Additional studies by angle-resolved XPS are continuing in order to determine quantitative surface concentrations of surface titanium species and to probe the identity of organic adsorbates in these reactions. Our studies to date demonstrate that (1) carbon–carbon bond formation reactions with synthetic utility can occur even under UHV conditions; (2) surface science approaches can identify active sites for novel heterogeneous syntheses; and (3) carbonyl coupling to olefins on oxophilic metals under reducing conditions occurs at mild temperatures and may be important in selective hydrocarbon synthesis with oxide-promoted metal catalysts.

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Reductive Activation of the η^5-Methylcyclopentadienyl Ligand in $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_3]$ and Evidence for a Ring-Slipped Intermediate Containing an η^3-Methylcyclopentadienyl Ligand

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We recently reported that the η^6-arene ligands in complexes such as $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) and $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ (**2**$^+$) can be activated toward electrophiles by two-electron naphthalenide reduction, and we have proposed that the highly reduced intermediates contain η^4-arene ligands.[1-3] Cymantrene, $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_3]$ (**3**), is isoelectronic with **1** and **2**$^+$, and it occurred to us that it might also be possible to induce a hapticity change in the η^5-methylcyclopentadienyl ligand in **3**, and that this might similarly result in activation of the aromatic ligand toward electrophiles. We now report (Scheme I) that **3** undergoes a reduction to give a complex formulated as $[Mn(\eta^3\text{-}C_5H_3)(CO)_3]^{2-}$ (**4**$^{2-}$), and that **4**$^{2-}$ can be protonated to give a cyclopentadiene complex $[Mn(\eta^4\text{-}C_5H_5CH_3)(CO)_3]^-$ (**5**$^-$) which undergoes facile naphthalene substitution.

Reduction of $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_3]$ (**3**) (0.30 g, 1.38 mmol) was best carried out with the alkalide [K(18-C-6)]K, freshly prepared as reported by Dye.[4] Dropwise addition of 13.8 mL of a 0.2 M solution of [K(18-C-6)]K in tetrahydrofuran (THF) to a solution of **3** in 30 mL of THF at 0 °C resulted in color changes from yellow through orange to purple, just before the alkalide blue began to persist. The loss of CO stretching absorptions at 2021 (s) and 1929 (vs) cm^{-1} (Figure 1a) showed that **3** had been consumed and had been replaced by a species with a single broad, very strong absorption at 1630 cm^{-1} (Figure 1b).[5] This is a very low carbonyl stretching absorption, and the shift of ca. 250 cm^{-1} is consistent with the formation of a dianionic complex. The spectrum is not, however, at all like that of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2]^{2-}$ (the only previously reported dianion in this system[7]).

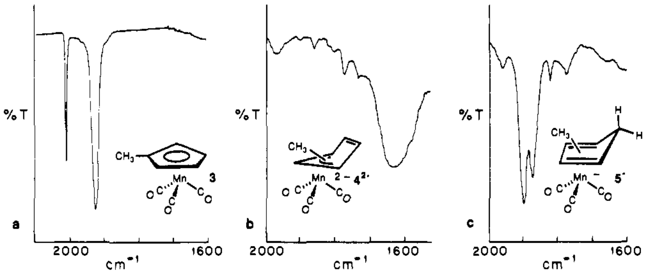
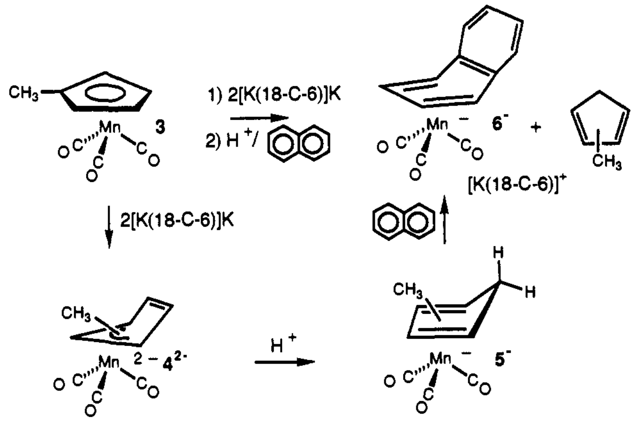


Figure 1. IR spectra in C≡O stretching region of a solution of $[Mn(\eta^5\text{-}C_5H_4CH_3)(CO)_3]$ (**3**) at various stages of the reduction/protonation sequence: (a) before reduction; (b) following dropwise addition of 2 equiv of [K(18-C-6)]K at 0 °C; (c) following further addition of 3 equiv of triflic acid at 0 °C.

