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

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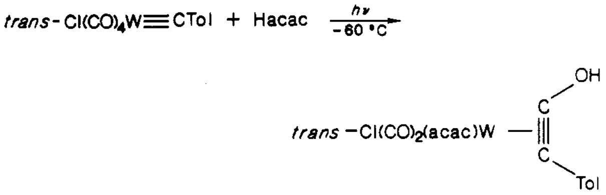
UV irradiation of solutions of $Cp(CO)_2W{\equiv}CTol$ (1) (Tol = $p\text{-}C_6H_4CH_3$; Cp = $\eta\text{-}C_5H_5$) in the presence of CO induces carbonylation of the carbyne ligand and formation of the binuclear complex $[Cp(CO)_2W]_2(\mu\text{-}TolCC\{O\}CTol)$ (2). Complex 2 has been crystallographically characterized: triclinic, $P\bar{1}$, $a = 8.773$ (2) Å, $b = 12.042$ (3) Å, $c = 14.866$ (5) Å, $\alpha = 91.81$ (2)°, $\beta = 94.12$ (2)°, $\gamma = 110.32$ (2)°, $R_F = 4.63\%$, $R_{wF} = 5.62\%$ for 3075 reflections with $F_o \geq 3\sigma(F_o)$. The bridging ligand of 2 consists of two carbyne units linked by a CO with the latter not bonded to either metal. Irradiation of 1 in the presence of PPh_3 leads to rapid formation of the known ketenyl complex $Cp(CO)(PPh_3)W(\eta^2\text{-}TolCCO)$ (5). Complex 5 reacts further with CO to form the η^1-ketenyl species $Cp(CO)_2(PPh_3)W(\eta^1\text{-}TolCCO)$. Photolysis of 1 in the presence of dppe (dppe = 1,2-bis(diphenylphosphino)ethane) yields the η^1-ketenyl species $Cp(CO)(dppe)W(\eta^1\text{-}TolCCO)$, which readily loses dppe to give the novel binuclear η^2-ketenyl derivative $[Cp(CO)W(\eta^2\text{-}TolCCO)]_2(\mu\text{-dppe})$.

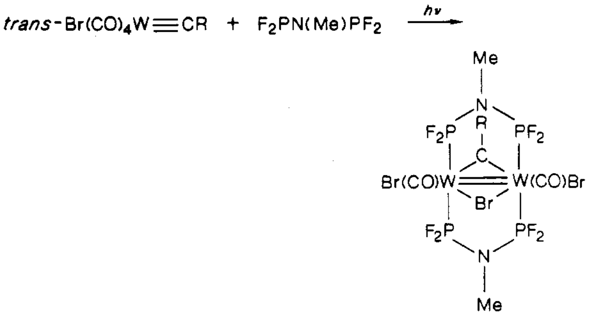
Introduction

In contrast to the well-developed thermal chemistry of carbyne complexes,[1] relatively little is known about their photochemical properties.[2] This class of compounds should have a rich photochemistry due to the unsaturated character of the metal–carbyne functional group and the presence of long-lived and low-lying metal-to-carbyne charge-transfer (MLCT) excited states.[3] Only a few photochemical studies of carbyne complexes have been published,[4-8] but these studies do indicate much promise for this area.

In early work Fischer and co-workers demonstrated the novel photoinduced conversion of a carbyne into a hydroxyalkyne ligand, eq 1,[4] and also the photoinduced formation of a binuclear carbyne complex, eq 2,[5] but no mechanistic suggestions were made for either reaction.

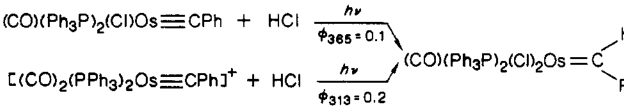


(1)



(2)

Vogler et al. observed the photoinduced protonation of the carbyne ligands in $[(CO)_2(PPh_3)_2Os{\equiv}CPh]^+$ and $(CO)Cl(PPh_3)_2Os{\equiv}CPh$ upon irradiation in the presence of HCl, eq 3.[6] Protonation was suggested to occur on "bent" carbyne ligands in MLCT excited states of these complexes as illustrated in eq 4.



