Intensities of the ethyl signals when compared to the deuteriated pyrrole signal at −17.6 ppm were consistent with the respective methylene and methyl assignments. A methyl proton NMR signal for the ethyliron(III) tetratolylporphyrin complex at −117 ppm (20 °C) has been reported recently.[5c] The far upfield and downfield deuterium signals exhibit Curie-like chemical shift behavior[7] with deviation from linearity at low temperature.

The ability to detect coordinated alkyl deuteron signals provided a convenient tool for demonstration of a novel alkyl interchange reaction. An 8 mM solution of (d_8-TPP)Fe(CH_3) was prepared in toluene by the Grignard route. An upfield pyrrole deuteron signal is seen for this species in Figure 1a. Within 5 min of preparation, excess C_2D_5I was added (to a concentration of 0.52 M) under anaerobic conditions. Deuterium spectra were recorded over a period of 4 h at 25 °C (each spectrum required only minutes for acquisition). Figure 1 reveals the appearance and growth of far downfield and upfield signals due to a coordinated d_5-ethyl group. The apparent half-life for this process for the specific solution conditions is approximately 100 min. In a separate proton NMR experiment (with d_8-toluene solvent) the expected appearance of CH_3I was confirmed.

The interchange process is independent of contamination by unreacted (TPP)FeCl (the precursor to the methyl complex), contamination by iron(II) porphyrin (generated by addition of excess Grignard reagent), or preparative route for the alkyliron(III) complex (Grignard route vs oxidative addition of RI to $TPPFe(I)^-$). In separate experiments the interchange of a proteo-alkyl ligand with a like deuterio-alkyl ligand was also demonstrated. Light is not required to effect the alkyl group interchange. No *N*-alkyliron porphyrin products are detected, and in the absence of oxidants and reductants there appears to be no relationship to the intramolecular alkyl exchange described for cobalt porphyrins.[8]

In separate experiments it was demonstrated that iron(II) tetraphenylporphyrin reacts slowly with alkyl iodides to produce equivalent amounts of the alkyliron(III) and iodoiron(III) derivatives. The high-spin (TPP)FeI complex exhibits a pyrrole deuteron NMR signal at 80 ppm. Absence of this signal for a period of days in solutions of (TPP)FeR and excess R'I indicates that the iron(II)/R'I reaction is not a significant route for alkyl group interchange.

One possible way to rationalize the interchange reaction between alkyliron(III) and iodoalkanes involves a known facile homolysis,[9] with subsequent alkyl radical iodine atom abstraction and radical–iron(II) recombination:

$$(TPP)Fe^{III}R \rightleftarrows (TPP)Fe^{II} + R^{\bullet} \quad (1)$$

$$R'I + R^{\bullet} \rightleftarrows RI + R'^{\bullet} \quad (2)$$

$$(TPP)Fe^{II} + R'^{\bullet} \rightleftarrows (TPP)Fe^{III}R' \quad (3)$$

However, as is described below, some conditions must be placed on this three-step mechanism in order to account for iodoalkane stabilization of the alkyliron(III) complex. The rate constant for the second reaction where R• is the methyl radical and R'I is iodoethane is 5.4×10^4 M^{-1} s^{-1} in toluene solvent at ambient temperature.[10] Hence, iodine atom abstraction is made competitive with rapid radical–iron(II) recombination (nearly diffusion controlled[11]) by virtue of the large excess of iodoalkane.

An unexpected feature of alkyliron(III) porphyrin chemistry in the presence of excess respective iodoalkane is the stabilization of the alkyliron(III) state. For example, the ethyliron(III) tetraphenylporphyrin complex is converted to the square planar iron(II) derivative with a half-life of less than 1 day,[12] but in the presence of 0.5 M iodoethane the half-life is extended to several days. The stabilization effect where R = R' (the "identity" reaction) may be explained in terms of the mechanism shown above provided one or more of the following conditions are met: (i) restriction of the reactions to a radical cage; (ii) preassociation of an iodoalkane with the iron porphyrin; (iii) formation of an R•/RI complex such that the radical would be sequestered from loss by coupling, disproportionation, or solvent hydrogen atom abstraction. The possibility of a radical cage or other concerted process may be suggested by literature reports that demonstrate the weak (and structurally undefined) complex formation between iodoalkanes and both iron(II)[13] and iron(III)[14] porphyrins.