Scheme I



The reduction product would appear to have retained three carbonyl ligands and the cyclopentadienyl ligand, as indicated by I_2 (2.5 equiv of I_2) oxidation of a solution of the dianion in THF at room temperature to give **3** in 70% yield (absorption-mode IR), and we propose that the reduction gives the ring-slipped dianion $[Mn(\eta^3\text{-}C_5H_4CH_3)(CO)_3]^{2-}$ (**4**$^{2-}$).

As in the case of $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$,[1,2] the product of two-electron reduction of **1**, the aromatic ligand in **4**$^{2-}$ is activated toward electrophiles. This has been demonstrated by the reaction of $[K(18\text{-}C\text{-}6)]_2$·**4** [freshly prepared from 0.31 g (1.42 mmol) of **3**] with 3.0 equiv of triflic acid in THF at 0 °C. The broad, strong carbonyl stretching absorption of **4**$^{2-}$ at 1630 cm^{-1} is slowly replaced by a two-band pattern at 1898 (vs) and 1874 (s) cm^{-1} (Figure 1c), indicating formation of a complex with a considerably less electron rich transition-metal center which we propose to be the cyclopentadiene complex $[Mn(\eta^4\text{-}C_5H_5CH_3)(CO)_3]^-$ (**5**$^-$). Attempts to isolate this material as a $[K(18\text{-}C\text{-}6)]^+$, $[Ph_3PNPPh_3]^+$, or $[NEt_4]^+$ salt have been unsuccessful to date, but we have been able to prepare a stable derivative by carrying out the protonation in the presence of 10 equiv of naphthalene. This gave an orange crystalline compound, isolated by precipitation from THF by addition of ether and recrystallization from THF/ether. The product was shown (IR, ^{1}H NMR, ^{13}C NMR) to be the η^4-naphthalene complex $[K(18\text{-}C\text{-}6)][Mn(\eta^4\text{-}C_{10}H_8)(CO)_3]$ ([K(18-C-6)]·**6**, 0.47 g, 60%) (Scheme I), which we have previously prepared as a [PPN]$^+$ salt by another route.[3]

X-ray diffraction studies have established that [PPN]·**6** contains an η^4-naphthalene ligand,[3] and **6**$^-$ could reasonably be formed by substitution of naphthalene for the methylcyclopentadiene ligand in **5**$^-$. Such a reaction would be analogous to the facile substitution which we have reported of η^4-naphthalene for the η^4-benzene in $[Cr(\eta^4\text{-}C_6H_6)(CO)_2]^{2-}$.[8] The diene substitution is unprecedented and involves replacement of an unstrained diene with a highly

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[5] This band does not have a Lorentzian envelope and is probably a composite of a number of absorptions. This would be a typical consequence of the existence of the anion in THF as a mixture of several ion pairs with distinct IR spectra, as often observed in solutions of carbonylmetalates.[6] If the complex is $[Mn(\eta^3\text{-}C_5H_5)(CO)_3]^{2-}$, as proposed below, we would expect more than one carbonyl absorption in its IR spectrum. The details of the IR spectrum of the tricarbonyl may, however, be masked by such ion-pairing effects.

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strained η^4-naphthalene, but this is not unreasonable since the η^4-naphthalene should be a significantly better π-acceptor. The displacement of methylcyclopentadiene from the protonation product has been confirmed by HPLC of a 100-μL aliquot of a reaction mixture protonated at 0 °C, maintained at this temperature for 2 h, and then cooled to −78 °C. This unambiguously established the formation of a 90 ± 3% yield of monomeric methylcyclopentadiene.

The suggestion that the methylcyclopentadienyl ligand in **4**$^{2-}$ adopts an η^3 conformation is partially based on 18-electron considerations: as noted in an authoritative recent review,[9] the η^3-cyclopentadienyl ligand was a controversial species for a number of years, but there is now a structurally characterized example of this bonding mode,[10] and Casey's work on PMe_3 addition to $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ provides an example in which kinetic data implicate an η^3-cyclopentadienyl complex as a labile intermediate following coordination of a two-electron donor.[11] The importance of ring slippage to the η^3-coordination mode in reactions of cyclopentadienyl complexes also receives circumstantial support from the recent body of work establishing that indenyl ligands can readily adopt η^3-coordination modes.[12]

The reduction of **3** to **4**$^{2-}$ would suggest that reductively induced hapticity changes of the type established for arene ligands[1-3,13] can also be induced with other aromatic ligands such as the cyclopentadienyl ligand and that, as in the arene case, such hapticity shifts result in ligand activation toward electrophiles.[14] The only prior evidence for reductive activation of a cyclopentadienyl ligand comes from the electrochemical studies of cobaltocene reduction by El Murr, in which he establishes that $[Co(C_5H_5)_2]^-$ can be trapped by exo CO_2 addition and esterification to give $[Co(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_5CO_2CH_3)]$.[15] Reductively induced hapticity shifts of cyclopentadienyl ligands have important implications for synthetically interesting sequences like those employed by Jonas, in which complexes of highly reduced transition-metal centers are formed by reduction of η^5-cyclopentadienyl precursors like ferrocene[16] (and more specifically for the observation by Ellis that Na/HMPA reduction of $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ gives $[Mn(CO)_4]^{3-}$[17]), and suggest that such reductions probably involve a series of discrete intermediates differing by two-electron hapticity shifts.