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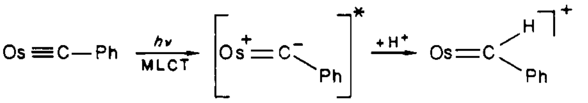
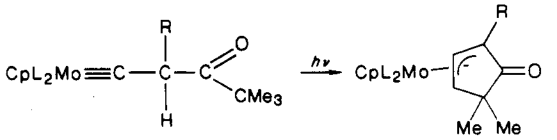


(4)

Green and co-workers[7] recently reported the interesting photoinduced rearrangement shown in eq 5, which was also suggested to occur via a bent carbyne ligand in a MLCT excited state.



(5)

Such an intermediate would have a 16e molybdenum center, which was suggested to activate a C–H bond of the *t*-BuCO group to allow rearrangement to the observed product. The only other reported photoreactions of carbyne compounds involved the hydrogenation of the μ_3-alkylidyne ligands in the clusters $Co_3(\mu_3\text{-}CR)(CO)_9$ (R = H, Me, Ph) upon photolysis in the presence of H_2.[8] The detailed mechanism of this reaction was not elucidated, but photoinduced

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[1] For reviews see: (a) Heesook, P. K.; Angelici, R. J. *Adv. Organomet. Chem.*, in press. (b) Evans, J. *Ann. Rep. Prog. Chem., Sect. A.: Inorg. Chem.* **1979**, *76*, 213. (c) Tirouflet, J.; Dixneuf, P.; Braunstein, P. *Actual. Chim.* **1975**, 3.

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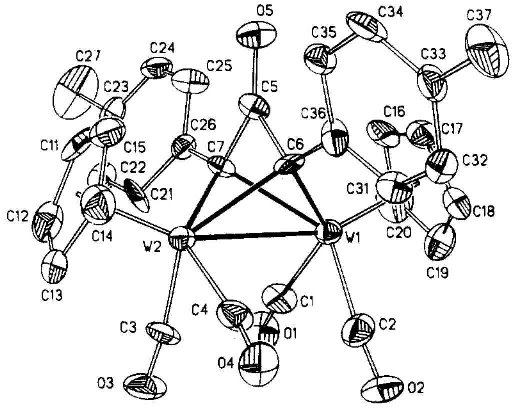


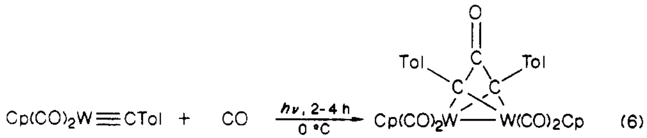
Figure 1. An ORTEP drawing of $[Cp(CO)_2W]_2(\mu\text{-}TolCC\{O\}CTol)$ (2). Thermal ellipsoids are drawn at the 40% probability level.

metal–metal bond homolysis was suggested as the first step.

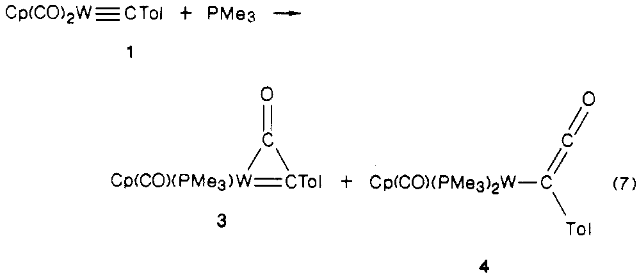
We have undertaken a study of the photochemical properties of a series of carbyne complexes in order to further develop this potentially important area. Herein is described the photoinduced carbonylation of the carbyne ligand in $Cp(CO)_2W{\equiv}CTol$ (1) to give ketenyl and ketenyl-derived products. This work also provides a mechanistic basis for the previously reported reaction shown in eq 1.[4] A portion of this work has been previously communicated.[9]

