eV, $W(4f_{5/2})$ = 36.7 and 37.7 eV in a 2:1 ratio].

To this solution was added 0.5 mL of dry, deoxygenated 2-heptene. The solution was allowed to stand 24 h at room temperature. Analysis of the reaction by GLC (10 ft × $^1/_8$ in. diameter, 10% Carbowax, 20M, 5% potassium hydroxide on 80–100-mesh Chromosorb P) showed no detectable amount of 5-decene, thus confirming the inactivity of the solution for the olefin metathesis reaction.

The reaction was quenched by addition of 1.0 mL of deoxygenated water. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was removed in vacuo to leave 100 mg of a yellow oily residue: ^{1}H NMR (CDCl$_3$) δ 7.2–6.7 (1 H, m), 1.5 (4 H, m), 1.25 (17 H, m), 0.9 (11 H, m). The structure of this high molecular weight material is unknown, but it appears to be formed by a nonmetathesis oligomerization of 2-heptene or alkylation of the solvent. This indicated that the spent metathesis catalyst was able to convert simple olefins into higher molecular weight species by some type of oligomerization process.

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Synthesis and Electrophilic Reactivity of Dicarbonylnitrosyl(cyclohexadienyl)manganese Cations: Double Nucleophilic Addition to Coordinated Arenes

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Abstract: Treatment of (cyclohexadienyl)Mn(CO)$_2$L (L = CO, PBu$_3$) with NOPF$_6$ provides a convenient synthesis of (cyclohexadienyl)Mn(CO)(NO)L$^+$ cations (3; X = Me, OMe; R = H, Me, Ph, CN, CH$_2$COCMe$_3$; L = CO, PBu$_3$). Reaction of **3** with nucleophilic reagents gives attack at the ring to yield (cyclohexadiene)Mn(CO)(NO)L complexes (**4**). Phosphorus and nitrogen nucleophiles add to **3** in a regio- and stereospecific manner (exo at C-5). Hydride donors add to **3** stereospecifically endo to the metal; **3** is the first class of coordinated cyclic π-hydrocarbon complexes that reacts with hydride in this manner. While NaCH(CO$_2$Me)$_2$ reacts with **3** in the normal way to give exo addition, many other carbon donor nucleophiles react by what appears to be a single electron-transfer pathway that ultimately gives a variety of products, including (cyclo-hexadienyl)Mn(CO)$_2$L. Ways to eliminate the undesirable side reactions with carbon donors are discussed. Overall, this report describes a simple procedure for the manganese-mediated conversion of coordinated arenes to difunctionalized coordinated cyclohexadienes by the addition of a nucleophile to (arene)Mn(CO)$_2$L$^+$ to give **2**, reaction with NOPF$_6$ to give **3**, and finally addition of a second nucleophile.

The electrophilic activation of π-hydrocarbons by coordination to a transition-metal moiety represents a fundamental process in organometallic chemistry. Studies of nucleophilic addition to π-hydrocarbons activated in this manner have led to significant synthetic and mechanistic applications.[1] With cyclic π-hydrocarbons the best known reactions involve the addition of a single nucleophile to a coordinated arene or cyclohexadienyl ring to give monofunctionalized products. The addition of *two* nucleophiles to coordinated rings would be a synthetically useful reaction, particularly if the two nucleophiles could be varied independently. Not surprisingly, such double additions are rare because the electrophilicity of the π-hydrocarbon is weakened or lost after the first nucleophile adds. However, we recently discovered[2] what appears to be a general procedure for the addition of two nucleophiles to coordinated arenes to yield difunctionalized coordinated cyclohexadienes. Scheme I illustrates the process. To effect double addition to the arene in **1**, the complex obtained after the first addition must be reactivated. NOPF$_6$ performs this function cleanly by converting **2** to **3**, which then reacts with a

Scheme I
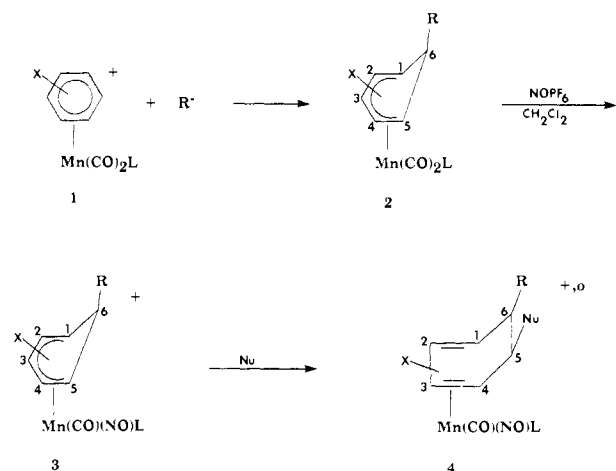
second nucleophile (Nu) to give the diene. In this paper we report details of the chemistry in Scheme I.

Table I. IR and ^{1}H NMR Data for (Cyclohexadienyl)Mn(CO)$_2$L Complexes (**2**)^a

X	R	L	ν_{CO}, cm^{-1}	^{1}H NMR (δ)	anal.^{b}
2-Cl	Me	CO	2028, 1960, 1950^c	5.38 (d, J = 5, H^3), 3.91 (dd, J = 7, 5, H^d), 3.06 (d, J = 6, H^1), 2.41 (dd, J = 7, 6, H^5), 2.15 (m, H^6), 0.05 (d, J = 6.5, Me)^{d,e}	
1-Cl	Me	CO	2028, 1960, 1950^c	4.68 (dd, J = 6, 5, H^3), 4.51 (d, J = 6, H^2), 3.86 (dd, J = 6, 5, H^4), 2.73 (m, H^{5,6}), 0.29 (d, J = 6.5, Me)^{d,f}	
1,2,4,5-Me	Ph	CO	2007, 1931, 1923^c	6.99 (m, Ph), 4.78 (s, H^3), 3.67m (s, H^6), 1.48 (s, Me^{2,4}), 1.40 (s, Me^{1,5})^d	C, 65.2 (65.1); H, 5.4 (5.4)^g
1,2,3,4-Me	Ph	CO	2009, 1939, 1927^c	6.97 (m, Ph), 3.55 (d, J = 6, H^5), 2.86 (d, J = 6, H^6), 1.98 (s, Me), 1.61 (s, Me), 1.53 (s, Me), 1.49 (s, Me)^d	C, 65.2 (65.1); H, 5.4 (5.4)^g
H	H	PPh$_3$	1943, 1884^h	5.56 (t, J = 5, H^3), 4.33 (q, J = 6, H^{2,4}), 2.65 (m, H^{6-endo}), 2.33 (t, J = 6, H^{1,5}), 1.94 (dd, H^{6-exo})	
H	H	PBu$_3$	1935, 1875^h		
H	Me	PPh$_3$	1944, 1884^c	5.52 (t, J = 5, H^3), 4.36 (q, J = 5, H^{2,4}), 2.76 (t, J = 6, H^{1,5}), 2.64 (m, J = 6, H^6), 0.39 (d, J = 6, Me)^i	C, 69.33 (69.53); H, 5.36 (5.19)
H	Me	PBu$_3$	1935, 1874^c	5.42 (t, J = 5.5, H^3), 4.36 (q, J = 5, H^{2,4}), 2.76 (t, J = 6, H^{1,5}), 2.53 (m, J = 6, H^6), 1.42–0.89 (m, Bu), 0.34 (d, J = 6, Me)^i	
H	Ph	PPh$_3$	1943, 1884^j		

