# Photoinduced Carbonylation of the Carbyne Ligand in $(\eta\text{-}C_5H_5)(CO)_2W{\equiv}CTol$

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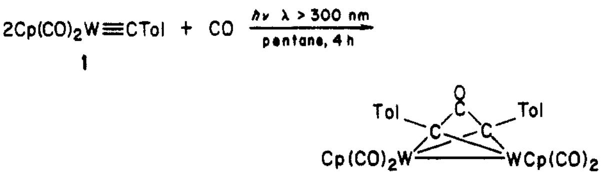
*Summary:* UV irradiation of solutions of $Cp(CO)_2W{\equiv}CTol$ (**1**, Tol = $p\text{-}C_6H_4CH_3$) in the presence of CO induces carbonylation of the carbyne ligand and formation of the binuclear complex $(Cp(CO)_2W)_2(\mu\text{-}C\{Tol\}C\{O\}CTol)$ (**2**). The bridging ligand of **2** consists of two carbyne units linked by a CO, but the latter is not bonded to the metal. Irradiation of **1** in the presence of $PPh_3$ leads to rapid formation of the known ketenyl complex $Cp(CO)(PPh_3)W(\eta^2\text{-}C\{Tol\}CO)$ (**3**) which reacts further with CO to form the $\eta^1$-ketenyl species $Cp(CO)_2(PPh_3)W(\eta^1\text{-}C\{Tol\}CO)$ (**4**).

The electronic character of ligands attached to metals can often be significantly altered by photoexcitation, particularly if charge-transfer (CT) excited states involving those ligands are populated.[1] Metal carbene and carbyne complexes generally possess low-lying CT states, and the potential exists for photoinducing unique interactions of these ligands with added substrate molecules. Metal-to-carbene charge-transfer excited states have been shown to give facile isomerization of carbene ligands,[2] and such states may be important in the photoinduced synthesis of $\beta$-lactams with $(CO)_5Cr{=}C(OR)R'$.[3] Likewise, metal-to-carbyne charge-transfer excitation has been shown to induce protonation of the carbyne ligand[4] and, apparently, to induce a novel carbyne ligand rearrangement.[5] We have discovered a further example which involves the *photoinduced carbonylation* of the carbyne ligand in $Cp(CO)_2W{\equiv}CTol$ (1) to give ketenyl and ketenyl-derived products as reported herein.


(1)

2 (63%)

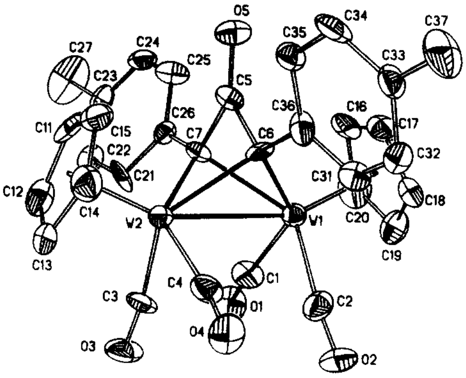
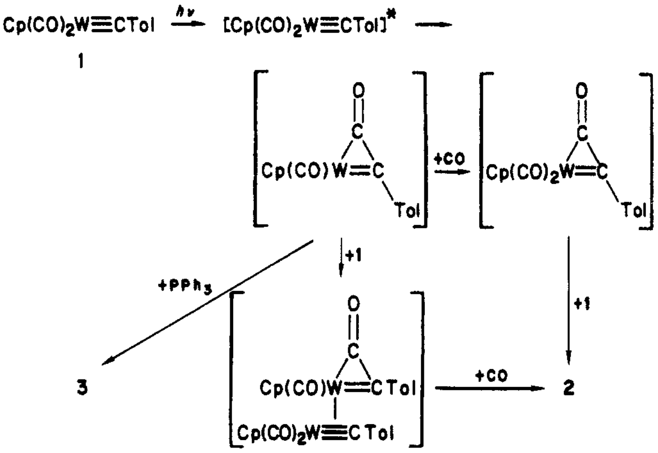


**Figure 1.** An Ortep drawing of 2. Important bond lengths (Å) and angles (deg) are as follows: W(1)–W(2), 2.956 (1); W(1)–CNT(1), 2.01 (1); W(2)–CNT(2), 1.99 (1); W(1,2)–C(6,7), 2.22 (1) (av); W(1,2)–C(1,4), 2.01 (av); C(5)–C(6), 1.52 (2); C(5)–C(7), 1.53 (2); C(5)–O(5), 1.22 (2); C(6)–W(1,2)–C(7), 62.2 (5) (av); W(1)–C(6,7)–W(2), 83.7 (4) (av); C(6)–C(5)–C(7), 98 (1); CNT(1,2)–W(1,2)–W(2,1), 155.5 (7) (av); CNT–W(1,2)–C(7,6), 116.4 (7) (av); CNT–W(1,2)–C(6,7), 109.8 (7) (av); dihedral angle [W(1)–W(2)–C(6)]–[W(1)–W(2)–C(7)], 87.7 (5)°; torsion angle CNT(1)–W(1)–W(2)–CNT(2), 29.6 (5)°. CNT(1) = center of $C_5H_5$ ring attached to W(1);; CNT(2) = center of $C_5H_5$ ring attached to W(2).