Acknowledgment. We thank the National Science Foundation for financial support through Grant CHE-8722424 and Professor Jim Dye for encouragement and helpful advice concerning the synthesis and use of alkalide reductants.

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Nitrite-Bound Five-Coordinate Low-Spin Iron(II) Model Complex for the Prosthetic Group of Nitrite Reductase with an Unusually Large Quadrupole Splitting. Synthesis, Mössbauer Properties, and Molecular Structure of the Complex (Nitro)(α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphinato)iron(II)

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We report the synthesis, molecular structure, and Mössbauer properties of a new N-bound five-coordinate (nitro)(porphinato)iron(II) complex which is relevant as a model for enzymatic nitrite reduction. Most interestingly, the ferrous iron is low spin ($S = 0$) and its Mössbauer spectrum shows an unusually large quadrupole splitting for low-spin (porphinato)iron(II). Such large splittings have been previously observed only for oxygenated hemes such as oxyhemoglobin.

Crystalline $[K(222)][Fe(NO_2)(TpivPP)]\cdot H_2O\cdot C_6H_5Cl$[2] was prepared by reaction, under argon, of $[Fe(SO_3CF_3)(H_2O)(TpivPP)]$[3] (0.08 mmol) and 1 mL of zinc amalgam in 10 mL of C_6H_5Cl and filtered into a solution of Kryptofix-222 (0.8 mmol) and KNO_2 (2.4 mmol) in C_6H_5Cl (10 mL).[4] The red-yellow solution was filtered, and crystals were prepared by diffusion of pentane into the C_6H_5Cl. The crystalline material was washed with several portions of degassed water and then with pentane. UV-vis (C_6H_5Cl): λ_{max} (log ϵ) 428 (5.01) (sh), 441 (5.11), 543 (4.01) (sh), 569 (4.17), 608 (3.83).

An X-ray crystal structure determination[6] shows that the complex is five-coordinate with an N-coordinated nitrite ion in the ligand binding pocket of the picket fence porphyrin (Figure 1). An adventitious water molecule is found at the mouth of the ligand-binding pocket; the $O(w)\cdots O(NO_2)$ distances of 3.17 and 3.36 Å suggest a weak hydrogen bond. Figure S1 (supplementary material) shows average bond distances in the porphinato core and atom displacements from the 24-atom mean plane.[9] Both the short average $Fe-N_p$ bond distance of 1.970 (4) Å and the small (0.18 Å) displacement of iron out-of-plane are consistent with those expected[10,11] for a low-spin five-coordinate iron(II)

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(1) (a) University of Notre Dame. (b) Emory University.

(2) Abbreviations used: H_2TPP, *meso*-tetraphenylporphyrin; $H_2TpivPP$, picket fence porphyrin; Kryptofix-222 or 222, 4,7,13,16,21,24-hexaoxo-1,10-diazabicyclo[8.8.8]hexacosane.

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(4) Kryptofix-222 was recrystallized from benzene, and KNO_2 was recrystallized from distilled water, dried under vacuum, and stored under argon. These compounds must be carefully recrystallized to remove the halide impurities known to coordinate[5] to Fe(II) porphyrin species.

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(6) The complex crystallizes in the monoclinic space group $P2_1/n$, $a = 17.715\ (7)$ Å, $b = 21.341\ (5)$ Å, $c = 22.838\ (11)$ Å, $\beta = 101.86\ (3)°$, $V = 8450$ Å^3, $Z = 4$. A total of 15 263 $h,k,\pm l$ reflections were measured at 123 K, and 7722 reflections having $\sin\theta/\lambda < 0.602$ and $F_o \geq 3.0\sigma(F_o)$ were taken as observed. The structure was solved by using the coordinates for the iron porphyrin and [K(222)] cation of the isomorphous nitrato[7] and acetato[8] structures. The remaining atoms were found from difference Fouriers. Least-squares refinement of the model based on 917 variables with anisotropic thermal parameters for all non-hydrogen atoms and fixed, idealized hydrogen atoms leads to $R_1 = 0.079$, $R_2 = 0.087$. Confer Table SI (supplementary material).

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