^{a} See structure **2** for numbering scheme. ^{b} Calculated values in parentheses. ^{c} In hexane. ^{d} In C$_6$D$_6$. ^{e} ^{13}C NMR (ppm) in C$_6$D$_6$: 26.2 (Me), 32.1 (C^6), 58.3, 58.6 (C^{1,5}), 78.1 (C^4), 91.0 (C^3), 94.2 (C^2), 220 (CO). ^{f} ^{13}C NMR (ppm) in C$_6$D$_6$: 22.8 (Me), 39.9 (C^6), 59.1 (C^5), 74.2 (C^4), 80.7 (C^1), 92.4 (C^2), 93.9 (C^3), 220.7 (CO). ^{g} Mass spectral mol wt = 350; calcd = 350. ^{h} In pentane. ^{i} In CDCl$_3$. ^{j} In cyclohexane.

**Table II.** IR and Analytical Data for [(Cyclohexadienyl)Mn(CO)(NO)L]PF$_6$ Complexes (**3**)^a

X	R	L	% yield	ν_{CO}, cm^{-1}	ν_{NO}, cm^{-1}	anal.^{b}
H	Ph	CO	78	2112, 2078	1843^c	C, 38.27 (38.12); H, 2.56 (2.51); N, 3.07 (3.18)
H	Me	CO	83	2109, 2073	1840^c	C, 28.24 (28.52); H, 2.37 (2.39); N, 3.27 (3.69)
H	CH$_2$COCMe$_3$	CO	71	2105, 2072, 1700	1835^d	C, 35.15 (36.30); H, 3.49 (3.69); N, 2.54 (3.02)
2-OMe	Me	CO	56	2107, 2073	1835^c	
2-OMe	Ph	CO	81	2108, 2074	1840^c	C, 38.15 (38.32); H, 2.75 (2.57); N, 3.12 (2.98)
1-Me,4-OMe	Ph	CO	84	2103, 2068	1833^c	C, 39.42 (39.61); H, 3.20 (3.21); N, 2.69 (2.89)
H	CN	CO	23^e	2120, 2082	1858^c	
1,2,3,4,5-Me	Me	CO	76	2089, 2051	1818^c	C, 36.87 (36.62); H, 3.88 (4.14); N, 2.95 (3.05)
1,2,3,4,5,6-Me	H	CO	f	2085, 2040	1810^c	
1,2,4,5-Me	Ph	CO	89	2094, 2056	1824^d	C, 42.9 (43.5); H, 3.8 (3.8); N, 2.6 (2.8)
1,2,3,4-Me	Ph	CO	60	2097, 2062	1822^d	C, 43.0 (43.5); H, 4.0 (3.8); N, 2.0 (2.8)
2-OMe	Me	CO	67^g	2108, 2067	1830^d	
H	Ph	CO$_2$Me	54	2019, 1649	1778^h	C, 54.9 (55.0); H, 4.4 (4.3); N, 3.7 (4.3)
H	Me	P(OMe)$_3$		2041	1793^d	C, 27.99 (27.81); H, 4.51 (3.82); N, 2.73 (5.95)
H	Me	P(C$_2$H$_4$CN)$_3$		2031	1786^c	
H	H	PPh$_3$	33^i	2056	1805^c	
H	H	PBu$_3$	i	2042	1795^c	
H	Ph	PPh$_3$	90	2038	1790^c	
H	Me	PBu$_3$		2025	1778^d	
H	Ph	PBu$_3$	85	2028	1783^c	C, 48.61 (48.79); H, 6.05 (6.22); N, 2.22 (2.27)

^{a} See structure **3** for the numbering scheme. ^{b} Calculated values in parentheses. ^{c} In CH$_3$NO$_2$. ^{d} In CH$_2$Cl$_2$. ^{e} Product obtained as 1:1 mixture of [(C$_6$H$_6$CN)Mn(CO)$_2$NO]PF$_6$ and [(C$_6$H$_6$)Mn(CO)$_3$]PF$_6$. ^{f} Product obtained as a 2:1 mixture of [(C$_6$Me$_6$)Mn(CO)$_3$]PF$_6$ and [(C$_6$Me$_6$H)Mn(CO)$_2$NO]PF$_6$. ^{g} BF$_4$$^-$ salt. ^{h} In hexane. ^{i} Product obtained as mixtures of [(C$_6$H$_6$)Mn(CO)$_2$L]PF$_6$ and [(C$_6$H$_7$)Mn(CO)(NO)L]PF$_6$.

