Table III. Quantum Yields of Disappearance of 4-Nitrophenyl Azide in the Presence of *n*-Butylamine[a]

set	λ, nm[b]	[*n*-butylamine], M	[biphenyl], M	Φ
I	313	0	0	514
	313	0.12	0	113
	254	0.12	0.096	228
II	254	0	0.092	74
	254	0.10	0.092	124
	254	0.045	0.092	109

[a] 0.1 M 4-nitrophenyl azide in acetonitrile deoxygenated by nitrogen bubbling. [b] Wavelength of excitation, $I(254\ \text{nm}) = 2.7 \times 10^{13}$ photons/s. $I(313\ \text{nm}) = 9.27 \times 10^{13}$ photons/s.

changes at low conversions, corresponding azobenzenes are the photoproducts. Plots of Φ vs. azide concentration show an exponential increase in Φ with increasing concentration for all four azides. Thus, a photoinitiated autocatalytic chain decomposition (PACD) reaction occurs for each substituted phenyl azide, as has been reported for phenyl azide.[1,5,7]

Since Φ values for 4-bromophenyl azide and 2,4,6-tribromophenyl azide greatly exceed unity, a triplet species is suggested as the PACD reaction chain propagator: an accelerated intersystem crossing due to an internal heavy atom effect is expected to promote formation of the triplet states of these species. 2,4,6-Tribromophenyl azide cleanly affords the triplet nitrene.[23] 4-Nitrophenyl azide also affords the triplet nitrene,[24,25] further suggesting this intermediate as the PACD reaction chain propagator.

Triplet-sensitized Φ values of 4-nitrophenyl azide were measured with benzophenone and biphenyl as sensitizers, adjusting concentration ratios such that >90% of the exciting light (254 nm) was absorbed by the sensitizer and that >90% of the monitoring light (313 nm) was absorbed by 4-nitrophenyl azide.[26] All Φ values measured greatly exceed unity, Table II. Triplet-sensitized Φ values exceed values measured upon direct excitation; however, this probably results from the lower lamp intensities in the sensitized experiments, since lower light intensities result in greater Φ values.[7] Thus, triplet 4-nitrophenylnitrene is thought to be the PACD reaction chain propagator.

Finally, Φ was determined upon direct excitation and biphenyl triplet sensitization of 4-nitrophenyl azide in the presence and absence of *n*-butylamine, since such nucleophilic species have been used to chemically trap singlet reaction intermediates.[12-15] Φ values greatly exceed unity whether or not *n*-butylamine is present, Table III. *n*-Butylamine reduces Φ values only upon direct excitation; it does not affect Φ values measured upon triplet sensitization. This can be understood if triplet 4-nitrophenylnitrene reacts with 4-nitrophenyl azide to produce *two* triplet nitrenes, the PACD reaction. Since added *n*-butylamine reduces measured Φ values upon direct excitation but not upon triplet sensitization, Table III, a singlet species is thought to be trapped: singlet nitrene precursor[25] to the PACD reaction triplet propagator and/or the singlet species thought responsible for polymer formation[13,27] since polymer is not formed upon triplet sensitization of phenyl azide.[1,27]

Thus, results of quantum yield measurements of 4-bromo-, 2,4,6-tribromo-, and 4-nitrophenyl azide and of triplet-sensitized studies of 4-nitrophenyl azide in the presence and absence of *n*-butylamine all indicate that triplet phenylnitrene intermediates act as the propagator of the photoinitiated autocatalytic chain decomposition (PACD) reaction.

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(21) Φ values were measured for room temperature acetonitrile solutions by exciting with monochromatic light from a 450-W Hg lamp and Schoeffel GM-252 1/4-m monochromator, using ferrioxalate actinometry[22] to determine the photon flux and using absorption spectral changes to determine changes in concentration;[1,5,7] volumetric dilutions were necessary to determine absorption spectral changes for concentrated ($>10^{-3}$ M) solutions.

