18 H, $C_6Me_6$) ppm.

**Preparation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNH)]BF_4$.** Prepared as above from **3A** and $HBF_4$: yield = 55%; $^1H$-NMR ($CD_2Cl_2$) 5.61 (s, 1 H, CNH), 2.40 (s, 18 H, $C_6Me_6$) ppm.

**Preparation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNBF_3)]$.** Prepared as above from **3A** and $BF_3$ (etherate): yield = 75%; $^1H$-NMR ($CD_2Cl_2$) 2.32 ppm. Anal. Calcd for $C_{15}H_{18}NO_2BF_3Mn$: C 49.1; H 4.95; N 3.82. Found: C 49.2; H 5.11; N 3.81.

**Preparation of $[(\eta^6\text{-Mesitylene})Mn(CO)_2(CNEt)]OTf$.** Prepared as above from **3B** and EtOTf: yield = 46%; $^1H$-NMR ($CD_2Cl_2$) 5.63 (s, 3 H, aryl), 3.82 (q, $J$ = 7.3, 2 H, $CH_2$), 2.39 (s,

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9 H, $Me_{mes}$), 1.42 (t, $J = 7.2$, 3 H, Me) ppm. Anal. Calcd for $C_{15}H_{17}NO_5SF_3Mn$: C 41.4; H 3.94; N 3.22. Found: C 41.3; H 3.82; N 3.18.

**Preparation of $[(\eta^6\text{-Mesitylene})Mn(CO)_2(CNCPh_3)]PF_6$.** Prepared as above from **3B** and $Ph_3CPF_6$: yield = 88%; $^1$H-NMR ($CD_2Cl_2$) 7.2 (m, 15 H, Ph), 5.61 (s, 3 H, aryl), 2.29 (s, 9 H, $Me_{mes}$) ppm.

**Preparation of $[(\eta^6\text{-}C_6H_6)Mn(CO)_2(CNMe)]OTf$.** Prepared as above from **3C** and MeOTf: yield = 67%; $^1$H-NMR ($CD_2Cl_2$) 6.22 (s, 6 H, aryl), 3.53 (s, 3 H, CNMe) ppm.

**Preparation of $[(\eta^6\text{-}C_6H_6)Mn(CO)_2(CNCPh_3)]PF_6$.** Prepared as above from **3C** and $Ph_3CPF_6$: yield = 81%; $^1$H-NMR ($CD_2Cl_2$) 7.2 (m, 15 H, Ph), 6.17 (s, 6 H, aryl) ppm.

**Preparation of Copper(I) Complexes.** **3A** (0.145 g, 0.485 mmol) and $[Cu(NCMe)_4]PF_6$ (0.181 g, 0.485 mmol) were dissolved in 50 mL of $CH_2Cl_2$. IR indicated immediate formation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(\mu\text{-}CN)Cu(NCMe)]PF_6$. This species could be isolated at this stage by precipitation using diethyl ether: yield = 98%; $^1$H-NMR ($CD_2Cl_2$) 2.29 (s, 18 H, $C_6Me_6$), 2.27 (s, 3 H, NCMe) ppm. Anal. Calcd for $C_{16}H_{21}N_2PO_2F_6CuMn$: C 37.2; H 3.86; N 5.11. Found: C 38.1; H 4.16; N 5.47.

Addition of 0.382 g (1.46 mmol) $PPh_3$ produced no change in the yellow color, but a significant IR shift was evident. Concentration in vacuo to about 10 mL, filtration, and precipitation with diethyl ether gave a yellow powder. This was further purified by overnight Soxhlet extraction using diethyl ether. The product became highly crystalline: 0.422 g were collected from the thimble (0.326 mmol, 67% yield); $^1$H-NMR ($CD_2Cl_2$): 7.3 (s, 45 H, $PPh_3$), 2.13 (s, 18 H, $C_6Me_6$) ppm. Anal. Calcd for $C_{69}H_{63}NP_4O_2F_6CuMn$: C 64.0; H 4.91; N 1.08. Found: C 63.2; H 5.02; N 1.08.