Double nucleophilic addition to coordinated arenes has been reported with several other complexes, but usually the reported procedure cannot be readily generalized to include a variety of nucleophiles for both R and Nu. The most significant work in this area is due to Brookhart et al.,[3-7] who found that double hydride addition to (arene)Mn(CO)$_3$$^+$ is possible with strong hydride donors. The resultant (cyclohexadienyl)Mn(CO)$_3$$^-$ complexes react with methyl iodide to give a cyclohexenyl complex that can be deprotonated to give a methyl-substituted cyclohexadienyl. Double addition of methoxide and cyclopentadienide to (C$_6$H$_6$)Co(Cp)$^{2+}$ is known, but extension to other nucleophiles does not appear possible.[8] Double addition of hydride to the benzene in (C$_6$H$_6$)Ru(C$_6$Me$_6$)$^{2+}$, (C$_6$H$_6$)Rh(C$_5$Me$_5$)$^{2+}$, and (C$_6$H$_6$)Ir(C$_5$Me$_5$)$^{2+}$ is also known.[9] Conversion of (C$_6$H$_6$)$_2$Fe^{2+} to the monofunctionalized cyclohexadiene (C$_6$H$_7$R)Fe(C$_6$H$_6$) is possible by hydride addition followed by carbanion addition; however, difunctionalized is not possible because electron transfer occurs when the first nucleophile is a carbanion.[10]

Functionalized cyclohexadienes are also available via nucleophilic addition to the well-known[11-13] (cyclohexadienyl)Fe(CO)$_3$$^+$ complexes (eq 1). Complexes **5** are synthesized by hydride
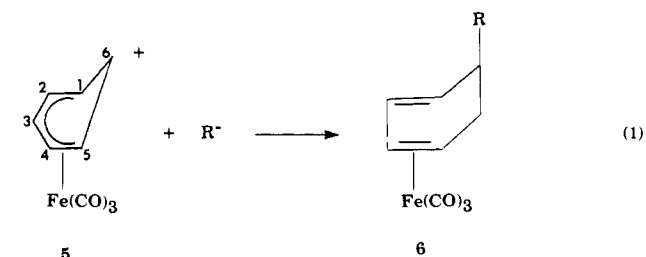
abstraction from **6** (R = H), which in turn are made by complexation of the free diene. It is difficult to prepare **5** with a substituent other than hydrogen at C-6,[14] and accordingly eq 1

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Table III. ^{1}H NMR Data^a for [(Cyclohexadienyl)Mn(CO)(NO)L]PF$_6$ Complexes (3)^b

X	R	L	^{1}H NMR (δ)
H	Ph	CO	7.35, 7.14 (Ph), 6.99 (t, J = 6, H^3), 6.22 (t, J = 6, H^{2,4}), 4.22 (t, J = 6, H^6), 5.05 (t, J = 6, H^{1,5})^c
H	Me	CO	6.98 (t, H^3), 6.02 (t, H^{2,4}), 4.81 (t, H^{1,5}), 2.94 (m, J = 6, H^6), 0.78 (d, J = 6, Me)^e
H	CH$_2$COCMe$_3$	CO	7.04 (t, J = 6, H^3), 5.92 (t, J = 6, H^{2,4}), 4.72 (t, H^{1,5}), 3.21 (q, J = 6, H^6), 2.30 (d, J = 7, CH$_2$), 1.03 (s, Me)^d
2-OMe	Me	CO	6.75 (br, H^3), 6.05 (br, H^4), 4.75 (br), 3.10 (br), 3.89 (OMe), 0.80 (d, J = 6, Me)^c
2-OMe	Ph	CO	7.33, 7.10 (Ph), 6.75 (br, H^3), 6.21 (br, H^4), 5.03 (br), 3.94 (OMe)^c
1-Me,4-OMe	Ph	CO	7.35, 7.00 (Ph), 6.65 (br, H^3), 5.73 (br, H^2), 4.28, 4.14 (br, H^{5,6}), 3.87 (OMe), 1.96 (s, Me)^d
1,2,4,5-Me	Ph	CO	7.15 (m, Ph), 6.69 (s, H^3), 4.26 (s, H^6), 2.26 (s, Me^{2,4}), 2.00 (s, Me^{1,5})^c
1,2,3,4-Me	Ph	CO	7.02 (, Ph), 4.57 (d, J = 6, H^5), 4.10 (d, J = 6, H^6), 2.79 (s, Me), 2.35 (s, Me), 2.32 (s, Me), 2.18 (s, Me)^c
H	Ph	CO$_2$Me	6.90 (m, Ph), 6.46 (dd, H^3), 5.39, 5.09 (dd, J = 7; dd, J = 7; H^{2,4}), 3.75, 3.46 (m; dd; H^{1,5}), 3.58 (s, OMe), 2.90 (dd, J = 6,6,H^6)^e
H	Me	P(OMe)$_3$	5.73 (q, J = 7, H^3), 5.35, 5.04 (m; t, J = 7; H^{2,4}), 3.75, 3.56 (m; m, J = 6; H^{1,5}), 2.60 (q, J = 6, H^6), 3.83 (d, J = 11, OMe), 0.64 (d, J = 6, Me)^d
H	Me	PBu$_3$	6.59 (br, H^3), 5.59, 4.99 (br, H^{2,4}), 3.42. 2.63 (br, H^{1,5}), 2.22 (br, H^6), 1.8–1.0 (Bu), 0.66 (Me)^d
H	Ph	PBu$_3$	6.57 (H^3), 5.77, 5.46 (H^{2,4}), 5.20, 3.83, 3.67 (H^{1,5,6}), 1.9–0.9 (Bu)^d

^{a} All spectra recorded at room temperature unless otherwise noted. ^{b} See structure 3 for numbering scheme. ^{c} In CD$_3$NO$_2$. ^{d} In CD$_2$Cl$_2$. ^{e} In toluene-d_8 at –60 °C.

in effect permits only monofunctionalization. In contrast to this, the manganese complexes **3** are readily synthesized with a non-hydrogen substituent at C-6.

Experimental Section

All solvents were purified by standard methods and all synthetic procedures were done under a nitrogen or argon atmosphere. The [(arene)Mn(CO)$_3$]PF$_6$ complexes (**1**; L = CO, PPh$_3$, PBu$_3$; X = H, Cl, Me, OMe) were synthesized as previously described.[15,16] Following published procedures,[16–19] nucleophilic addition of NaBH$_4$, NaCN, MeMgCl, PhMgBr, and LiCH$_2$COCMe$_3$ to **1** gave the corresponding cyclohexadienyl complexes **2**. Several of these are new or have not been completely characterized in the past, and accordingly some selected spectroscopic data are given in Table I.

[(Cyclohexadienyl)Mn(CO)(NO)L]PF$_6$ (**3**). All of these complexes were synthesized by the same procedure except for those with L = P-(OMe)$_3$ and P(C$_2$H$_4$CN)$_3$. The following is a typical synthesis: to (C$_6$H$_6$Me)Mn(CO)$_3$ (0.23 g, 0.99 mmol) in 10 mL of CH$_2$Cl$_2$ at room temperature NOPF$_6$ (0.19 g, 1.1 mmol) was added and the mixture was stirred for 30 min. Several milliliters of CH$_3$NO$_2$ were then added and the solution filtered. Excess diethyl ether was added to precipitate the product as yellow-orange crystals, which were washed with diethyl ether and dried. The yield was 0.31 g (83%) of [(C$_6$H$_6$Me)Mn(CO)$_2$(NO)]-PF$_6$. Tables II and III give analytical and spectroscopic data.