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(26) 4-Nitrophenyl azide was chosen since it possessed both a long-wavelength first absorption maximum (313 nm) and a low absorbance at 254 nm: hence a sensitizer that absorbs strongly at 254 nm, but not at 313 nm, could be used with 254-nm excitation and a wavelength of 313 nm could be used to quantitatively monitor the disappearance of 4-nitrophenyl azide. Concentrations were adjusted so that >90% of the 313-nm light was absorbed by 4-nitrophenyl azide and >90% of the 254-nm light was absorbed by benzophenone or biphenyl: $A_{254\,\text{nm}}$(azide/sensitizer) = 0.10; $A_{313\,\text{nm}}$(azide/sensitizer) = 44.6. The quantum yield of triplet energy transfer (Φ_{ET}) from benzophenone to 4-nitrophenyl azide was determined from the phosphorescence spectrum of benzophenone monitoring its intensity as a function of added azide and using a Stern–Volmer analysis of the data. At the azide concentrations used for quantum yield determinations $\Phi_{\text{ET}} = 0.99$, hence no correction was needed in calculating Φ.

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Nitrite-Induced Carbyne to Acyl Conversion. Unprecedented Formation of an Arylglyoxyl Ligand via Coupling of an Oxidized Carbyne with a Coordinated Carbon Monoxide

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Carbene complexes react with suitable oxygen donors to release the carbene ligand in the form of a free ester, amide, or ketone,[1] and this is usually the method of choice for removing a modified carbene from a metal in a complex organic synthesis.[2] Surprisingly, analogous oxidation reactions of carbyne complexes have not been reported. To explore this aspect of carbyne chemistry, we have examined the reactions of the carbyne complexes $[\text{Cp}(\text{CO})_2\text{M}{\equiv}\text{CR}]^+$ (M = Re (**1**)[3], Mn(**2**)[4]) with NO_2^-, a potential oxygen atom donor, and as described herein have observed the smooth conversion of the carbyne into an acyl ligand. Remarkably, this reaction with **2** gives a product containing an arylglyoxyl ligand that has been formed from the oxidized carbyne and a coordinated carbonyl ligand. Glyoxyl ligands have never before been assembled from coordinated ligands, and previous studies of glyoxyl complexes have led to the general conclusion that such ligands are not likely to form by migration of an acyl ligand to a coordinated CO.[5]

Our initial studies with the carbyne complex I showed that addition of 1 equiv of $[\text{PPN}][\text{NO}_2]$ $\{\text{PPN} = (\text{Ph}_3\text{P})_2\text{N}\}$ to this species gave smooth, immediate conversion to the acyl complex **3**,[6] eq 1. Formally, this reaction involves addition of O^- to the

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(6) (a) **3**: Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{NO}_3\text{Re}$: C = 39.23, H = 2.80, N 2.90(%). Found: C = 39.00, H = 2.80, N = 2.70(%). IR (CH_2Cl_2): ν(CO) 1993 (s), ν(NO) 1717 (s), ν(acyl) 1578 (w), 1561 (w) cm^{-1} {two bands, attributed to rotational isomers, have been observed for other acyl complexes, ref 5a and 6b}. ^{1}H NMR (CDCl_3): δ 2.36 (3 H, s, Me), 5.78 (5 H, s, Cp), 7.21 (2 H, d, J = 8 Hz, tolyl), 7.45 (2 H, d, J = 8 Hz, tolyl). ^{13}C NMR (CDCl_3): δ 21.3 (Me), 93.9 (Cp), 126.6, 128.7, 140.7, 152.3 (tolyl), 201.7 (CO), 238.5 (acyl CO). Mass spectrum: m/z 429 (M^+, ^{187}Re). (b) Calderazzo, F.; Noack, K.; Schaerer, U. *J. Organomet. Chem.* **1966**, *6*, 265.