The unusual stabilization effect has implications for crystal growth experiments with organometallic species that are prone to undergo metal–carbon homolysis. Alkyl group interchange provides yet another synthetic route for systems in which Grignard reactions or two-electron oxidative-addition reactions are problematic.

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Vibrational and Electrochemical Properties of a Series of Stable Manganese(V)–Oxo Complexes

The importance of manganese complexes of oxidation state IV and above can be seen in their roles in stoichiometric and catalytic oxidations and biological redox enzymes. The significance of the permanganate ion in stoichiometric oxidations in which manganese(V)–oxo complexes are intermediates is well documented.[1] Manganese(V)–monooxo complexes are believed to be active intermediates in oxo transfer and related reactions with porphyrin and salen catalysts.[2] In biological systems, manganese–oxo complexes have a possible role in the oxygen-evolving complex in photosynthesis.[3] Because of inherent high reactivity, evidence for the existence of terminal monooxo complexes of manganese has been difficult to obtain. Careful spectroscopic studies have elucidated the existence of $Mn^{IV}(O)$(porphyrin) compounds.[2a,4]

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Table I

complex	IR[a] for ^{16}O, cm^{-1}	IR for ^{18}O, cm^{-1}	RR[b] for ^{16}O, cm^{-1}	RR for ^{18}O, cm^{-1}	E_{f_1},[c] V vs NHE	E_{f_2}, V vs NHE	λ_{max},[d] nm	ϵ
$[Et_4N][Mn(O)(\eta^4\text{-}\mathbf{1})]$	979	942	981	942	1.77 (1.59)	−0.27 (−0.44)	422	7410
$[Et_4N][Mn(O)(\eta^4\text{-}\mathbf{2})]$	972	934	972	934	irrev	−0.56	438	6200
$[Et_4N][Mn(O)(\eta^4\text{-}\mathbf{3})]$	973	936	976	939	1.39 (1.23)	irrev	468	5859
$[Et_4N][Mn(O)(\eta^4\text{-}\mathbf{4})]$	970	933	973	933	1.08 (0.96)	irrev	494	6950

[a] Nujol mull. [b] KBr pellet. [c] CH_3CN/0.1 M TBAP (values in parentheses are for CH_2Cl_2). Plots of peak current vs the square root of scan rate over the range 5–200 mV s^{-1} were made and found to be linear for systems other than those noted not to be reversible. [d] CH_3CN as solvent.

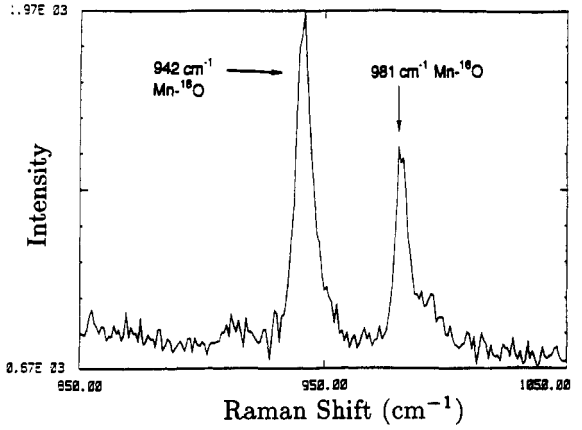
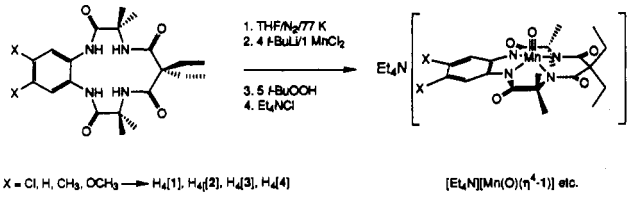


Figure 1. Resonance Raman spectrum of $[Et_4N][Mn(O)(\eta^4\text{-}\mathbf{1})]$ (λ_{ex} = 406.7 nm; KBr pellet) showing both ^{16}O and ^{18}O-labeled species.