[(C$_6$H$_6$Ph)Mn(CO)(NO)CO$_2$Me]. To a stirred solution of NaOMe (0.09 g, 1.74 mmol) in methanol (100 mL) at –78 °C was added [(C$_6$H$_6$Ph)Mn(CO)$_2$(NO)]BF$_4$ (0.52 g, 1.36 mmol). The yellow suspension was stirred for 1 h at –78 °C and the resulting orange solution evaporated to dryness at low temperature. Extraction into pentane (50 mL) and cooling to –78 °C over a period of 3 h yielded the product as an orange crystalline solid (0.09 g, 20%). Further product was obtained on evaporation to dryness of the pentane mother liquor (0.15 g, 34%). The product is thermally unstable above 0 °C and is air sensitive.

[(C$_6$H$_6$Me)Mn(CO)(NO)L]PF$_6$ [L = P(OMe)$_3$, P(C$_2$H$_4$CN)$_3$]. IR studies showed that P(OMe)$_3$ and P(C$_2$H$_4$CN)$_3$ react with [(C$_6$H$_6$Me)-Mn(CO)$_2$NO]PF$_6$ to give a mixture of products derived from CO substitution and from addition to the cyclohexadienyl ring. The relative amounts of these products varied from experiment to experiment, although IR spectra showed that the ring addition product is formed initially. In a typical experiment, stirring excess P(OMe)$_3$ and [(C$_6$H$_6$Me)Mn(CO)$_2$NO]PF$_6$ in CH$_2$Cl$_2$ for 1 h followed by addition of diethyl ether gave a precipitate that was put through a neutral alumina column (1:1 CH$_2$Cl$_2$–CH$_3$NO$_2$). Solution concentration and precipitation with diethyl ether gave [(C$_6$H$_6$Me)Mn(CO)(NO)P(OMe)$_3$]PF$_6$ in an overall 25% yield. The original reaction solution (CH$_2$Cl$_2$–Et$_2$O) slowly precipitated additional material that was shown by IR to be a 3:1 mixture of the ring adduct and the CO displaced product.

Addition of PR$_3$ to [(Cyclohexadienyl)Mn(CO)$_2$NO]PF$_6$ (**3**). IR spectral studies showed that tertiary phosphines add quantitatively to the ring in **3** to give cyclohexadiene complexes **4**. Several of these phosphine adducts were synthesized by the following typical procedure: to a slurry of [(C$_6$H$_6$Ph)Mn(CO)$_2$NO]PF$_6$ (0.15 g, 0.34 mmol) in CH$_2$Cl$_2$ (10 mL) was added PBu$_3$ (0.072 g, 0.36 mmol) with vigorous stirring. The reaction mixture became a homogeneous solution within a few seconds as the CH$_2$Cl$_2$ soluble product formed. The addition of excess diethyl ether gave orange crystals of [(C$_6$H$_6$Ph PBu$_3$)Mn(CO)$_2$NO]PF$_6$ (0.16 g, 73%). An X-ray structural study showed[20] that the PBu$_3$ is exo as depicted in structure **4**. A similar synthesis with P(4-MeOC$_6$H$_4$)$_3$ gave the adduct in 75% yield. The phosphine adducts of [(C$_6$H$_6$Me)Mn(CO)$_2$NO]PF$_6$ were also prepared by this procedure. Although these products were stable enough for spectral characterization, storage in solution or as a solid at room temperature led to decomposition. The synthetic procedure outlined above presented a difficulty in that the diethyl ether induced precipitation sometimes produced oils rather than crystalline materials. Whether an oil or a crystalline solid was obtained was dependent on concentration and temperature factors. The oily products (which were spectrally pure) could sometimes be crystallized by slow reprecipitation.

Tables IV and V give analytical and spectroscopic data for all the cyclohexadiene complexes **4** reported in this study.

Addition of Nitrogen Donors to [(Cyclohexadienyl)Mn(CO)$_2$NO]PF$_6$ (**3**). IR spectra showed that nitrogen donors such as pyridine and N-methylimidazole rapidly react with **3** to give ring adducts **4**. Attempts to synthesize these complexes followed the procedure described above for the phosphine adducts. Although crystalline materials were obtained and characterized via IR, the products were thermally unstable at room temperature and within 1 day had significantly decomposed.

Addition of Hydride Donors to [(Cyclohexadienyl)Mn(CO)(NO)L]PF$_6$ (**3**). Most of the complexes **4** with Nu = H$^-$ were synthesized by the following procedure: to a stirred suspension of dienyl complex **3** in MeCN/THF (1:2) at –5 °C was added a slight excess of NaBH$_4$. After stirring for ca. 1 h, the solution was evaporated to dryness and extracted with pentane. Evaporation of the pentane generally gave a pure product. In several cases a mixture of isomeric products was obtained, and these were separated via TLC (silica gel G) with hexane or via an alumina column with pentane. (C$_6$H$_7$CN)Mn(CO)$_2$NO was synthesized by treating a mixture of [(C$_6$H$_6$)Mn(CO)$_3$]PF$_6$ and [(C$_6$H$_6$CN)Mn(C-O)$_2$NO]PF$_6$ (obtained in the reaction of NOPF$_6$ and (C$_6$H$_6$CN)Mn-(CO)$_3$) with NaBH$_4$ and chromatographing through alumina. Hexane eluted (C$_6$H$_7$)Mn(CO)$_3$ and CHCl$_3$ eluted the desired product.

A number of other hydride donors was tried, including NaBH$_3$CN, NaH, LiAlH$_4$, and LiB(C-HMeEt)$_3$. Hydride donors stronger than NaBH$_4$ frequently led to decomposition or converted **3** to **2** (vide infra). With the strong donor LiB(CHMeEt)$_3$ the outcome of the reaction seemed to depend on the electrophilicity of the starting complex **3**. Thus the more electrophilic [(C$_6$H$_6$Ph)Mn(CO)$_2$NO]PF$_6$ did not yield any hydride adduct **4**, while the much less electrophilic [(C$_6$H$_6$Ph)Mn-(CO)(NO)PBu$_3$]PF$_6$ reacted smoothly to give **4**.