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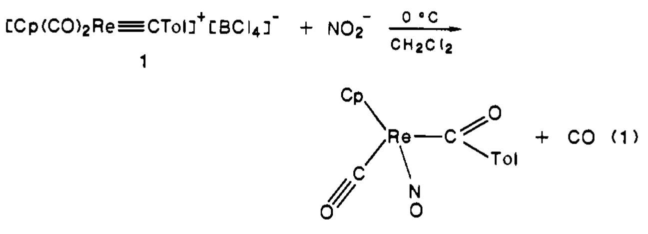
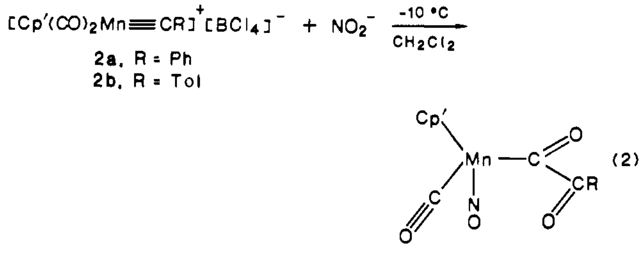


3 (74%)

cationic carbyne ligand followed by substitution of NO for CO. Although simple in composition, acyl complex **3** has not been previously reported, although its PPh_3 analogue $Cp(PPh_3)(NO)ReC\{O\}R$ has been well studied.[7]

Surprisingly, repetition of the same reaction with $[Cp'(CO)_2Mn{\equiv}CR]^+$ (**2**, $Cp' = MeC_5H_4$) gave the novel arylglyoxyl complex **4**, eq 2, a reaction which involves the formal coupling of an acyl and a CO ligand.



4a, R = Ph, 51%
4b, R = Tol

Complex **4b** has been structurally characterized,[8] Figure 1, and has the three-legged piano-stool geometry typical of this family of complexes with the tolylglyoxyl ligand bound in an η^1 fashion. All bond distances and angles within the complex appear normal, although the O(1)-C(1)-C(2)-O(2) torsion angle of 102° differs from the near 180° angles found for the other two structurally characterized glyoxyl complexes.[5a,c] Spectroscopic data for **4**[9] are consistent with the determined structure. That the α-CO of the glyoxyl ligand was an original metal carbonyl was confirmed by the exclusive ^{13}C enrichment of this carbon when reaction 2 was repeated using ^{13}CO-enriched **2a**.

The mechanism by which the glyoxyl ligand is formed is of obvious interest since all other relevant studies have led to the conclusion that formation of such a ligand via acyl migration to a carbonyl ligand is unlikely.[5] We do not believe that such reaction occurs here and instead suggest that the formation of both **3** and **4** occurs via the mechanism outlined in Scheme I. Both **1** and **2** are known to readily add anionic nucleophiles (e.g., CN^-, Cl^-, SCN^-) to the carbyne carbon to give neutral carbene complexes,[10] and a similar species (**5**) should initially form with NO_2^-. Indeed, reaction of **2** with NO_2^- at -78 °C gave a solution which showed two bands at 2002 and 1942 cm^{-1} similar to those of other neutral carbene complexes prepared from **2**,[10] and this species gave **4** upon warmup. Migration of NO from the carbene to rhenium either simultaneous or subsequent to CO loss would account for the formation of **3**.

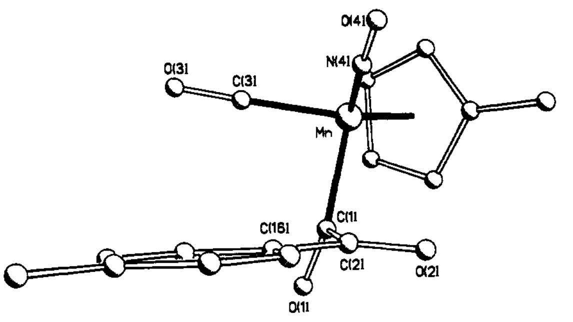
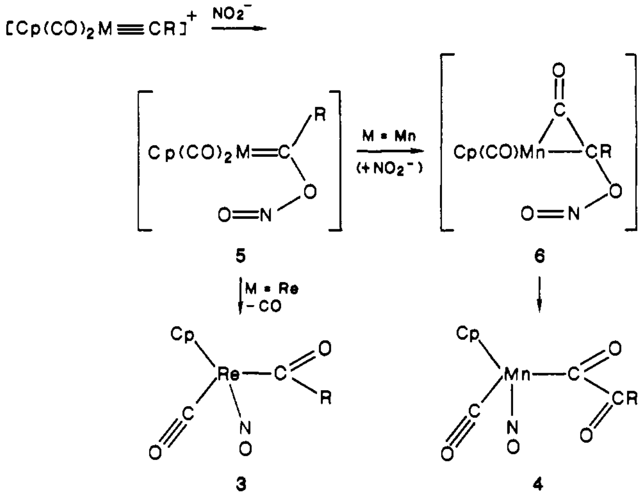