Results

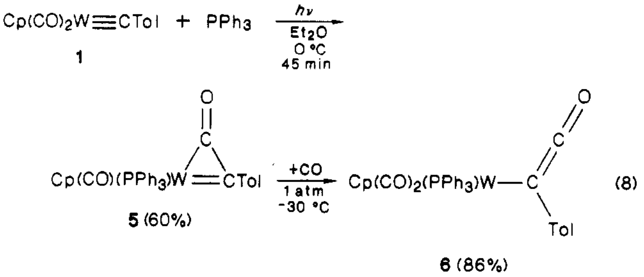
Irradiation of $Cp(CO)_2W{\equiv}CTol$ under a CO Atmosphere. When hexane solutions of 1 were irradiated in the absence of added ligand, trace amounts of a red crystalline compound 2 were produced, along with copious quantities of a brown insoluble precipitate. The yield of 2 was markedly improved by photolysis under a CO atmosphere, eq 6. Complex 2 was previously isolated by Stone, et al.[10] as a minor byproduct from the thermal reaction of 1 with a binuclear WRh alkylidyne complex, with its structure being deduced from spectroscopic data. Its IR spectrum shows a band at 1568 cm^{-1} assigned to the carbonyl within the bridging TolCC{O}CTol ligand, and its ^{13}C NMR spectrum shows resonances at δ 78.0 and 177.3, respectively, attributed to the Tol*C* and *C*O carbons of this ligand. The structure of 2 was further confirmed by the X-ray diffraction study described below, the results of which are shown in Figure 1. That the reaction of eq 6 is a photochemical transformation rather than a thermally induced reaction was shown by the formation of only traces of 2 when 1 was heated under 2 atm of CO in hexane at 100 °C for 10 h. This latter reaction gave mostly recovered 1 along with several other unidentified products.



Irradiation of $Cp(CO)_2W{\equiv}CTol$ in the Presence of PPh_3. Kreissl and co-workers have previously shown that complex 1 rapidly reacts with PMe_3 to give a mixture of the η^1- and η^2-ketenyl compexes 3 and 4, eq 7, depending on the PMe_3 concentration.[11] The similar reaction with PPh_3 was reported to occur much more slowly (2 days, 25 °C) to give the PPh_3 analogue of 3 in 82% yield.[11] We have found that the latter reaction only occurs well under photochemical conditions. When a mixture of 1 and PPh_3 was kept rigorously in the dark, $Cp(CO)(PPh_3)W(\eta^2\text{-}TolCCO)$ (5) was formed in low yield as one component in a mixture of products after 6–7 days at 25 °C. The other unidentified species formed were the same as those produced when complex 1 was allowed to stand alone under these conditions.



However, irradiation of diethyl ether solutions of 2 in the presence of PPh_3 gave rapid formation of the η^2-ketenyl complex 5, eq 8. This species was formed in good yield and characterized by comparison of its spectroscopic data to those reported by Kreissl and co-workers.[11] In the course of this study we also observed that complex 5 takes up added CO to form the η^1-ketenyl complex 6, eq 8. Although this latter complex has not been previously reported, the observed reaction parallels that which is known to occur for its PMe_3 analogue.[12] Complex 6 was spectroscopically characterized. It shows a strong IR absorption at 2035 cm^{-1} assigned to the ketenyl CO stretch, a ^{31}P NMR singlet at δ 33.8 for the PPh_3 ligand, and ^{13}C NMR resonances at δ 13.4 and 158.2 attributed to the ketenyl C and CO carbons, respectively. Complex 6 is an air and thermally sensitive material which produces a mixture of decomposition products upon warmup above −10 °C.



Irradiation of $Cp(CO)_2W{\equiv}CTol$ in the Presence of dppe. Kreissl and co-workers[13] have shown that complex 1 readily reacts with added 1,2-bis(dimethylphosphino)ethane (dmpe) even at −40 °C to form the η^1-ketenyl complex $Cp(CO)(dmpe)W(\eta^1\text{-}TolCCO)$. We have found that a similar reaction slowly occurs with the less basic phosphine 1,2-bis(diphenylphosphino)ethane (dppe) to form the η^1-ketenyl complex 7, eq 9, if the solution is maintained in the dark. However, as indicated in eq 9 the reaction is markedly photoaccelerated. Under the photochemical conditions shown in eq 9, complex 7 is the only product. However, lower concentrations of 1 or dppe resulted in slower rates of reaction and greater overall de-

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[9] Sheridan, J. B.; Geoffroy, G. L.; Rheingold, A. R. *Organometallics* **1986**, *5*, 1514.