Addition of Carbon Donors to [(Cyclohexadienyl)Mn(CO)(NO)L]PF$_6$ (**3**). The reaction of **3** (L = CO) with carbon donor nucleophiles was briefly examined. Nucleophiles such as MeLi, CdMe$_2$, MeMgCl, Li-CuMe$_2$, and KCH$_2$NO$_2$ in THF or diethyl ether gave mixtures of prod-

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Table IV. IR and Analytical Data for (Cyclohexadiene)Mn(CO)(NO)L Complexes (4)[a]

X	R	Nu	L	% yield	ν_{CO},cm^{-1}	ν_{NO},cm^{-1}	anal.[b]
H	Me	PPh$_3$	CO	c	2047, 1998	1761[d]	
H	Ph	PPh$_3$	CO	c	2048, 1999	1762[d]	
H	Me	PBu$_3$	CO	c	2043, 1992	1755[d]	C, 43.50 (43.40); H, 6.19 (6.24); N, 2.53 (2.41)
H	Ph	PBu$_3$	CO	73[c]	2045, 1999	1755[d]	C, 48.53 (48.53); H, 6.01 (5.9); N, 2.24 (2.18)
H	Me	CH(CO$_2$Me)$_2^-$	CO	33	2041, 1993	1752[e]	C, 46.3 (46.0); H, 4.5 (4.4); N, 3.9 (3.8)
2-OMe	Me	CH(CO$_2$Me)$_2^-$	CO	38	2039, 1989	1750[e]	
1,2,4,5-Me	Ph	H$^-$	CO	28	2024, 1972	1737[e]	C, 60.8 (61.2); H, 5.7 (5.7); N, 3.6 (4.0)
H	Ph	H^{-f}	CO	80	2035, 1987	1750[e]	C, 55.57 (56.58); H, 4.45 (4.07); N, 4.61 (4.71)
H	Me	H^{-f}	CO	75	2033, 1985	1749[e]	C, 45.94 (45.98); H, 4.45 (4.29); N, 6.08 (5.96)
2-OMe,5-Me	Ph	H$^-$	CO	53	2034, 1983	1748[e]	C, 56.50 (56.32); H, 4.90 (4.72); N, 4.00 (4.10)
1-Me,4-OMe	Ph	H$^-$	CO	36	2029, 1968	1739[e]	
H	CN	H^{-f}	CO	35	2045, 1997	1763[g]	C, 44.62 (43.92); H, 2.96 (2.87); N, 11.23 (11.38)
1,2,3,4,5-Me	Me	H$^-$	CO	97	2020, 1968	1732[g]	
H	Ph	N-MeIM	CO	c	2050, 1998	1755[h]	
H	Me	N-MeIm	CO	c	2045, 1995	1753[d]	
H	Ph	pyridine	CO	c,i	2052, 1998	1759[h]	
H	Me	P(OBu)$_3$	CO	c,i	2045, 1995	1752[h]	
H	Ph	P(OBu)$_3$	CO	c,i	2045, 1996	1755[h]	
H	H	H$^-$	PBu$_3$	j	1948	1693[g]	
H	Ph	H^{-f}	PBu$_3$	70[k]	1949	1697[g]	

[a]See structure 4 for the numbering scheme. All cationic complexes have PF$_6^-$ as the counterion. [b]Calculated values in parentheses. [c]Yield is quantitative by IR. [d]In CH$_2$Cl$_2$. [e]In hexane. [f]Deuterium analogue also synthesized. [g]In pentane. [h]In CH$_3$NO$_2$. [i]Complex made in solution only; not isolated. [j]Made by adding NaBH$_4$ to a mixture of [(C$_6$H$_6$)Mn(CO)$_2$PBu$_3$]PF$_6$ and [(C$_6$H$_7$)Mn(CO)(NO)PBu$_3$]PF$_6$ and separating the products by TLC. [k]Made using NaBH$_3$CN; all other hydride adducts made with NaBH$_4$.

Table V. ^{1}H NMr Data for (Cyclohexadiene)Mn(CO)$_2$NO Complexes (4)[a]

X	R	Nu	^{1}H NMR (δ)
H	Me	PPh$_3$	5.66, 5.55 (t; t; H^{2,3}), 4.20 (t, J = 12, H^5), 3.26 (H^6), 3.07 (H^{1,4}), 0.83 (d, J = 7, Me)[b]
H	Ph	PPh$_3$	5.85 (H^{2,3}), 4.70 (H^5), 4.17 (H^6), 3.20 (H^{1,4})[b]
H	Me	PBu$_3$	5.76, 5.65 (H^{2,3}), 3.26 (H^5), 2.94 (H^{1,4}), 2.78 (H^6), 1.21 (d, J = 6, Me), 2.15-1.00 (Bu)[b]
H	Ph	PBu$_3$	5.94 (t, H^{2,3}), 3.97 (t, J = 12, H^5), 3.30 (m, H^1), 3.22 (d, J = 12, H^6), 3.04 (m H^4), 1.8-0.9 (Bu)[b]
H	Me	CH(CO$_2$Me)$_2^-$	4.91 (dd, J = 6.5, 5, H^3), 4.72 (dd, J = 6.5, 5, H^2), 3.29 (m, H^5, H^{CH}), 3.24 (s, Me), 3.22 (s, Me), 2.98 (ddd, J = 6.5, 2, 1.5, H^4), 2.43 (ddd, J = 6.5, 3, 1.5, H^1), 2.24 (m, J = 9, H^6), 0.55 (d, J = 7, Me)[c,d]
2-OMe	Me	CH(CO$_2$Me)$_2^-$	4.86 (dd, J = 7, 2, H^3), 3.31 (m, H^{CH}), 3.25 (s, Me), 3.21 (s, Me), 3.12 (m, H^1), 2.95 (s, OMe), 2.92 (m, H^5), 2.54 (m, J = 10, 4, H^6), 2.35 (dd, J = 7, 3, H^4), 0.82 (d, J = 7, Me)[c,e]
1,2,4,5-Me	Ph	H$^-$	6.99 (Ph), 5.38 (s, H^3), 3.64 (d, J = 11, H^6), 2.48 (m, J = 11, 7, H^5), 2.20 (s, Me), 1.60 (s, Me), 1.41 (s, Me), 0.41 (d, J = 7, Me)[f,g]
H	Ph	H$^-$	7.1-6.85 (Ph), 4.96, 4.82 (t; t; J = 5.5; J = 5.5; H^{2,3}), 3.06 (dt, J = 11, 3, H^6), 2.76 (m, H^{1,4}), 2.07 (m, J = 15, 11, 4, H^{5-exo}), 1.58 (d, J = 15, H^{5-exo})[c]
H	Me	H$^-$	4.86, 4.74 (t; t; J = 5.5; J = 5.5; H^{2,3}), 2.65 (, H^{1,4}), 1.83 (m, H^6), 1.75 (m, J = 15, 10.5, 4, H^{5-endo}), 1.01 (dm, J = 15, H^{5-exo}), 0.63 (d, J = 7, Me)[c]
2-OMe,5-Me	Ph	H$^-$	5.43 (dd, J = 4, 2.5, H^3), 3.73 (dd, J = 11, 2.5, H^6), 3.67 (s, OMe), 3.63 (t, J = 2.5, 2.5, H^1), 2.64 (dd, J = 7, 3.5, H^4), 2.18 (m, H^5), 0.36 (d, J = 7, Me)[f]
1-Me,4-OMe	Ph	H$^-$	5.83 (d, J = 5, H^3), 4.93 (d, J = 5, H^2), 3.53 (s, OMe), 3.35 (m, H^6), 2.88 (dd, J = 11, 16, H^{5-endo}), 2.32 (dd, J = 5, 16, H^{5-endo}), 1.63 (s, Me)[f]
H	CN	H$^-$	5.65 (t, J = 7, H^{2,3}), 3.24, 3.19 (m; M; H^{1,4}), 2.97 (m, J = 10, H^6), 2.2 (m, H$^{5-exo,endo}$)[f]
1,2,3,4,5-Me	Me	H$^-$	2.16 (s, Me), 1.64 (s, Me), 0.80 (d, J = 7, Me^{5,6})[f]