Figure 1. View of Cp'(CO)(NO)Mn-C{O}C{O}Tol (**4b**) along the C(1)-C(2) bond. Important bond lengths (Å) and angles (deg) are as follows: Mn-C(1), 2.005 (4); C(1)-C(2), 1.527 (7); Mn-C(3), 1.820 (5); C(2)-O(2), 1.212 (5); Mn-N(4), 1.656 (4); C(1)-O(1), 1.203 (6); C(1)-Mn-C(3), 89.0 (2); C(1)-Mn-N(4), 98.0 (2); C(3)-Mn-N(4), 96.2 (2); Mn-C(1)-O(1), 128.5 (3); Mn-C(1)-C(2), 112.6 (3); O(1)-C(1)-C(2), 118.8 (3); C(1)-C(2)-O(2), 118.8 (4); C(1)-C(2)-C(16), 118.6 (4); O(2)-C(2)-C(16), 122.6 (4); O(1)-C(1)-C(2)-O(2), 101.7; O(1)-C(1)-C(2)-C(16), -77.2; Mn-C(1)-C(2)-O(2), -75.3; Mn-C(1)-C(2)-C(16), 105.9.

Scheme I



With manganese, we suggest that CO migrates to the carbene ligand to yield the ketene intermediate **6**, which would give **4** upon NO migration to the vacant manganese coordination site. Formation of ketene ligands from carbene and carbonyl ligands is well precedented,[11] particularly for manganese,[11b] although the factors which influence this reaction are not well understood.[11a] We have observed that a slight excess of NO_2^- must be used in the synthesis of **4**, as otherwise low yields are obtained due to the observed intermediate **5** decomposing to other unidentified products. The role of the additional NO_2^- may be to promote CO migration to the carbene ligand by an oxidation process, similar to the known oxidative promotion of CO insertion into metal-alkyl bonds.[12] Such carbene oxidation reactions are currently under investigation in our laboratory to further probe this effect.

Alternative pathways involving CO insertion into acyl intermediates are less likely on the basis of literature data which imply

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(8) Crystal data for **4b**: $C_{16}H_{14}MnNO_4$, orange, triclinic, $P\bar{1}$, $a = 6.928$ (3) Å, $b = 7.425$ (3) Å, $c = 16.153$ (6) Å, $\alpha = 94.32$ (3)°, $\beta = 97.70$ (3)°, $\gamma = 110.73$ (3)°, $v = 763.3$ (5) Å^3, $Z = 2$, $\mu(Mo\ K\alpha) = 8.45$ cm^{-1}. Of 2367 reflections collected at ambient temperature (Nicolet R3, $4° < 2\theta < 47°$), 2263 were unique, of which 1855 had $F_o \geq 3\sigma(F_o)$ and were used in the solution (Patterson) and refinement. Final refinement included all non-hydrogen atoms as anisotropic and hydrogen atoms as idealized isotropic contributions. For 231 parameters, $R_F = 4.74\%$, $R_{wF} = 5.25\%$, GOF = 1.118, and highest peak (final map) = 0.30 e Å^{-3}, SHELXTL programs (Nicolet Corp., Madison WI).