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

[11] Kreissl, F. R.; Eberl, K.; Uedelhoven, W. *Chem. Ber.* **1977**, *110*, 3782.

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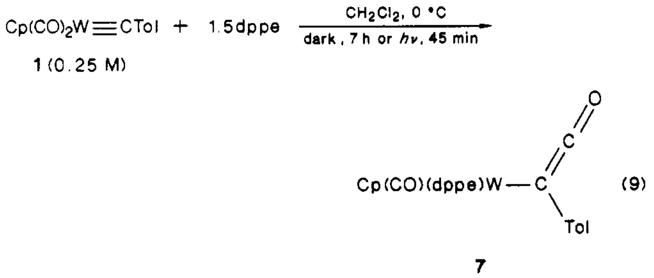
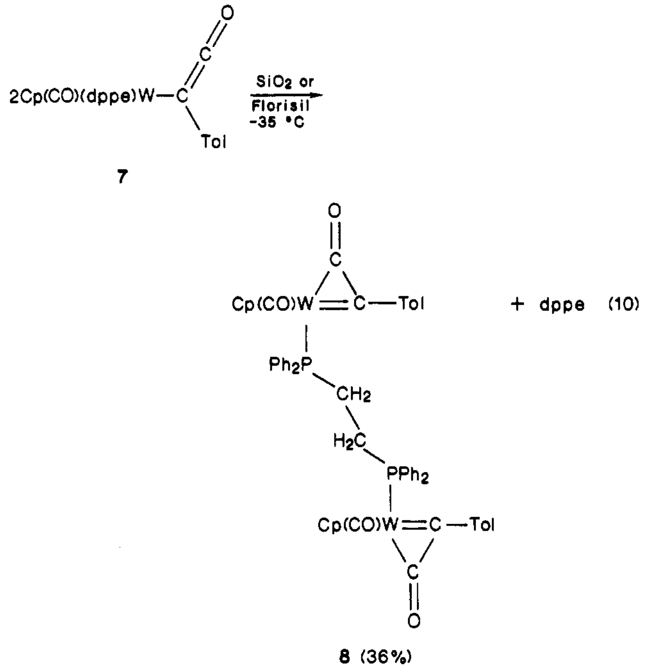


composition. Complex 7 was identified by comparison of its IR, ^{31}P, and ^1H NMR spectra (see the Experimental Section) to those of its dmpe analogue.[13]

Attempts to separate complex 7 from the excess dppe by chromatography on silica gel, deactivated alumina, or Florisil gave partial loss of dppe from 7 and formation of the unusual dppe-bridged, η^2-ketenyl dimer 8, eq 10.



Complex 8 has two chiral metal centers and was formed as a 1:2.3 mixture of diastereomers. Spectroscopic and analytical data for the complex are listed in the Experimental Section with ^{13}C NMR and IR data clearly indicating an η^2-ketenyl structure. Particularly diagnostic of the dimeric structure of 8 are the 1158 amu ion in its mass spectrum ($M^+ - 2CO$) and the presence of a *single* ^{31}P NMR resonance for each diastereomer. A monomeric η^2-ketenyl complex containing a monodentate dppe ligand would show *two* ^{31}P NMR resonances. The identity of 8 was further indicated by its reaction with excess dppe to cleanly reform 7.

Photolysis of 1 with Other Substrates. In like manner to reactions 6 and 8, complex 1 was irradiated in the presence of *t*-BuNC, CyNC, C_2H_4, $(MeO_2C)HC{=}CH(CO_2Me)$, 1,5-cyclooctadiene, PhC≡CPh, $MeO_2CC{\equiv}CCO_2Me$, bipyridine, H(Ph)C=NMe, $CH_3C\{O\}CH_3$, and CH_3CN. In each case rapid decomposition of 1 was observed along with the formation of trace amounts of the dinuclear species 2, but no other identifiable products were obtained.