[a]See structure 4 for the numbering scheme. All cationic complexes have PF$_6^-$ as the counterion. [b]In CD$_2$Cl$_2$. [c]In C$_6$D$_6$. [d]^{13}C NMR (ppm) in C$_6$D$_6$: 21.8 (Me), 33.6 (C^6), 40.0 (C^5), 52.0 (2Me), 57.5 (CH), 66.7, 73.6 (C^1,C^4), 86.5, 89.4 (C^2,C^3), 168.8, 168.9 [Co(malonate)], 223 (CO). [e]^{13}C NMR (ppm) in C$_6$D$_6$: 21.5 (Me, 35.3 (C^6), 40.0 (C^5), 52.0 (2Me), 54.2 (OMe), 57.2 (C^1), 57.5 (CH), 65.0, 68.4 (C^3,C^4), 141.8 (C^2), 168.9 [CO(malonate)], 226.6 (CO). [f]In CDCl$_3$. [g]^{13}C NMR (ppm) in CDCl$_3$: 19.3 (Me^5), 21.6, 21.7 (Me^1, Me^4), 23.8 (Me^2), 41.3 (C^5), 56.4 (C^6), 82.0, 84.8 (C^1, C^4), 89.1 (C^3), 103.6 (C^2), 126.0, 127.1, 127.8, 128.0, 130.7, 143.8 (Ph), 224.4, 226.7 (CO).

ucts that included tricarbonyl complexes 2, free arene, and at best small amounts of the desired adduct 4. However, recent results show that these problems may be eliminated by choosing alternative solvents and by deactivating 3 by having L = PBu$_3$ instead of CO (vide infra).[21]

The relatively mild nucleophile NaCH(CO$_2$Me)$_2$ reacted successfully with 3 according to the following procedure: to a solution of NaCH-(CO$_2$Me)$_2$ (0.38 g, 2.50 mmol) in THF (40 mL) at 0 °C was added [(C$_6$H$_6$Me)Mn(CO)$_2$NO]PF$_4$ (0.50 g, 1.6 mmol). The solution was stirred for 15 min and evaporated to dryness yielding a brown residue. Extraction into toluene (30 mL) and chromatography on a alumina column eluting with 1:3 diethyl ether–hexane gave an orange solution. Evaporation to dryness gave the product (4, Nu = CH(CO$_2$Me)$_2^-$) as an orange crystalline solid (yield 0.19 g, 33%). The same reaction with 3 (X = 2-OMe, R = Me, L = CO) gave a 38% yield of 4 with the addition being stereo- and regiospecific (exo at C-5).

Results and Discussion

**Synthesis of (Cyclohexadienyl)Mn(CO)(NO)L+ Cations (3).** The primary synthetic interest in the (cyclohexadienyl)Mn-(CO)(NO)L+ salts is their utility as intermediates in the conversion of arenes to difunctionalized cyclohexadienes via a double addition procedure. In this context it is important to note that mild procedures exist[22] for complexing arenes to form (arene)Mn(CO)$_2$L+ salts (1). Thus, a wide variety of arene ring substituents can be tolerated. The addition of hydride or carbon donor nucleophiles to 1 is generally a simple and high yield reaction to give (cyclohexadienyl)Mn(CO)$_2$L (2).[18] Depending on the arene ring substituents, the additions can be highly regioselective.[18] The ring in 2 is not electrophilic to a significant extent and reactivation is generally required in order to add a second nucleophile. We found that NOPF$_6$ in CH$_2$Cl$_2$ accomplishes this by rapidly substituting a carbonyl ligand in 2 to give nitrosyl salts 3, which are thermally and air-stable yellow-orange solids. As long as the exo substituent at C-6 in 2 is not H or CN, the yields are good (Table II). While NO+ reacts with many metal carbonyls to give oxidation rather than CO substitution products,[23-25] this is not the

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case with **2**. The NO^+ is tolerant of a variety of functional groups on **2**, e.g., R = Me, Ph, CN, CH_2COCMe_3; X = Me, OMe; L = CO, PR_3.[26]

Although the reaction **2** → **3** goes in good yield in most cases, when the C-6 substituent is R = H the reactivation step with $NOPF_6$ gives **1** as the major or sole product; i.e., instead of CO substitution the exo hydride on C-6 is abstracted. This is clearly shown by the observation that complex **7** reacts smoothly with

7

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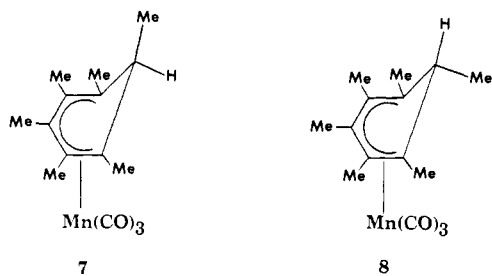
$NOPF_6$ to give **3** while **8** gives mostly $(C_6Me_6)Mn(CO)_3^+$. The amount of hydride abstraction from **2** was found to decrease as electron releasing groups are substituted at C-1 to C-5 (Me instead of H) or at the metal (PBu_3 instead of CO). Interestingly, hydride abstraction by $NOPF_6$ does not occur with the analogous seven-membered ring complexes, $(C_7H_8R)Mn(CO)_2L$.[21]

