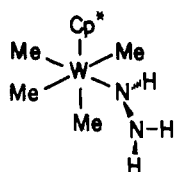Figure 1. ^{1}H NMR spectrum in C_6D_6 of the crude reaction mixture produced upon reduction of "WCp*Me$_3$Cl" under N$_2$ showing ∼20% [WCp*Me$_3$]$_2$(μ-N$_2$).

structure being one in which W, N$_\alpha$, H$_\alpha$, N$_\beta$, H$_\beta$, and H$_\beta'$ *all lie in a plane* that is not a molecular plane, viz.,


An alternative 18e$^-$ structure containing an η^2-NHNH$_2$ ligand[1d] is less likely for steric as well as electronic reasons. This is the least ambiguous example of a complex containing the extremely rare parent [NHNH$_2$]$^-$ ion.[9] Due to the instability of **2** (see below) we have not yet been able to show whether the three protons equilibrate by an intra- or an intermolecular process. Limited stability of **2** also has prevented accurate elemental analyses. We have shown, however, that **2** is hydrolyzed rapidly by aqueous HCl to give 0.85 (5) equiv of hydrazine.

In polar solvents such as dichloromethane **2** decomposes quantitatively (by ^{1}H NMR) to **3** (eq 2).[6] **3** is a fully characterized
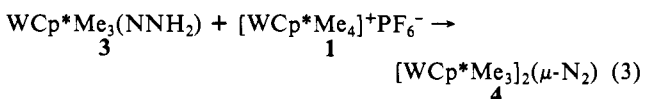
$$\text{WCp*Me}_4(\text{NHNH}_2) \rightarrow \text{CH}_4 + \text{WCp*Me}_3(\text{NNH}_2) \quad (2)$$
$$\textbf{2}\textbf{3}$$
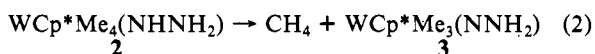
red-orange, pentane-soluble complex whose NMR spectra are consistent with a square-pyramidal structure, viz.
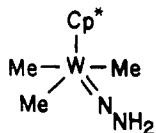
Its NNH$_2$ protons are found at δ 4.59 in C_6D_6. In the presence of aqueous HCl **3** is hydrolyzed immediately to give 0.85 (5) equiv of hydrazine.[8]

The reaction between [WCp*Me$_4$]$^+$PF$_6^-$ and **3** in ether produces a red-orange complex in ∼50% yield that is physically quite similar to **3** but that has neither ν_{NH} peaks in its IR spectrum nor NH resonances in its ^{1}H NMR spectrum.[10] We propose that it is the μ-N$_2$ complex **4** (eq 3), with a structure related to that

$$\text{WCp*Me}_3(\text{NNH}_2) + [\text{WCp*Me}_4]^+\text{PF}_6^- \rightarrow$$
$$\textbf{3}\textbf{1}$$
$$[\text{WCp*Me}_3]_2(\mu\text{-N}_2) \quad (3)$$
$$\textbf{4}$$

of **3**.[8] A preliminary X-ray structural study confirms that this

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(10) Typically WCp*Me$_3$(NNH$_2$) (0.2 g, 0.51 mmol) and [WCp*Me$_4$]$^+$PF$_6^-$ (0.26 g, 0.51 mmol) are stirred together in diethyl ether (15 mL) for 12 h. The mixture is then filtered and the ether removed from the filtrate in vacuo to give 0.22 g of red [WCp*Me$_3$]$_2$(μ-N$_2$). [WCp*Me$_3$]$_2$(μ-N$_2$) can be recrystallized from pentane.

is the case.[11] Interestingly, however, **4** in ether is not readily hydrolyzed upon being shaken with 1 N NaOH overnight. Also, no hydrazine is liberated when an ether solution of **4** is treated with aqueous or gaseous HCl. A red precipitate forms that we are in the process of identifying. The stability of **4** toward hydrolysis might be ascribed to the hydrophobic coordination sphere and/or what are apparently relatively nonbasic formal electron pairs on what is believed to be essentially a μ-N$_2^{4-}$ ligand.

An interesting question is whether **4** can be prepared by reducing WCp*Me$_3$Cl under molecular nitrogen. WCp*Me$_3$Cl is unknown. We attempted to prepare it by the conproportionation between WCp*Me$_4$ (three parts) and WCp*Cl$_4$ (one part) in dichloromethane for 20 h. The solvent was removed from the resulting red solution and the residue was dissolved in THF. One equivalent of sodium amalgam was added and the mixture was stirred under N$_2$ (40 psi) overnight. The mixture was filtered and the THF removed in vacuo to give a red semisolid whose ^{1}H NMR spectrum showed ∼20% of the diamagnetic product mixture to consist of **4** (Figure 1). **4** was *isolated* from this mixture by recrystallization from pentane in 5–10% yield. We hesitate to suggest a mechanism for this reaction in view of the number of unknowns, but the fact that any **4** is observable, whatever the mechanism might be, is intriguing. It *is* possible, however, that a relatively high oxidation state complex (e.g., WCp*Me$_3$) *does* scavenge N$_2$ at a rate that competes with other reactions involving the methyl groups.