(9) **4b**: Anal. Calcd for $C_{16}H_{14}MnNO_4$: C = 56.63, H = 4.13, N = 4.13(%). Found: C = 56.54, H = 4.01, N = 3.88(%). IR (CH_2Cl_2): ν(CO) 2016 (s), ν(NO) 1759 (s), ν(glyoxyl) 1665 (w), 1615 (m), 1607 (m), 1590 (w) cm^{-1} {four bands, attributed to s-cis and s-trans rotational isomers, have been observed for other glyoxyl complexes, ref 5e}. ^1H NMR ($CDCl_3$): δ 1.99 (3 H, s, MeCp), 2.41 (3 H, s, MeTol), 4.97 (2 H, s, Cp'), 5.08 (1 H, s, Cp'), 5.16 (1 H, s, Cp), 7.29 (2 H, d, J = 7 Hz, tolyl), 7.82 (2 H, d, J = 7 Hz, tolyl). ^{13}C NMR ($CDCl_3$): δ 12.8 (MeCp), 21.7 (MeTol), 92.4, 93.5, 93.9, 94.5, 110.2 (Cp'), 128.0, 129.6, 130.1, 144.6 (tolyl), 189.2 (COCOR), 226.7 (CO), 273.2 (COCOR).

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that Cp(NO)(CO)Mn–C{O}Ph does not insert CO to form a glyoxyl ligand even when maintained under 150 atm of CO.[13] We also observed that complex **3** did not insert CO to form a glyoxyl ligand when subjected to 1000 psi CO nor when the synthesis of **3** (eq 1) was conducted under 3 atm of CO. The synthesis of **4** could be envisaged to occur via NO_2^--induced oxidation of **2** to form NO^+ and $[Cp(CO)_2Mn\text{–}C\{O\}R]^-$ (**7**), followed by CO insertion and addition of NO^+ to **7**. However, this is not the case since **4** was not produced when authentic **7**[14] was allowed to react with $[NO]BF_4$.

This study has shown that the carbyne ligands in **1** and **2** are readily oxidized to form acyl ligands and also describes the first synthesis of a glyoxyl ligand from the assembly of other coordinated ligands, although we do not believe that this occurs via insertion of CO into a metal-acyl bond. The generality of this reaction is currently under exploration.

Acknowledgment. The donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8501548) are acknowledged for support of this research. The diffractometer at the University of Delaware was purchased with partial support from the National Science Foundation.

Supplementary Material Available: Tables of crystallographic and atomic positional parameters for **4a** (3 pages). Ordering information is given on any current masthead page.

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Heteropoly "Browns" as Class I Mixed Valence (W(IV,VI)) Complexes. Tungsten-183 NMR of W(IV) Trimers

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Reduction of many heteropoly tungstates yields dark blue mixed-valence species ("heteropoly blues") in which electrons undergo "hopping" delocalization at a rate that is rapid on the ESR and NMR time scales.[1] More highly reduced polyanions, especially under acidic conditions, are transformed to brown species that are less sensitive to oxidation than the blues and which display quite different electrochemistry. Launay[2] has suggested that the brown complexes contain tungsten(IV) atoms in trigonal metal–metal bonded W_3O_{13} groups. This suggestion is supported, but not unequivocally, by X-ray photoelectron spectroscopy[3] of 6-, 12- and 24-electron reduced metatungstate anion, $[(H_2)W_{12}O_{40}]^{6-}$, and by a disordered crystal structure[4] of the 6-electron reduced salt $Rb_4H_8[(H_2)W_{12}O_{40}]_{aq}$.

In the course of our investigations of the aqueous and nonaqueous redox chemistry of highly reduced heteropolyanions, we have examined solutions of the 6-electron reduced "browns" of the three Keggin anions α-$SiW_{12}O_{40}^{4-}$, α-$BW_{12}O_{40}^{5-}$, and α-$(H_2)W_{12}O_{40}^{6-}$ by ^{183}W NMR spectroscopy.[5] The spectra not only confirm Launay's proposal concerning stoichiometry but also demonstrate other electronic and molecular structural features that distinguish the "browns" from the "blues".