Addition of Nucleophiles to (Cyclohexadienyl)Mn(CO)(NO)L$^+$ Cations (3). As determined from IR spectra, most phosphorus and nitrogen donor nucleophiles react quantitatively with **3** to give cyclohexadiene ring adducts **4**. The nucleophiles $P(OMe)_3$ and $P(CH_2CH_2CN)_3$ attack the ring and the metal with CO displacement, while most nitrogen donors (pyridines, anilines, imidazoles) give adducts **4** that are thermally unstable at room temperature with respect to decomposition products. Kinetic studies[27] of these reactions show that the ring in **3** is activated by $Mn(CO)_2NO$ to almost exactly the same degree as cyclohexadienyl rings are activated by the $Fe(CO)_3$ moiety in **5**. Hence, one can reasonably expect that the range of nucleophiles that react according to eq 1 will also be possible for reactions of **3** with the significant difference that the products (**4**) derived from **3** are difunctionalized.

Methoxide ion in methanol at −78 °C attacks $[(C_6H_6Ph)Mn(CO)_2NO]BF_4$ at a CO to give $(C_6H_6Ph)Mn(CO)(NO)(CO_2Me)$ as a thermally unstable solid. This reaction is analogous to methoxide attack at a CO in $(C_6H_6)Mn(CO)_3^+$ [16] and $(C_6H_7)Os(CO)_3^+$,[28] and to hydroxide attack on $(C_6H_7)Fe(CO)_3^+$.[29]

Hydride addition to **3** occurs readily with $NaBH_4$ in $MeCN/THF$ (1:2) at −5 °C. The stronger hydride donor $NaB(CHMeEt)_3H$ reacts normally with $[(C_6H_6Ph)Mn(CO)(NO)PBu_3]PF_6$, but with the more electrophilic $[(C_6H_6Ph)Mn(CO)_2NO]PF_6$ the primary reaction product is $(C_6H_6Ph)Mn(CO)_3$. We suspect that the tricarbonyl product is formed whenever single electron transfer to **3** becomes more facile than nucleophilic attack. Similar observations apply with carbon donors (vide infra).

Hydride addition to **3** produced a most unexpected result in that the addition was found to occur in a stereospecific endo manner. This conclusion was initially based on the ^1H NMR spectra of the deuteride adducts of $(C_6H_6R)Mn(CO)_2NO^+$ (R = Me, Ph, CN) and $(C_6H_6Ph)Mn(CO)(NO)PBu_3^+$. A com-

parison of the hydride and deuteride adducts showed that upon deuteration the endo H-5 resonance and the vicinal endo-H-5,H-6 coupling (ca. 11 Hz) disappear (**9**; Table V). $^2H\{^1H\}$ NMR (38.4

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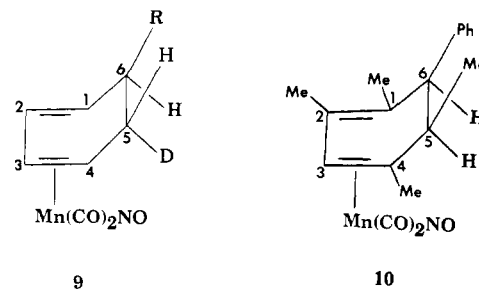
MHz) verified that the hydride addition is stereospecifically endo, meaning that the endo adduct is the *kinetic* product. Determination of the stereochemistry of hydride addition to **3** does not require deuteration if the carbon being attacked bears a substituent. Thus, hydride addition to **3** (X = 1,2,4,5-Me; R = Ph; L = CO) gives a product with a H-5,H-6 coupling constant of 11 Hz, which implies that H-5 is endo as shown in structure **10**. An attempt to verify these conclusions by subjecting **10** to a X-ray diffraction study was frustrated by the difficulty of obtaining suitable crystals.[30] However, it proved possible to obtain the X-ray structure of the product of reaction 2, and this confirmed that

(2)
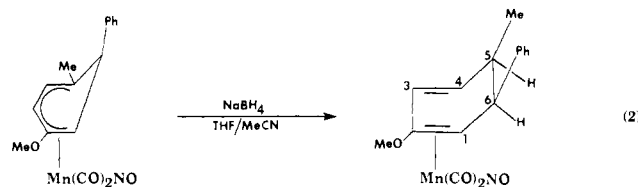
hydride adds endo as shown.[19] Recent results indicate that hydride addition also occurs endo with the seven-membered ring complexes $[(cyclohexadienyl)Mn(CO)(NO)L]PF_6$.[21] In contrast to these results with hydride, the NMR spectra as well as the X-ray structure[20] indicate that phosphine addition to **3** occurs exo.

Virtually all carbon, nitrogen, oxygen, phosphorus, and sulfur nucleophiles are known to add exo to coordinated cyclic π-hydrocarbons.[1] Similarly, exo hydride addition has been confirmed in many cases.[19] There are, however, several reports[6,31-33] of hydride addition yielding a mixture of exo and endo products, with the amounts of endo being at most 50%. Because of the reaction conditions, some of these results may reflect thermodynamic exo/endo equilibration. The unique feature of hydride addition to **3** is the *stereospecific* endo nature of the reactions.[34] The endo stereochemistry suggests an initial interaction at the metal or a CO followed by migration to the ring. The presence of a nitrosyl ligand may be important since it can act as an electron sink if the metal is attacked by hydride. The mechanistic aspects of these reactions will be the subject of a future publication.