Photolyses of Other Carbyne Complexes. Irradiation of solutions of the complexes $[(Bpy_4)(CO)_2W{\equiv}CTol]$ (py = pyrazolyl), $[Cp(CO)_2M{\equiv}CTol]^+$ (M = Mn, Re), and $[(\eta^6\text{-}C_6H_6)(CO)_2Cr{\equiv}CTol]^+$ in either the presence or the absence of added substrates resulted in no reaction. By contrast the complexes *trans*-$Cl(CO)_4W{\equiv}CTol$ and *trans*-$Cl(CO)_2(TMEDA)W{\equiv}CTol$ (TMEDA = tetramethylethylenediamine) showed rapid photoreactivity with a number of substrates (e.g. CO, PPh_3, but-2-yne), but the reactions were not clean and none gave tractable products.

Table I. Crystallographic Data for $[Cp(CO)_2W]_2(\mu\text{-}TolCC\{O\}CTol)$ (2)

mol wt	844.23
(a) Crystal Parameters	
crystal system	triclinic
space group	$P\bar{1}$
a, Å	8.773 (2)
b, Å	12.042 (3)
c, Å	14.866 (5)
α, deg	91.81 (2)
β, deg	94.12 (2)
γ, deg	110.32 (2)
V, $Å^3$	1466.4 (7)
Z	2
μ, cm^{-1}	83.1
ρ, g cm^{-3} (calcd)	1.88
size, mm	0.04 × 0.22 × 0.34
color	orange
(b) Data Collection	
diffractometer	Nicolet R3
radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite
2θ scan range, deg	4–50
scan type	ω
scan speed, deg min^{-1}	var 4–20
temp, K	294
std rflcns	3 std/197 rflcns, < 1% var
(c) Data Reduction and Refinement	
rflcns collected	5016
unique rflcns	4802
unique rflcns with $F_o \geq 3\sigma(F_o)$	3075
R(int), %	1.71
R_F,[b] %	4.63
R_{wF},[a] % (*g* = 0.001)	5.62 (*g* = 0.0025)
GOF	1.47
highest peak, final diff Fourier, e $Å^{-3}$	1.6 [1.2 Å from W(2)]
Δ/σ	0.02
N_o/N_v	10.8

[a] $w^{-1} = \sigma^2(F_o) + g(F_o^2)$; $R_F = \sum|\Delta|/\sum|F_o|$; $R_{wF} = \sum(|\Delta|w^{1/2})/\sum(|F_o|w^{1/2})$; $\Delta = |F_o| - |F_c|$.

X-ray Crystal Structure of $[Cp(CO)_2W]_2(\mu\text{-}TolCC\{O\}CTol)$ (2). An ORTEP drawing of 2 is shown in Figure 1, and the important structural parameters are given in Tables I–III. Each tungsten is ligated by a Cp, two carbonyls, and the bridging TolCC{O}CTol ligand, and the two metals are joined by a metal–metal bond (2.956 (1) Å). The *C*Tol carbon atoms of the bridging TolCC{O}CTol ligand and the two tungsten atoms form a "butterfly" structure with a [W(1)–W(2)–C(6)]–[W(1)–W(2)–C(7)] dihedral angle of 87.7 (5)°. The carbonyl group C(5)O(5) is bonded to each of the original carbyne carbons C(6) and C(7) with this ligand symmetrically bridging the two metals.

The only other complex with a similar μ-RCC{O}CR ligand is $Pt_2(CN\text{-}t\text{-}Bu)_4(\mu\text{-}PhCC\{O\}CPh)$ (9) which was isolated from the reaction of $Pt_3(CN\text{-}t\text{-}Bu)_6$ with diphenylcyclopropenone.[14] Although the structures of 2 and 9 are similar, there are important differences in details of the μ-RCC{O}CR ligands. The C(5)–C(6) and C(5)–C(7) distances in 2 average 1.52 Å, a typical C–C single bond value, whereas the corresponding distances in 9 are significantly shorter, averaging 1.43 Å. The latter is a typical η^3-allyl C–C distance. This was taken to indicate an η^3-allyl coordination of the PhCC{O}CPh ligand in 9 involving an interaction of the central carbon of this ligand with the

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[14] Carroll, W. E.; Green, M.; Howard, J. A. K.; Pfeffer, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1978, 1472.