Each spectrum consists of just three narrow lines (Figure 1, Table I) of intensity 1:1:2. Two of these (3 W, 6 W) have chemical shifts very close to that of the oxidized anion while the third (3 W) is deshielded by about 1500 ppm and is attributed to the W(IV) atoms. This assignment is supported by our measurement of the chemical shift of the W(IV) cation $W_3O_4(H_2O)_9^{4+}$ (also shown in Table I).[8,9] A three-line spectrum for the heteropoly anions requires that the reduced anions have C_3 or C_{3V} symmetry and that the W(IV) atoms occupy either an edge-shared or corner-shared group of the Keggin skeleton. The magnitude of the tungsten–tungsten couplings[10] unambiguously excludes the second possibility; the low-field line shows $^2J_{W-W}$ of 14–15 Hz (corner-shared) whereas the other line of intensity corresponding to three tungstens has J = 4–6 Hz (edge-shared). The highst field line (6 W) has both couplings as expected. The shielding pattern of the two tungsten(VI) lines (δ(6 W) < δ(3 W)) is analogous to that observed for the W resonances of the 1,4,9 isomer of $PV_3W_9O_{40}^{6-}$ [11] in which the three vanadiums also occupy an edge-shared triad of the Keggin structure. The reverse pattern (δ(6 W) > δ(3 W)) is observed for 1,2,3-$PV_3W_9O_{40}^{6-}$ and -$SiV_3W_9O_{40}^{7-}$ [10] in which the vanadium atoms occupy a corner-shared triad.

We note not only that all the lines are much narrower than those recently reported by Kozik et al.[12] for heteropoly blues but also that the change in chemical shift of the unreduced tungsten atoms adjacent to the tungsten(IV) atoms is very small (−1 to −6 ppm, vs. −172 ppm for unreduced tungstens in $P_2W_{18}O_{62}^{8-}$). Both of these observations underline the difference in electronic structure of the diamagnetic "blues" and the "browns". In the former, pairs of electrons defining W(V) atoms are antiferromagnetically coupled and are delocalized on the NMR time scale (class II mixed-valence behavior). The electron motion and the local paramagnetism lead to greatly reduced relaxation times and increased line widths. In contrast the spectra reported here for the "browns" are consistent with complete localization of W(IV) and W(VI) valences (class I behavior). The spectra show a modest temperature dependence of +0.1 ppm/°C for the W(VI) and +0.5 ppm/°C for the W(IV).[13]

The 6-electron reduced anions have six additional protons and Launay has argued that these constitute terminal aquo ligands on the W(IV) atoms. The following results support this view. Three (and only three) of these protons may be neutralized[6,7,14] and titration of $SiW_{12}O_{40}H_6^{4-}$ to $SiW_{12}O_{40}H_3^{7-}$ (presumed conversion of $W\text{–}OH_2$ to W–OH) results in a change of chemical shift of +200 ppm for the W(IV) resonance while the W(VI) resonances are unaffected.

The metatungstate anion contains two nonlabile protons within the central tetrahedron.[15] During reduction in D_2O/DCl, partial

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[5] The reduced compounds were prepared as ca. 0.15 M solutions in 0.5 M DCl/D_2O by literature methods.[4,6,7] Spectra were recorded on a Bruker AM-300 WB spectrometer at 12.505 MHz using 20-mm tubes. The upfield and downfield regions were scanned separately (SW = 2000 Hz) to minimize acoustic ringing and to optimize resolution. About 30 000 scans were taken. Chemical shifts are given relative to saturated Na_2WO_4.

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[9] W(IV) complexes have chemical shifts in the range 1100–1600 ppm. We note that for all diamagnetic tungsten oxo complexes δ_W appears to be roughly diagnostic of oxidation state: tungstates(VI), +60 − −250 ppm; $W^{III}_2(O\text{-}t\text{-}Bu)_6$, +4408; $W^{II}_2(O_2CCF_3)_4$, +6760. (Minelli, M.; Enemark, J.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169.)

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