**Reaction of 3A with Other Metal Cations.** $[Mn(CO)_5]BF_4$ and $[CpFe(CO)_2]BF_4$ were prepared from $[Mn(CO)_5Br]$ and $[CpFe(CO)_2I]$, respectively, using $AgBF_4$ in $CH_2Cl_2$. After filtration to remove silver halide, the solution was added to the **3A**. Infrared analysis (see Table I) indicated formation of the cyano-bridged complex in solution. However precipitation using diethyl ether at room temperature or −78 °C provided only unreacted **3A**.

**Attempted Reaction of 3A with Weak Electrophiles.** Treatment of **3A** with excess benzoyl chloride in room temperature or refluxing $CH_2Cl_2$ led to a slight increase in IR frequency of about 10 cm$^{-1}$. However the starting material was always recovered. Other unreactive electrophiles included acetyl chloride, methyl tosylate, tropylium hexafluorophosphate, *p*-nitrophenyldiazonium tetrafluoroborate, and acetic anhydride.

**Preparation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNCMe_3)]PF_6$ Using Free Isonitrile.** Excess *tert*-butyl isocyanide (about 0.5 mL) in 50 mL of $CH_2Cl_2$ was added to $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(THF)]PF_6$ (0.0947 g, 0.203 mmol). Within 10 min the solution color had changed from purple to yellow-orange. After 0.5 h the solution was concentrated in vacuo to 10 mL, filtered, and precipitated with diethyl ether. The product was a pale yellow powder (0.0567 g, 0.133 mmol, 56% yield).

**Preparation of $[(\eta^5\text{-}1,3,5\text{-}C_6Me_3H_4)Mn(CO)_2(CNCPh_3)]$.** **3B** (0.0537 g, 0.209 mmol) and trityl hexafluorophosphate (0.0994 g, 0.294 mmol) were dissolved in 20 mL of $CH_2Cl_2$. As the solvent was added to the solids, the orange color of the trityl cation immediately gave way to a medium yellow. After stirring for 5 min, the solution was cooled to 0 °C and 2 mL of $CH_2Cl_2$ containing 0.0711 g (0.276 mmol) $(^nBu)_4NBH_4$ were added via syringe. No change in color was apparent. IR indicated complete reaction. After 10 min, the mixture was concentrated to about 5 mL in vacuo. Byproduct $(^nBu)_4NPF_6$ was precipitated by the addition of excess diethyl ether and was filtered off. The yellow oil which remained after solvent evaporation was crystallized from diethyl ether/hexane solution at −78 °C; 0.0833 g were obtained (0.166 mmol, 79% yield): IR ($C_6H_{14}$) 2073(m,br), 1940(s), 1900(s) cm$^{-1}$; $^1$H-NMR ($CDCl_3$) (see **11** for numbering scheme) 7.2 (mult, 15 H, Ph), 4.44 (s, 2 H, $H_{2,4}$), 2.38 (s, 3 H, $Me_3$), 2.29 (d, $J = 12$, 1 H, $H_{6\text{-endo}}$), 1.42 (s, 6 H, $Me_{1,5}$), 1.34 (d, $J = 12$, 1 H, $H_{6\text{-exo}}$) ppm.