We believe that these preliminary studies show that high oxidation state tungsten μ-N$_2$ complexes can be prepared and that they are likely to have some unique properties and reactivities. We expect to encounter other examples soon.

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(11) Churchill, M. R., personal communication.

Bimetallic-Mediated Reaction of Carbon Monoxide and Dioxygen

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The reaction of dioxygen and carbon monoxide is slow in the absence of catalysts. The role of a single metal atom to activate CO and O$_2$ and to mediate their reaction has been suggested,[1] but one of the most effective homogeneous catalysts for the reaction is the Rh$_6$(CO)$_{16}$ cluster.[2] Spectral studies of the reaction of CO and O$_2$ on Pt/SiO$_2$ led to a proposal of a multi metal atom mechanism involving dissociative adsorption of O$_2$ and subsequent reaction with coordinated CO.[3] We describe experiments which provide evidence for a bimetallic-mediated pathway for the reaction of CO and O$_2$.

Gaseous dioxygen was observed not to react with [Pt-(PPh$_3$)$_2$(CO)Cl]BF$_4$ (**2**), but the dioxygen complex Pt(PPh$_3$)$_2$O$_2$ (**1**) in CH$_2$Cl$_2$ reacts rapidly with **2**. The reaction proceeds with loss of ν(CO) of **2** at 2115 cm^{-1} and formation of a strong IR band at 1521 cm^{-1}. Gas chromatographic assay on molecular sieves

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(1) (a) Roundhill, D. M.; Allen, G. H.; Bechtold, R. A.; Bealieu, W. B. *Inorg. Chim. Acta Lett.* **1981**, *54*, 299. (b) Huber, H.; McIntosh, D.; Ozin, G. A. *Inorg. Chem.* **1978**, *16*, 975.

(2) (a) Mercer, G. D.; Beaulieu, W. B.; Roundhill, D. M., *J. Am. Chem. Soc.* **1977**, *99*, 6551. (b) Chin, C.-S.; Sennett, M. S.; Vaska, L. *J. Mol. Catal.* **1978**, *4*, 375.

(3) Grant, N. W.; Donaldson, R. A. *J. Catal.* **1981**, *71*, 320.

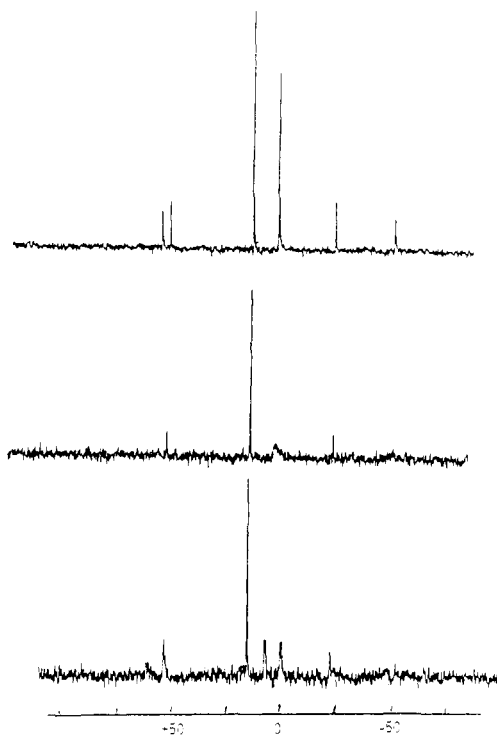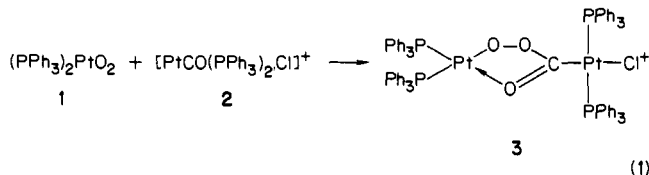**Figure 1.** $^{31}P\{^{1}H\}$ NMR spectra of 3 in CH_2Cl_2 at (A) 298, (B) 233, and (C) 193 K (ppm vs. external 85% H_3PO_4).

and Poropak Q columns indicated that no CO or CO_2 is given off. A colorless product 3 can be isolated and recrystallized from

CH_2Cl_2/Et_2O in 83% yield. Anal. Calcd for $C_{73}H_{60}O_3BClF_4P_4Pt_2$: C, 54.06, H, 3.73, P, 7.64. Found: C, 53.84; H, 4.00; P, 7.80, mp 180 °C dec.