**Scheme I**



The electronic absorption spectrum of 1 shows an intense band at λ 325 nm ($\epsilon$ 10730 L mol$^{-1}$ cm$^{-1}$) which can be attributed to a tungsten-to-carbyne CT transition.[6] Irradiation of hydrocarbon solutions of 1 under a CO purge with λ > 300 nm gives rapid precipitation of the red binuclear complex 2 (eq 1). Complex 2 was isolated in 63% yield and identified by X-ray crystallography (Figure 1)[7] and by its spectroscopic data.[8] This species was previously isolated by Stone et al.[9] as a minor byproduct from the thermal reaction of 1 with a binuclear WRh alkylidyne complex, its structure being deduced from spectroscopic data. The bridging ligand in 2 is derived from the two carbyne ligands and a CO, with the structural parameters indicating no interaction between the "organic" carbonyl and the metals [W(1)–C(5) = 2.64 (2) and W(2)–C(5) = 2.65 (2) Å]. This contrasts with the only other complex containing such a bridging ligand, $Pt_2(CN\text{-}t\text{-}Bu)_4(\mu\text{-}(PhC)_2CO)$, prepared by the reaction of $Pt_3(CN\text{-}t\text{-}Bu)_6$ with

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[7] Crystal data: $C_{31}H_{24}O_4W_2$, triclinic, $P1$, $a = 8.773$ (2) Å, $b = 12.042$ (3) Å, $c = 14.866$ (5) Å, $\alpha = 91.81$ (2)°, $\beta = 94.12$ (2)°, $\gamma = 110.32$ (2)°, $V = 1466.4$ (7) Å$^3$, $Z = 2$, $\mu(MoK\alpha) = 83.1$ cm$^{-1}$. Of 5016 reflections collected (Nicolet R3, $4° \leq 2\theta \leq 50°$), 4802 were unique, of which 3075 had ($F_o \geq 3\sigma(F_o)$ and were used in the solution (Patterson) and refinement. All non-hydrogen atoms anisotropic and hydrogen atoms idealized as isotropic contributions. For 344 parameters, $R_F = 4.63\%$, $R_{wF} = 5.62\%$, GOF = 1.47, and highest peak (final map) = 1.0 e Å$^{-3}$ (1.16 Å from W(2); SHELXTL programs (Nicolet Corp., Madison, WI).

[8] **2**: IR ($CH_2Cl_2$) $\nu$(CO) 2020 (s), 1977 (m), 1935 (m), 1586 (w) cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.30 (6 H, s, Me), 5.04 (10 H, s, Cp), 7.02 (4 H, d, $J$ = 8 Hz, tolyl), 7.57 (4 H, d, $J$ = 8 Hz, tolyl); $^{13}$C NMR ($C_6D_6$) $\delta$ 21.0 (Me), 78.0 (*C*-Tol, $J(^{13}C^{183}W)$ = 40 Hz), 9.12 (Cp), 128.3, 128.8, 128.9, 133.5 (Tol), 177.3 (C{Tol}*C*{O}C{Tol}), 215.5 (CO, $J(^{13}C^{183}W)$ = 149 Hz); *m/z* 844 ($M^+$), 816 ($M^+ - CO$), 788 ($M^+ - 2CO$), 760 ($M^+ - 3CO$).

[9] Green, M.; Howard, J. A. K.; Porter, S. J.; Stone, F. G. A.; Tyler, D. C. *J. Chem. Soc., Dalton Trans.* **1984**, 2553.

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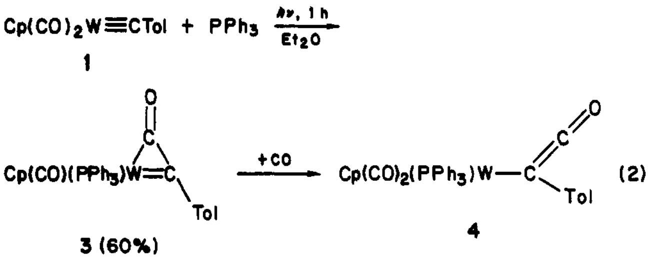
diphenylcyclopropenone and for which a weak metal carbonyl interaction was suggested.[10] Of particular interest in **2** is the acute C(6)–C(5)–C(7) angle of 98°, considering the assumed $sp^2$ hybridization of C(5). Complex **2** also forms in trace quantities along with unidentified brown decomposition products when solutions of **1** are irradiated in the absence of added CO.

