Formation of Cyclopentenone upon Photo-oxidation of the Cyclopropyl (c-C_3H_5) Carbyne Complex [(η^5-C_5H_5){P(OMe)$_3$}(CO)W≡C(c-C_3H_5)]

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Photo-oxidation of the carbyne complex [(η^5-C_5H_5){P(OMe)$_3$}(CO)W≡C(c-C_3H_5)] by irradiation in $CHCl_3$ results in formation of [(η^5-C_5H_5){P(OMe)$_3$}(CO)WCl_3] and partial recovery of the lost cyclopropyl carbyne ligand as cyclopentenone.

We recently reported that photolysis of the carbyne complex [(η^5-C_5H_5){P(OMe)$_3$}$_2$Mo≡CPh] (**1**) in the presence of $CHCl_3$ and PMe_3 results in photo-oxidation of (**1**) followed by ligand exchange and halogen atom abstraction to give the cationic carbyne complex (**2**) (Scheme 1).[1] The mechanistic steps of this process are characteristic of the reactions of metal radicals. Under the same conditions, [(η^5-C_5H_5)-{P(OMe)$_3$}(CO)W≡C(c-C_3H_5)] (**3**) undergoes analogous metal radical reactions to yield (**4**) (Scheme 2).[2] However, in the absence of PMe_3, photolysis of (**3**) in $CHCl_3$ results in rearrangement and loss of the carbyne ligand to give [(η^5-C_5H_5){P(OMe)$_3$}(CO)WCl_3] (**6**) and cyclopentenone (**5**) as the final products. Thus, the change in reaction conditions induces a shift in the site of radical reactivity from the metal atom to the carbyne ligand, where it is detected as rearrangement of the cyclopropyl group.

Several types of photochemical reactions of carbyne complexes have been observed, including coupling of the carbyne ligand to a carbonyl,[3,4] formation of a cyclopropenyl complex by addition of an alkyne,[5] conversion of the carbyne ligand into a π-allyl,[6] and protonation of the carbyne carbon.[7] The formation of cyclopentenone (**5**) demonstrates another mode of photoinduced reactivity for metal carbynes: photo-oxidation followed by rearrangement and loss of the carbyne ligand as a stable organic product.

Photo-oxidation of the carbyne complex (**3**)† in $CDCl_3$ results in disappearance of starting material and formation of a 58% yield of complex (**6**)† in which the carbyne ligand has been lost and three chlorine atoms have been abstracted from the solvent. The lost carbyne ligands appear in part as a 38% yield of cyclopentenone (**5**). The reaction also produces a significant amount of intractable material and the only other identifiable product is a 25% yield of methyl chloride. Methyl chloride is produced upon reaction of P(OMe)$_3$ with chlorocarbons, a process that is initiated by light or radicals,[9] both of which are present during the reaction.

In the cyclopentenone product, the hydrogen that is not derived from the original cyclopropyl group is in part

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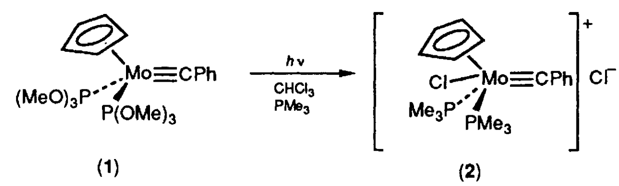
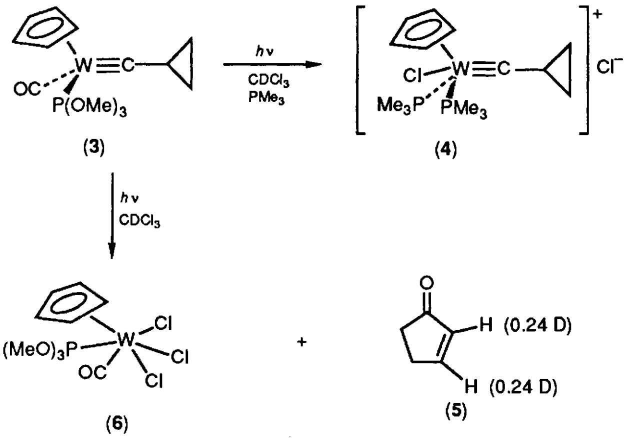
† *Spectral data* for (**3**): IR: ν_{CO} (CD_3CN) 1883 cm^{-1}; NMR: ^1H (C_6D_6) δ 0.45 (m, 2H, C_3H_5), 0.95 (m, 3H, C_3H_5), 3.44 [d, 9H, P(OMe)$_3$, *J*(PH) 12.1 Hz], and 5.19 (s, 5H, C_5H_5); ^{13}C (C_6H_6) δ 9.9, 10.5, 33.3 (C_3H_5), 52.0 [P(OMe)$_3$], 89.4 (C_5H_5), 234.0 (CO), and 301.2 [W≡C, *J*(CP) 18.1 Hz]; ^{31}P (C_6D_6) δ 175.0 ppm [*J*(PW) 674 Hz].

Spectral data for (**6**): IR: ν_{CO} (KBr) 2021 cm^{-1}; NMR: ^1H ($CDCl_3$) δ 3.96 [d, 9H, P(OMe)$_3$, *J*(PH) 10.2 Hz] and 5.70 [d, 5H, C_5H_5, *J*(PH), 3.7 Hz]; ^{31}P ($CDCl_3$) δ 91.2 ppm [*J*(PW) 375 Hz]; FAB MS: m/z 436, $(M - Cl_2)^+$. The molybdenum congener of (**6**) is characterized in ref. 8.

Satisfactory elemental analyses were obtained for (**3**) and (**6**).



Scheme 1



Scheme 2

abstracted from the solvent. Mass spectral analysis of (**5**) indicates that the material is 48% $^2H_1$. Integration of ^1H NMR spectra shows the deuterium to be located on the vinyl group, evenly distributed between the 2- and 3-positions. The product yields appear to be limited by the amount of available CO, as (**5**) and (**6**) each contain a carbonyl and the starting material can only provide one equivalent.

These results contrast with the carbyne-to-vinylidene conversion observed by Green upon one-electron oxidation of $[(\eta^5\text{-}C_5H_5)\{P(OMe)_3\}_2Mo{\equiv}CCH_2Bu^t]$.[10] A similar pathway triggered by the photo-oxidation of (**3**) to the 17 e species $(\mathbf{3})^+$ would lead to a vinylidene complex where the ligand is the highly strained cyclopropylidenecarbene. Instead, formation of (**5**) from the cyclopropyl carbyne ligand of (**3**) implies a multistep pathway including ring opening, carbonyl insertion, and hydrogen abstraction.

Mechanistic studies on this reaction are still in progress, but cleavage of the cyclopropyl ring in the metal radical $(\mathbf{3})^+$ appears to be related to the facile ring opening of cyclopropylmethyl radicals.[11] Other plausible steps on the pathway to (**5**) such as carbonyl insertion into the ligand[12,13] and reductive elimination of the product from a metallacyclic intermediate[14] should also be accelerated in the cationic species resulting from oxidation of (**3**).

In summary, we have observed formation of cyclopentenone upon photo-oxidation of the cyclopropyl carbyne complex (**3**). This demonstrates a new mode of reactivity for metal carbynes in which photo-oxidation of the complex triggers rearrangement in the carbyne moiety instead of the ligand exchange and atom abstraction processes characteristic of metal radicals. Further studies on the scope and mechanism of these reactions are in progress.

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