Scheme I. Synthesis of Manganese(V)–Oxo Complexes



Our work has shown that it is possible to synthesize stable manganese(V)–monooxo complexes by using acyclic diamide/dialkoxide and macrocyclic tetraamido-*N* ligands designed to be strongly donating and resistant to oxidative destruction.[5] We have been studying these species to learn about spectral and chemical characteristics associated with the $Mn^V{\equiv}O$ unit. In this report, we describe $Mn^V{\equiv}O$ resonance Raman signatures and reversible electrochemical oxidations and reductions associated with a series of stable manganyl complexes.

The syntheses of the macrocycles and manganyl complexes[5,6] have been reported previously, and the new manganyls employed here, $[Mn(O)(\eta^4\text{-}\mathbf{2})]^-$, $[Mn(O)(\eta^4\text{-}\mathbf{3})]^-$, and $[Mn(O)(\eta^4\text{-}\mathbf{4})]^-$, are synthesized in an analogous manner to $[Mn(O)(\eta^4\text{-}\mathbf{1})]^-$ (Scheme I).[5b] Manganyl ^{18}O-labeling was accomplished either by stirring the Li^+ salts in $H_2{}^{18}O$ or by stirring the $[Et_4N]^+$ salts in $CH_3CN/H_2{}^{18}O$ (1:10). The results of infrared and resonance Raman studies are shown in Table I. The isotopic shifts are approximately equal to that expected for a diatomic Mn–O harmonic oscillator. Figure 1 shows the Raman spectrum of $[Mn(O)(\eta^4\text{-}\mathbf{1})]^-$ (natural abundance and ^{18}O-labeled), employing photoexcitation at 406.7 nm. The excitation wavelength falls within a broad absorption feature of the complex. The protio, methyl, and methoxy derivatives, $[Mn(O)(\eta^4\text{-}\mathbf{2})]^-$, $[Mn(O)(\eta^4\text{-}\mathbf{3})]^-$, and $[Mn(O)(\eta^4\text{-}\mathbf{4})]^-$, exhibit similar intense Raman signatures with excitation at 488.0 nm (λ_{max} is shifted to the red with increasingly donating ligand substituents; see Table I). For all compounds studied, low-intensity vibrational bands are seen throughout the 200–1800-cm^{-1} spectral region. Selective excitation studies indicate that the $Mn^V{\equiv}O$ stretches are clearly resonance enhanced while other modes are not. Such an enhancement could arise if the broad visible region absorption feature is either an n $\rightarrow \pi^*$ ($d_{xy} \rightarrow d_\pi$) or $\pi \rightarrow \pi^*$ (O p $\rightarrow$ Mn d) transition, although the relatively large ϵ values suggest the latter assignment.

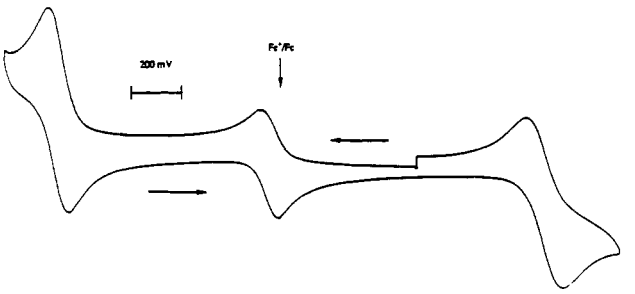


Figure 2. Cyclic voltammogram of $[Et_4N][Mn(O)(\eta^4\text{-}\mathbf{1})]$ (CH_2Cl_2/0.1 M TBAP; ferrocene internal standard).