The $^{31}P\{^{1}H\}$ NMR spectrum of 3 at 298 K has two singlet resonances (with ^{195}Pt satellites) at δ 16.22 $^{1}J(PtP)$ = 1918 Hz and δ 4.85 $^{1}J(PtP)$ = 1358 Hz. Cooling the sample to 258 K leads to collapse of the higher field singlet (Figure 1) and further cooling to 218 K leads to reappearance of the resonance as a doublet δ 8.21 and 1.21 $^{2}J(P,P)$ = 24.4 Hz. From these data, it may be deduced that compound 3 is a peroxy carbonyl complex in which the cis phosphorus atoms are equivalent on the NMR time scale. This may arise from dissociation of the Pt–carbonyl oxygen bond and rotation about the Pt–O bond. The singlet resonance at δ 16.2 for the trans P atoms in 3 remains sharp and unchanged at lower temperatures. Lithium chloride or phosphoric acid reacts with 3 to give CO_2. The addition of PPh_3 to 3 in CH_2Cl_2 leads to a substitution of the carbonyl oxygen ligand and formation of 4.[4]
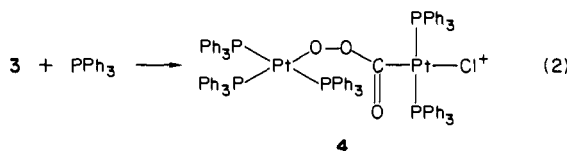
A preliminary survey to asses the generality of the MO_2 + MCO reaction indicated that the dioxygen metal complexes 1, $Pd(PPh_3)_2O_2$, and $Ir(O_2)(PPh_3)_2(CO)Cl$ yield rapid CO_2 evolution

when mixed with CH_2Cl_2 solutions of $Pt(PPh_3)(CO)Cl_2$, [Fe-$(C_5H_5)(CO)_3]PF_6$, and $Pd(PPh_3)_2Cl_2$ first treated with CO. Intermediates analogous to 3 were not detected in these reactions. Reactions of the dioxygen complexes with $W(CO)_6$ and Ru-$(PPh_3)_2(CO)_2Cl_2$ were very slow and reactions were not discernible with $Ir(PPh_3)_2(CO)Cl$, $Rh(PPh_3)_2(CO)Cl$, and $[Fe(C_5H_5)(CO)_2]_2$. The CO in acyl complexes such as $Pt(PR_3)_2Cl(COR)$, R = CH_3, C_6H_5, was not oxidized by the dioxygen complexes.

The addition of the dioxygen complex 1 to $[Fe(C_5H_5)(CO)_2$-(CS)]PF_6 in CH_2Cl_2 results in rapid disappearance of $\nu(CS)$ at 1348 cm^{-1} and a slower decay of the $\nu(CO)$ centered at 2020 cm^{-1}. The formation of carbonyl sulfide (OCS) and CO_2 was confirmed by GLC and IR. The oxidation of the coordinated thiocarbonyl ligand has not previously been reported.[5]

The reactivity pattern that emerges from the observations described in this study is the reactions of the dioxygen complex $Pt(PPh_3)_2O_2$ as a nucleophile such as previously demonstrated in reactions with acids,[6] alkyl halides,[7] ketones, and aldehydes[8] which form the corresponding peroxides or ozonides. The dioxygen complexes thus react with metal carbonyl complexes which are susceptible to nucleophilic attack[9] to form a cycloperoxycarbonyl which subsequently decomposes to form CO_2. This new reactivity pattern thus provides new insights on a mechanism for the CO–O_2 reaction in which dioxygen is activated by a metal atom and CO is activated on a second metal atom.

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(7) Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.,* **1981,** *103,* 5832.
(8) (a) Hayward, P. J.; Saftich, S. J.; Nyman, C. J. *Inorg. Chem.* **1971,** *10,* 1311. Hayward, P. J.; Nyman, C. J. *J. Am. Chem. Soc.* **1971,** *93,* 617. (c) Ugo, R.; Zanderighi, G. M.; Fusi, A.; Carreri, D. *J. Am. Chem. Soc.* **1980,** *102,* 3745. (d) Beaulieu, W. B.; Mercer, G. D.; Roundhill, D. M. *J. Am. Chem. Soc.* **1978,** *100,* 1147.
(9) Angelici, R. J. *Acc. Chem. Res.* **1972,** *5,* 335.

Specific Side-Chain Cleavage of Tryptophan, Tryptophanyl Derivatives, and Tryptophanyl Dipeptides Using Hypervalent Iodine

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We wish to report a novel and specific cleavage reaction for L-tryptophan (1) and various derivatives (Table I) as exemplified by 1 → 2 (eq 1).
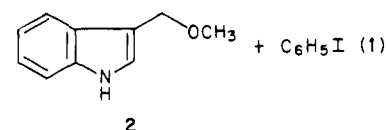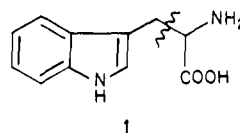
This process is a β-cleavage of the side chain and has not been observed, heretofore, in chemical systems; however, such a pathway

(4) IR 1680 cm^{-1}; $^{31}P\{^{1}H\}$ NMR δ 6.395 ($J(Pt-P)$ = 1849 Hz), 11.51 (d, $J(PP)$ = 11.51 Hz), 12.7 (t); Anal. Calcd for $Pt_2C_{91}H_{75}P_5O_2BF_4Cl$·$0.25CH_2Cl_2$: C, 58.0, H, 4.03, Cl, 2.82, P, 8.20. Found: C, 57.6; H, 4.17; Cl, 2.84; P, 8.35. mp 121 °C dec.