**Preparation of $[(\eta^5\text{-}1,2,3,4,5,6\text{-}C_6Me_6H)Mn(CO)_2(CNCPh_3)]$.** This complex was prepared as described above in 78% yield: IR ($C_6H_{14}$) 2064(m,br), 1934(s), 1893(s) cm$^{-1}$; $^1$H-NMR ($CDCl_3$) 7.2 (mult, 15 H, Ph), 2.40 (s, 3 H, $Me_3$), 2.14 (q, $J = 6.9$, 1 H, $H_{6\text{-exo}}$), 1.81 (s, 6 H, $Me_{2,4}$), 1.40 (s, 6 H, $Me_{1,5}$), 1.19 (d, $J = 7.2$, 3 H, $Me_{6\text{-endo}}$) ppm; $^{13}$C-NMR ($CDCl_3$) 16.3 ($Me_{6\text{-endo}}$), 16.4 ($Me_{1,5}$), 17.0 ($Me_{2,4}$), 17.1 ($Me_3$), 29.9 ($CPh_3$), 36.8 ($C_6$), 58.5 ($C_{1,5}$), 76.0 ($C_3$), 92.0 ($C_{2,4}$), 127.9–129.6 (Ph), 143.8 (CN), 229.3 (CO). Anal. Calcd for $C_{34}H_{34}NO_2Mn$: C 75.1; H 6.32; N 2.58. Found: C 75.6; H 6.33; N 2.37.

**Preparation of $[(\eta^5\text{-}C_6H_7)Mn(CO)_2(CNCPh_3)]$.** This complex was prepared as described above in 79% yield: IR ($C_6H_{14}$) 2085(m,br), 1953(s), 1910(s) cm$^{-1}$; $^1$H-NMR ($CDCl_3$) 7.2 (mult, 15 H, Ph), 5.72 (tt, $J = 5.2, 1.3$, 1 H, $H_3$), 4.61 (t, $J = 6.2$, 2 H, $H_{2,4}$, 2.63 (t, $J = 6.4$, 2 H, $H_{1,5}$), 2.50 (mult, $J = 12, 6$, 1 H, $Me_{6\text{-endo}}$), 1.99 (d, $J = 12$, 1 H, $H_{6\text{-exo}}$) ppm; $^{13}$C-NMR ($CDCl_3$) 24.7 ($C_6$), 10.0 ($CPh_3$), 48.2 ($C_{1,5}$), 78.4 ($C_3$), 98.0 ($C_{2,4}$), 128.1–128.6 (Ph), 143.4 (CN), 225.0 (CO). Anal. Calcd for $C_{28}H_{22}NO_2Mn$: C 73.2; H 4.84; N 3.05. Found: C 72.8; H 5.17; N 2.99.

**Preparation of $[(\eta^5\text{-}6\text{-}exo\text{-}MeC_6H_6)Mn(CO)_2(CNCPh_3)]$.** **3C** (0.0514 g, 0.239 mmol) and trityl hexafluorophosphate (0.102 g, 0.263 mmol) were combined in 20 mL of $CH_2Cl_2$ as described above. After cooling to −78 °C, 0.5 mL of 1.5 M methyllithium were added via syringe. The yellow color lightened slightly. The solution was stirred for 15 min and then warmed to 20 °C. The solvent was evaporated. The residue was suspended in diethyl ether and filtered through alumina to destroy excess nucleophile. Evaporation of the solvent left 0.0934 g of yellow solid (0.197 mmol, 83% yield): IR ($C_6H_{14}$) 2086(m,br), 1953(s), 1911(s) cm$^{-1}$; $^1$H-NMR ($CDCl_3$) 7.2 (mult, 15 H, Ph), 5.59 (tt, $J = 5.2, 1.3$, 1 H, $H_3$), 4.55 (dd, $J = 6.3, 5.3$, 2 H, $H_{2,4}$), 2.95 (td, $J = 6.6, 1.1$, 2 H, $H_{1,5}$), 2.41 (q, $J = 6.1$, 1 H, $H_{6\text{-endo}}$), 0.34 (d, $J = 6.5$, 3 H, $Me_{6\text{-exo}}$) ppm; $^{13}$C-NMR ($CDCl_3$) 28.4 ($Me_{6\text{-exo}}$), 30.0 ($CPh_3$), 30.1 ($C_6$), 57.1 ($C_{1,5}$), 78.0 ($C_3$), 95.6 ($C_{2,4}$), 128.2–128.5 (Ph), 143.5 (CN), 225.8 (CO). Anal. Calcd for $C_{29}H_{24}NO_2Mn$: C 73.6; H 5.12; N 2.96. Found: C 74.0; H 5.72; N 2.81.