A similar rapid photoinduced carbonylation of the carbyne ligand occurs when **1** is irradiated in the presence of $PPh_3$ to give the $\eta^2$-ketenyl complex **3** (eq 2). When the reaction is performed under a CO atmosphere, **3** is observed as an intermediate, but the final product of this reaction is the $\eta^1$-ketenyl complex **4**.[11] Complex **4** was independently shown to derive from **3** by a thermal reaction with CO. The **1** to **3** conversion has been previously reported to proceed thermally over 2 days at 25 °C,[12] but we find that if these solutions are rigorously maintained in the dark, **3** forms after 7–8 days and then only as one component in a mixture of decomposition products. In contrast, the similar reaction involving $PMe_3$ proceeds rapidly in the dark as well as upon irradiation.[12]



We suggest that these carbonylation reactions proceed via initial migration of a coordinated CO to the carbyne ligand in a tungsten-to-carbyne CT excited state. This would yield a coordinatively unsaturated $\eta^2$-ketenyl complex which could subsequently be scavenged by $PPh_3$ to yield **3** or alternatively by CO or the carbyne complex **1** to form binuclear **2** (Scheme I). Support for this suggestion comes from IR monitoring of the photolysis of **1** in the presence of $PPh_3$ under a $^{13}CO$ atmosphere. No incorporation of $^{13}CO$ into the $\eta^2$-ketenyl ligand of **3** was observed nor into the $\eta^1$-ketenyl ligand of **4** which eventually forms. Metal carbonyl enrichment of **4** did occur since exogenous CO is taken up by **3** to form **4**.[14]

The results described here may be of relevance to an earlier study by Fischer and co-workers in which photolysis of *trans*-$Cl(CO)_4W{\equiv}CPh$ with Hacac gave the hydroxyalkyne complex *trans*-$Cl(CO)_2(acac)W(\eta^2\text{-}HOC{\equiv}CPh)$.[15] Although the mechanism for this reaction was not defined, our studies suggest that it proceeds via photoinduced carbonylation of the carbyne ligand followed by protonation of the resulting ketenyl species by Hacac. A similar protonation of a ketenyl ligand has been described by Stone et al.[16]

It is assumed that carbon monoxide migrates from tungsten to the carbyne ligand in a MLCT excited state because of the increased electron density on the carbyne carbon atom. With carbyne complexes that do not possess CO ligands, it may prove possible to capture the "activated" carbyne with other substrates. Such systems are currently under investigation.

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**Registry No.** 1, 60260-15-3; 2, 95029-84-8; 3, 102615-19-0; 4, 102615-20-3.

**Supplementary Material Available:** Tables of crystallographic data and atomic positional parameters for 2 (28 pages). Ordering information is given on any current masthead page.

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[11] **4**: IR ($CH_2Cl_2$) $\nu$(CCO) 2035 (s) $cm^{-1}$, $\nu$(CO) 1946 (s), 1856 (s) $cm^{-1}$; $^{31}P$ NMR (acetone-$d_6$, −10 °C) $\delta$ 33.8 ($J_{P-W}$ = 188 Hz); $^{13}C\{^1H\}$ NMR (acetone-$d_6$, −10 °C) $\delta$ 20.7 ($CH_3$), 93.0 (Cp), 128–134 (aryl), 158.2 (CCO), 224.8, 224.9, 225.2 (CO); $^1H$ NMR (acetone-$d_6$, −10 °C) $\delta$ 2.23 (s, $CH_3$), 5.20 (d, $J_{H-P}$ = 2 Hz, Cp).

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[14] IR: $\nu$(CCO) 2035 (s) $cm^{-1}$; $\nu$(CO) 1946, 1856 (m) $cm^{-1}$; $\nu(^{13}CO)$ 1902, 1836 (m) $cm^{-1}$.

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## Synthesis of $[Ru(N)R_4][NBu_4]$, the First Alkyl Complexes of Ruthenium(VI)

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*Summary:* The nitridoalkylruthenium(VI) anions $[Ru(N)R_4]^-$, $[Ru(N)Me_2(CH_2SiMe_3)_2]^-$, and $[Ru(N)(CH_2SiMe_3)_2(OSiMe_3)_2]^-$ (where R = $CH_3$ or $CH_2SiMe_3$) have been prepared from either $[Ru(N)Cl_4]^-$ or $[Ru(N)(OSiMe_3)_4]^-$ and $Mg(CH_2SiMe_3)_2$ and/or $AlMe_3$. The alkyl complexes are thermally stable, yellow crystalline complexes. They react rapidly with $O_2$ in solution but are stable to $H_2O$ and MeOH in the absence of light.

Ruthenium tetraoxide is a powerful oxidizing agent, capable of oxidizing olefins to the cis diols or cleaving the C–C double bond to form aldehydes or carboxylic acids.[1] It has been proposed that metal oxides, like $RuO_4$, react with olefins to form high oxidation state organometallic complexes.[2] Ruthenium(VI) alkyls have also been proposed, recently, as intermediates in C–H activation of hydrocarbons with a ruthenium hydrido complex.[3] While there have been recent reports of osmium(VI) alkyl complexes, organometallic complexes ruthenium(VI) are unknown.[4-6] The most recent advances in Ru(VI) chemistry have been the preparation of nitrido complexes such as $[Ru(N)X_4]^-$ and trans dioxo complexes such as $[Ru(O)_2X_4]^{2-}$.[7]

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