Direct Observation of a Hydrogen Abstraction Product upon Photooxidation of a Tungsten Cyclohexenyl Carbyne Complex

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In previous work, we have demonstrated that photooxidation of carbyne complexes of the type $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}$-$M{\equiv}CR$ (M = Mo, W; R = alkyl) results in rearrangement and decoordination of the carbyne ligand to yield organic products such as cycloalkenones, olefins, and dienes.[1] Mechanistic studies suggested that these reactions shared the following two initial steps: (1) photoinduced electron transfer from the carbyne to the solvent and (2) hydrogen abstraction from the reaction medium to produce a metal carbene.[2] Despite the usual tendency of organometallic radicals to undergo ligand exchange and halogen abstraction at the metal center,[3] geometric distortions of the carbyne radical cations cause radical reactivity to occur at the carbyne carbon and the H-abstraction takes place at that site.[4] The resulting cationic carbene complexes are the reactive species in the reactions that produce organic products.

Although mechanistic studies were consistent with the intermediacy of cationic carbene complexes in the formation of organic products from photooxidized carbynes, to this point, carbene complexes had never actually been observed in the reaction mixtures. We now report that photolysis of the cyclohexenyl carbyne complex $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}W{\equiv}C$-$(c\text{-}C_6H_9)$ (**1**)[5] in the presence of CHCl$_3$ yields the tungsten carbene complex **2** (eq 1). Observation of **2** in the photooxi-

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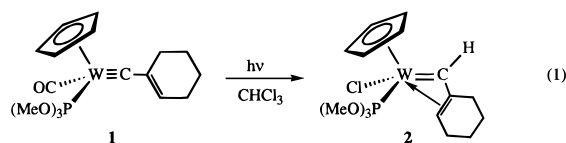
dation reaction mixtures provides the first direct evidence for the formation of carbene complexes in these reactions, providing additional support for H-abstraction at the carbyne carbon of the 17-electron $[(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}M{\equiv}CR]^{\bullet+}$ species.

The cyclohexenyl tungsten carbyne complex **1** was synthesized as shown in Scheme 1. The known carbene **3**[6] was readily converted to the tris(trimethyl phosphite) carbyne complex **4** using Fischer's method.[5,7] Reaction of CpNa with **4** produced

Scheme 1
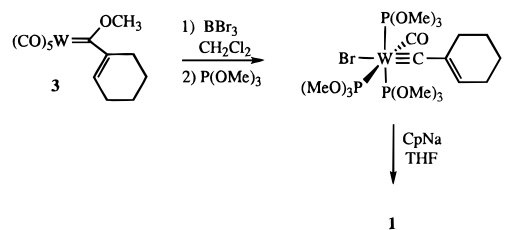
carbyne **1**[5] as a reddish-orange oil that can be stored for approximately 1 week at −30 °C.

Photolysis of carbyne **1** at −45 °C in CDCl$_3$ with a Hanovia medium-pressure mercury vapor lamp while monitoring the reaction progress by ^{1}H NMR spectroscopy resulted in observation of downfield shifts of the alkyl peaks and the formation of a new Cp peak. Since the reactivity of related carbyne complexes following photooxidation[1] suggested that **1**$^{\bullet+}$ had probably abstracted a deuterium atom from the CDCl$_3$ solvent, the experiment was repeated in CHCl$_3$ at −45 °C so that the abstracted H-atom could be located by ^{1}H NMR.[5] Upon completion of the photolysis as determined by disappearance of the initial carbyne **1** by TLC of the reaction mixtures, the CHCl$_3$ was pumped off at −45 °C and the residue was dissolved in cold CDCl$_3$ to obtain a ^{1}H NMR spectrum. The spectrum revealed a broad singlet at δ 15.35 which is characteristic of a proton on the carbene carbon of an electrophilic carbene complex.[15]

One obvious candidate for the photooxidation product was the cationic carbene complex **5**. Electron transfer from **1** to
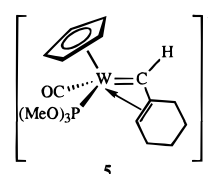
the solvent followed by H-abstraction at the carbyne carbon of **1**$^{\bullet+}$ would produce **5**. However, IR spectra of the reaction mixtures failed to show a new signal for a terminal CO ligand.[8−10] Once **5** had been ruled out as the observable species, the next obvious possibility would be displacement of the CO in **5** with Cl$^-$ to yield the neutral carbene **2**. Reaction mixtures from the photooxidation of **1** would contain Cl$^-$ since it is generated upon reduction of the CHCl$_3$ solvent[11] by the excited state of carbyne **1**.