For applications to synthesis the most important nucleophiles to be added to **3** are carbon donors. $NaCH(CO_2Me)_2$ was found to add to **3** (X = H or OMe, R = Me, L = CO) to give the cyclohexadiene complex. The large vicinal coupling constant J(H-5,H-6) of ca. 10 Hz shows that the $CH(CO_2Me)_2^-$ group is situated exo. Other carbon nucleophiles (MeLi, $CdMe_2$, MeMgCl, $LiCuMe_2$, and KCH_2NO_2) in THF or diethyl ether react with **3** (L = CO) but little or none of the desired ring adduct **4** is formed. Instead, large amounts of (cyclohexadienyl)Mn(CO)$_3$ are produced. Most likely this is due to initial electron transfer

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(26) The transformation 1 → 2 → 3 is also applicable to seven-membered rings. Thus, (cycloheptatriene)Mn(CO)$_2$L$^+$ cations are cleanly converted to $(C_7H_8R)Mn(CO)(NO)L^+$ (R = H, Me, Ph, CN; L = CO, PBu$_3$).[21]

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(34) There is also a recent report of endo hydride addition to the heterocyclic ring in $[(thiabenzene-1-oxide)Cr(CO)_2NO]PF_6$ to give a σ, π-allyl product: Weber, L.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 498.

from the nucleophile to **3** followed by loss of NO and attack by a second molecule of **3**. While this matter is yet to be fully investigated, the probable role of single electron transfer in these reactions is strongly implicated by the effect of replacing a CO ligand in **3** by a more electron-releasing one. Thus, preliminary experiments show[21] that (cyclohexadienyl)Mn(CO)(NO)PBu₃⁺ is much less susceptible to reduction to yield **2** (L = PBu₃) instead of **4** when treated with carbon donor nucleophiles. The replacement of a CO by PBu₃ has a dramatic effect on the diene product yields with the analogous seven-membered ring complexes.[21] Thus, it now appears likely to us that suitable procedures will soon be elaborated that permit the addition of carbon donors

to **3** in good yields. Full details of these carbon additions as well as procedures for removal of the diene from the products (**4**) will be published separately.

In conclusion, we have shown that the manganese mediated conversion of coordinated arenes to coordinated cyclohexadienes can be a facile and high-yield procedure that may prove quite useful in synthesis. We have also discovered the first class of compounds for which hydride addition to a coordinated cyclic π-hydrocarbon occurs stereospecifically endo to the metal.

Structure of Octaethylporphyrin N-Oxide and the Characterization of Its Nickel(II) and Copper(II) Complexes

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Contribution from the Department of Chemistry, University of California, Davis, California 95616. Received September 10, 1984

Abstract: The structure of octaethylporphyrin N-oxide has been determined by X-ray crystallography. It crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with one molecule per unit cell of dimensions a = 7.612 (3) Å, b = 9.740 (4) Å, c = 10.566 (4) Å, α = 91.61 (3)°, β = 98.49 (3)°, γ = 108.43 (3)° at 140 K. The structure was refined to R = 0.068 for 1588 reflections and 207 parameters. The molecules pack in a disordered fashion so that a center of symmetry is present. The oxygen atom, which is disordered over four positions, is out of the porphyrin plane by 0.97 Å and bound to one nitrogen with an N–O distance of 1.398 (7) Å. ¹H NMR spectra indicate that at room temperature in solution the oxygen atom rapidly inverts through the center of the porphyrin while remaining attached to one nitrogen atom. A nickel(II) complex of the porphyrin N-oxide has been prepared, isolated, and characterized by ¹H NMR, mass, infrared, and UV–visible spectroscopy to have a structure incorporating an Ni–O–N unit. A copper(II) complex has been isolated and characterized by infrared, UV–visible, and electron spin resonance spectroscopy.

The alternative structures **1** and **2** have been proposed for highly

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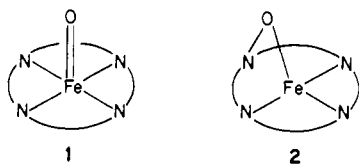
oxidized forms of heme proteins (particularly cytochrome P450 and the peroxidases) and as intermediates in heme catabolism.[1-3] Theoretical calculations have predicted that **2** may be significantly more stable than **1**.[4,5] Our approach to studying **2** began by examining the complexation of metal ions by porphyrin N-oxides. However, little information is available regarding these substances. Bonnett, Appelman, and co-workers have described the preparation of octaethylporphyrin N-oxide (**3**) by the attack of electrophilic oxygen on octaethylporphyrin.[6,7] In their characterization of this N-oxide, however, they point out "we have not succeeded in obtaining positive physical evidence for the existence of the N–O bond". A copper(II) complex was briefly described.[7] Here we

Table I. Atom Coordinates (×10⁴) and Thermal Parameters (Å² × 10³) for Octaethylporphyrin N-Oxide

atom	x	y	z	U
O(1)	306 (7)	−309 (6)	6271 (5)	24 (2)
O(2)	873 (35)	1294 (29)	4577 (24)	11 (9)
N(1)	−46 (4)	875 (3)	6830 (3)	21 (1)[a]
N(2)	2872 (4)	1276 (3)	5121 (3)	22 (1)[a]
C(1)	1375 (5)	2005 (4)	7503 (3)	20 (1)[a]
C(2)	3172 (5)	2578 (4)	7185 (3)	23 (1)[a]
C(3)	3895 (5)	2248 (4)	6124 (3)	21 (1)[a]
C(4)	3982 (4)	1220 (4)	4225 (3)	18 (1)[a]
C(5)	3381 (5)	331 (4)	3079 (3)	21 (1)[a]
C(6)	−1611 (5)	660 (4)	7388 (3)	19 (1)[a]
C(7)	−1139 (5)	1690 (4)	8512 (3)	19 (1)[a]
C(8)	693 (4)	2528 (4)	8570 (3)	17 (1)[a]
C(9)	5776 (4)	2860 (4)	2848 (3)	19 (1)[a]
C(10)	5835 (5)	2217 (4)	4696 (3)	20 (1)[a]
C(11)	−2446 (5)	1769 (4)	9421 (3)	24 (1)[a]
C(12)	−2407 (6)	793 (4)	10499 (4)	39 (2)[a]
C(13)	1834 (5)	3753 (4)	9540 (3)	25 (1)[a]
C(14)	3238 (5)	3363 (4)	10514 (4)	29 (2)[a]
C(15)	7320 (5)	4059 (4)	6666 (3)	22 (1)[a]
C(16)	7325 (5)	5549 (4)	6272 (4)	26 (1)[a]
C(17)	7486 (5)	2468 (4)	4011 (3)	23 (1)[a]
C(18)	7479 (5)	3505 (4)	2948 (4)	28 (1)[a]
H(1)	1654 (54)	703 (42)	5043 (37)	30

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

present the results of an X-ray diffraction study of octaethylporphyrin N-oxide, an examination of its structure in solution, and the preparation and detailed characterization of its nickel(II) and copper(II) complexes. Nickel(II), particularly, was chosen

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