**Preparation of $[(\eta^5\text{-}6\text{-}exo\text{-}PhC_6H_6)Mn(CO)_2(CNCPh_3)]$.** The reaction was run as above, except using phenylmagnesium bromide (3 M in THF) as the nucleophile at 0 °C. A 95% yield of a yellow oil was obtained: IR ($C_6H_{14}$): 2087(m,br), 1956(s), 1912(s) cm$^{-1}$; $^1$H-NMR ($CDCl_3$): 7.2 (mult, 18 H, Ph), 6.94 (d, $J = 7.7$, 2 H, $Ph_{6\text{-exo},ortho}$), 5.61 (tt, $J = 5.3, 1.2$, 1 H, $H_3$), 4.80 (dd, $J = 6.5, 5.4$, 2 H, $H_{2,4}$), 3.68 (t, $J = 6.0$, 1 H, $H_{6\text{-endo}}$), 3.23 (dd, $J = 7.2, 6.0$, 2 H, $H_{1,5}$) ppm; $^{13}$C-NMR ($CDCl_3$): 30.0 ($CPh_3$), 40.0 ($C_6$), 56.0 ($C_{1,5}$), 78.0 ($C_3$), 96.4 ($C_{2,4}$), 125.8–127.4 ($Ph_{6\text{-exo}}$), 128.2–128.5 (Ph), 143.4 (CN), 227.2 (CO). Anal. Calcd for $C_{34}H_{26}NO_2Mn$: C 76.3; H 4.90; N 2.62. Found: C 76.8; H 4.95; N 2.45.

**X-ray Diffraction Study of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2(CNMe)]OTf$.** Suitable crystals were grown by diffusion of diethyl ether into a $CH_2Cl_2$ solution of the compound at −5 °C. One of the yellow rod-shaped crystals was cut approximately in half, providing a fragment (1.0 × 0.53 × 0.28 mm) which was glued to a glass fiber. A Siemens P4 diffractometer (Mo K$\alpha$ radiation, 0.71073 Å, P3 software) was used to collect intensity data at −35 °C by $\omega$ scans technique. Scan rate was variable (4.0–29.3° min$^{-1}$). Three standard reflections were monitored every 100 reflections. Absorption correction was based on face indexing of the crystal. The structure was solved by direct methods using the Siemens SHELXTL PC program package. Non-hydrogen atoms were refined anisotropically to minimize $\Sigma w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F) + 0.0002F^2$. All hydrogen atoms were found in a difference Fourier map and then were placed in theoretical positions with $r = 0.96$ Å. The maximum residual electron density peak in the final difference Fourier map was 0.75 e Å$^{-3}$.

**X-ray Diffraction Study of $[(\eta^6\text{-}C_6H_6)Mn(CO)_2(CNCPh_3)]PF_6$.** Large, plate-like single crystals were grown as above. After cutting, the selected fragment (0.76 × 0.70 × 0.49 mm) was glued to a glass fiber. Data collection was carried out as above with the exceptions that the collection temperature was 25 °C and XSCANS software was used. Face indexing was again used as the basis for an absorption correction. The unit cell volume was found to be quite large (5731.7 Å$^3$). This was the result of two ion pairs and a $CH_2Cl_2$ molecule comprising the asymmetric unit. Extensive disorder in both $PF_6^-$ anions was modeled by two interpenetrating octahedra with fixed bond lengths. A disordered phenyl on the isonitrile was treated similarly. Nevertheless we were unable to model the disorder accurately enough to reduce the $R$ value below about 10%.

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**Supplementary Material Available:** H-Atom coordinates, isotropic and anisotropic displacement coefficients, and packing diagram for [($\eta^6$-$C_6Me_6$)Mn(CO)$_2$(CNMe)]OTf (4 pages). Ordering information is given on any current masthead page.

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