The results of cyclic voltammetry on the manganese(V)–oxo complexes are also shown in Table I and Figure 2. There is a substantial substituent effect manifested in the oxidation process which occurs over a range of 630 mV. Although based on a minimal number of data points, the formal potentials for this event correlate with the Hammett substituent σ^+ values (R = 0.99, $\rho/2$ = −13.7),[7] establishing that intramolecular electronic parameters arising from the ligand substituents determine the changes in formal potential values.[8] Oxidation of the manganyl monoanions is facilitated by the noninnocent character of the aromatic-ring-containing ligands,[6] and the neutral molecules should not be considered as Mn(VI) species. However, a formal oxidation state assignment of Mn(IV) is reasonable for the reduced complexes at the observed potentials. In some instances, bulk electrolysis gives stable products, and work is ongoing to isolate and characterize these species by vibrational and EPR spectroscopy.

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(7) When the formal potential values for the neutral molecule reductions are converted to equilibrium constants and plotted against the σ^+ values, the Hammett ρ value is −27 for the CH_3CN data. (There are two substituents per molecule.) The σ^+ substituent parameter is applicable when cationic centers are present in chemical processes. The parent process is the solvolysis of 2-chloro-2-phenylpropane.

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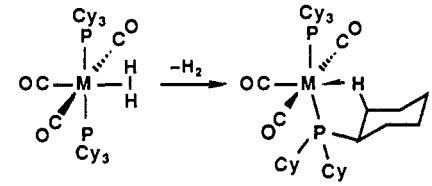
The Barrier to Rotation of Dihydrogen in $Cr(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$, a Complex with an Unusually High Difference in Solid- and Solution-State Stabilities

The details of the unique chemical bond[1,2] that is formed between the dihydrogen ligand and a metal are of major interest in the effort to elucidate the factors that govern stable η^2-H_2 binding as opposed to oxidative addition to hydrides. We have shown[3] in previous work that the barrier to rotation of η^2-H_2 is largely determined by the electronic interaction with the metal, or more specifically, that it is the dπ (metal) $\rightarrow$ σ^* (H_2) back-bonding that gives the metal-H_2 bond its directional property. The beauty of the H_2 ligand is its diminutive size ($\sim$20° "bite-angle") and lack of extraneous electrons, which eliminate "steric" factors such as repulsions between ligand π and metal a_2 orbitals in the case of ethylene rotation[4] on a ML_5 fragment. We have now synthesized the first-row member of our group 6 series, $Cr(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ (Cy = cyclohexyl), as a stable solid and measured its rotational barrier by an inelastic neutron scattering technique, which also is invaluable as an *unambiguous proof of dihydrogen binding*. Classical hydride ligands cannot give rotational spectra[5] and do not interfere in the measurements.

$Cr(CO)_3(PCy_3)_2(H_2)$ has previously been prepared by Hoff only in solution under >300 psi of H_2 and had been thought to be unstable under normal pressure.[6] However, we recently found that under proper conditions the solid complex could be isolated under 1 atm of H_2. H_2 addition to toluene or THF solutions of the 16-e precursor, $Cr(CO)_3(PCy_3)_2$,[6a] does not give the H_2 complex, *unless* the solution is highly concentrated or supersaturated. In this case the H_2 complex precipitates as bright yellow microcrystals, presumably because of its lower solubility. It immediately turns green in air, but is indefinately stable under H_2. The best method to synthesize $Cr(CO)_3(PCy_3)_2(H_2)$ is similar to that for $Cr(CO)_3(PCy_3)_2$[6a] (reaction of $Cr(CO)_3$(naphthalene) with 2 equiv of PCy_3 in THF), except for the use of an *H_2 atmosphere instead of argon*. $Cr(CO)_3(PCy_3)_2(H_2)$ precipitates in 81% yield upon stirring for 18 h. This synthesis is then analogous to that of the Mo and W congeners from $M(CO)_3$(cycloheptatriene).[7]