Complex **2** is formally the product of protonation of carbyne **1** at the carbyne carbon and Cl$^-$ substitution. Thus, it was not unreasonable to attempt its preparation by reaction of **1** with HCl, although protonation of metal carbynes is a complicated issue because proton attack can occur either at the metal or at the carbyne carbon.[12] Reaction of related $(\eta^5\text{-}C_5H_5)(CO)$-$\{P(OMe)_3\}M{\equiv}CR$ complexes with HCl generally leads to η^2-

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(8) A reviewer has suggested an alternative mechanism in which photochemical CO loss from **1** is followed by coordination of CHCl$_3$ and inner-sphere electron transfer. However, in the absence of electron acceptors, the CO ligands of $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}W{\equiv}CR$ complexes do not dissociate photochemically.[2b,e,9] This is consistent with the assignment of the lowest excited state as d → π* (W≡C).[10]
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acyl complexes of the type $(\eta^5\text{-}C_5H_5)Cl_2\{P(OMe)_3\}MCO\text{-}CH_2R$.[1,2,13] However, Kreissl's work on the mechanism of η^2-acyl formation points to the intermediacy of a metal carbene intermediate which then undergoes CO insertion.[14] This postulate was supported by the fact that when the aminocarbyne $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CNEt_2$ was reacted with HCl, the reaction stopped at the carbene.[13b] Although in the Kreissl work the carbene was only observable for the aminocarbyne case, which is electronically very different from **1**, the presence of the cyclohexenyl group in **1** opened the possibility of preventing CO insertion into the carbene ligand of intermediate **5** by chelation of the double bond.

As desired, protonation of the vinyl carbyne **1** with HCl (eq 2)[5] did not produce the η^2-acyl complex, but rather yielded the

$$(2)$$
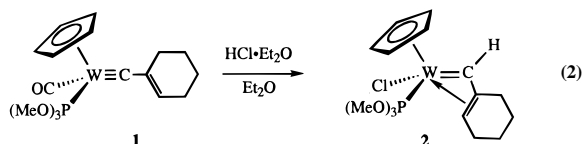
carbene complex **2** as a yellow powder which is thermally labile but stable at $-45\ ^\circ$C. Comparison of the ^{1}H NMR spectrum of the HCl product to the ^{1}H NMR spectra of the reaction mixtures from photooxidation of carbyne **1** provided confirmation that both routes had produced the same complex.

The ^{1}H NMR, ^{13}C NMR, and MS data for **2** support the proposed structure. In the ^{1}H NMR of **2** in CDCl$_3$ at $-50\ ^\circ$C, the proton on the carbene carbon appears as a singlet at δ 15.35, which is characteristic of conjugated electrophilic carbene complexes.[15] The ^{13}C NMR chemical shifts of δ 277.8 for the carbene carbon, δ 75.4 for the quaternary vinyl carbon, and δ

93.7 for the tertiary vinyl carbon strongly resemble the literature values for the tungsten η^3-vinyl carbene complex $(\eta^5\text{-}C_5H_5)$-(CO)(I)W{=}C(Ph)C(Ph)CHTol.[16] The electrospray MS of **2** in CH$_3$CN exhibited a molecular ion peak at 502.1, with an isotopic distribution pattern that matched the simulation for the molecular formula of **2**, $C_{15}H_{24}ClO_3PW$.

Photolysis of carbyne **1** at $-45\ ^\circ$C in CDCl$_3$ containing decane as a standard afforded carbene **2** in 25% yield as determined by integration of the Cp resonance in the ^{1}H NMR spectrum. To rule out photochemical formation of HCl as the source of **2** in the photooxidation reactions, **1** was photolyzed in CDCl$_3$ to which the hindered base 2,6-di-*tert*-butylpyridine had been added to scavenge any acid. 2,6-Di-*tert*-butylpyridine has been used by us[2d,e,4] and others[17] to distinguish radical cation chemistry from acid-induced reactions. The yield of the photolysis product was the same in the presence and the absence of the base, ruling out formation of **2** in the photolysis mixtures by reaction of **1** with HCl.

In summary, we have demonstrated that photooxidation of the cyclohexenyl carbyne **1** in CHCl$_3$ yields carbene complex **2**. This experiment represents the first direct observation of a carbene intermediate following single-electron oxidation of a carbyne complex and provides further evidence for H-abstraction at the carbyne carbon as a common mechanistic step in previously reported photooxidation reactions. Formation of **2** upon thermal reaction of **1** with HCl also provides additional support for the Kreissl mechanism for generation of η^2-acyl complexes from carbyne complexes and HCl by extending the range of observable carbene intermediates from amino derivatives to alkyl derivatives. Further chemistry of carbyne **1** will be reported in due course.

Supporting Information Available: Experimental procedures for the preparation of compounds **1**−**4**, photolysis procedure for **1**, and spectral data for the products (2 pages). See any current masthead page for ordering and Internet access instructions.

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