There is a large difference between solid- and solution-state stabilities here, at least in a practical if not thermodynamic sense. When the Cr-H_2 complex is dissolved in toluene, instantaneous complete dissociation of H_2 occurs (H_2 gas is evolved), *even under an H_2 atmosphere*, to give a deep blue-purple solution of $Cr(CO)_3(PCy_3)_2$. Only partial dissociation occurs for the Mo analogue while the more strongly bound W complex completely retains H_2 in solution. Crystal lattice stabilization energy could favor H_2 binding in the solid, but why does the small H_2 molecule not eventually dissociate and escape out of the lattice as it does in solution? The answer lies in the fact that the H_2 is not just leaving the coordination site in these complexes but is actually being "displaced" by a cyclohexyl ring C-H to give an agostic interaction, identified by X-ray crystallography (M = Cr,[8a] W[8b]):



In solution the molecule is much more flexible in its ability to move a cyclohexyl ring into position to displace the H_2, and weak solvent interactions[9] can also possibly aid in ousting the H_2. However, since the above reaction is reversible to some degree, driving forces such as solubility could "trap out" the H_2 complex in solid form. Once this occurs, the structural rigidity (e.g. crystal packing forces) could favor H_2 binding over intramolecular C-H binding, for which significant rearrangements and bond angle changes would have to occur.[8] The energies[10] of the metal σ-bond interactions in these complexes are so low ($\sim$10-15 kcal/mol) that entropic factors[10a] can even become important. A general analogy can be made to biological metal coordination sites wherein competition between external small molecule substrates and intramolecular protein residues occurs.

The rotational barrier can directly be determined essentially only from inelastic neutron scattering measurements of the low-lying rotational energy levels of the hindered dihydrogen rotor. In fact, it is the rotational tunnel splitting of the librational ground state[5] which is most sensitive to the barrier: for relatively weak hindering potentials the value of the tunnel splitting varies approximately exponentially with barrier height. This has been demonstrated[3] by the dramatic change observed when replacing W with Mo in $M(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$. Here the tunnel splitting was found to change by about a factor of three, from 0.89 to 2.82 cm^{-1}, with an attendant change in the barrier from 2.2 to 1.7 kcal/mol, where the latter value is somewhat uncertain because the H-H distance (and therefore the rotational constant B) is not known for the Mo analogue.

The barrier in these two complexes thus scales qualitatively as one might expect, i.e., that the ligand bond strength of W be

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(7) Kubas, G. J. *Inorg. Synth.* **1990**, *27*, 1. This synthesis does not work either for $Cr(CO)_3$(cycloheptatriene) or for $Cr(CO)_3$(naphthalene) in *toluene* (*THF* must be used) because PCy_3 will not displace toluene from the $Cr(CO)_3$(toluene) formed in situ. For steric reasons, THF is actually a weaker ligand in these systems than H_2 and does not bind to $Cr(CO)_3(PCy_3)_2$.
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(9) For steric reasons, toluene or any other aromatic solvent *cannot coordinate through π interactions* to the $M(CO)_3(PCy_3)_2$ fragment. Thus any metal-solvent interaction would have to involve a C-H bond of the solvent. We tried to test for possible C-H interactions by placing $Cr(CO)_3(PCy_3)_2(H_2)$ in bulky aromatic solvents such as 1,3,5-triisopropylbenzene and 3,5-di-*tert*-butyltoluene, hoping that the H_2 would *not* dissociate because the solvent would be too sterically encumbered to assist H_2 loss even by metal···H-C interactions. Unfortunately the complex was virtually insoluble in these solvents at room temperature. Raising the temperature to $\sim$45 °C did give some solubilization, but also H_2 loss, to form the blue-purple $Cr(CO)_3(PCy_3)_2$ (color is a clear indicator here). In this case thermally-induced loss of H_2 could be occurring, which would be indistinguishable from solvent effects. As for the toluene case, placing the H_2 complex in mesitylene (1,3,5-trimethylbenzene) at 23 °C also gave a blue color indicative of the agostic species, but much paler (lower solubility).
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