Table II. Atomic Coordinates and Temperature Factors for [Cp(CO)$_2$W]$_2$(μ-TolCC{O}CTol) (2)

	x	*y*	*z*	*U*[a]
W(1)	2197.2 (7)	888.2 (5)	2051.5 (4)	32 (1)
W(2)	3867.8 (6)	−858.6 (4)	2183.0 (4)	30 (1)
O(1)	−699 (17)	−920 (12)	782 (10)	78 (6)
O(2)	4034 (15)	1704 (11)	317 (8)	58 (5)
O(3)	1675 (18)	−2181 (11)	427 (8)	70 (6)
O(4)	6456 (14)	566 (10)	894 (10)	62 (5)
O(5)	3250 (13)	396 (10)	4414 (7)	50 (4)
C(1)	407 (18)	−322 (14)	1237 (11)	46 (6)
C(2)	3386 (23)	1353 (14)	948 (12)	55 (7)
C(3)	2392 (20)	−1638 (13)	1065 (10)	45 (6)
C(4)	5482 (19)	116 (13)	1357 (11)	46 (6)
C(5)	3199 (16)	233 (12)	3595 (10)	34 (5)
C(6)	4358 (16)	859 (11)	2911 (8)	30 (5)
C(7)	1884 (16)	−629 (11)	2929 (9)	29 (5)
C(11)	3797 (21)	−2144 (15)	3338 (12)	53 (7)
C(12)	3541 (22)	−2774 (14)	2495 (13)	55 (7)
C(13)	5025 (28)	−2319 (14)	2037 (13)	65 (9)
C(14)	6121 (23)	−1337 (15)	2680 (13)	55 (7)
C(15)	5289 (21)	−1325 (14)	3434 (11)	48 (6)
C(16)	1011 (22)	1676 (15)	3144 (12)	52 (7)
C(17)	2596 (21)	2515 (14)	3098 (11)	49 (7)
C(18)	2634 (23)	2886 (13)	2259 (12)	54 (7)
C(19)	1137 (29)	2348 (17)	1777 (15)	72 (10)
C(20)	56 (23)	1572 (18)	2317 (17)	75 (10)
C(21)	−429 (18)	−2511 (11)	2634 (12)	47 (6)
C(22)	−1811 (18)	−3388 (13)	2882 (12)	46 (6)
C(23)	−2438 (18)	−3264 (14)	3711 (12)	46 (6)
C(24)	−1691 (21)	−2276 (14)	4245 (11)	47 (6)
C(25)	−258 (18)	−1431 (15)	4009 (11)	47 (6)
C(26)	389 (16)	−1503 (11)	3198 (10)	32 (5)
C(27)	−3904 (24)	−4232 (23)	4057 (22)	111 (13)
C(31)	6697 (17)	2652 (13)	2592 (11)	40 (6)
C(32)	8150 (17)	3509 (12)	2793 (10)	36 (5)
C(33)	9035 (18)	3646 (11)	3623 (11)	40 (5)
C(34)	8282 (21)	2810 (14)	4247 (12)	51 (6)
C(35)	6783 (19)	1910 (13)	3998 (11)	41 (6)
C(36)	5976 (18)	1828 (12)	3167 (11)	42 (6)
C(37)	10694 (21)	4565 (14)	3858 (15)	67 (8)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table III. Selected Bond Distances and Angles for [Cp(CO)$_2$W]$_2$(μ-TolCC{O}CTol) (2)

(a) Bond Distances, Å			
W(1)–W(2)	2.956 (1)	C(5)–C(6)	1.516 (19)
W(1)–C(1)	2.021 (14)	C(5)–C(7)	1.526 (17)
W(1)–C(2)	1.998 (18)	C(5)–O(5)	1.222 (18)
W(1)–C(6)	2.221 (14)	C(1)–O(1)	1.143 (18)
W(1)–C(7)	2.229 (14)	C(2)–O(2)	1.147 (21)
W(2)–C(3)	2.017 (14)	C(3)–O(3)	1.146 (18)
W(2)–C(4)	2.020 (15)	C(4)–O(4)	1.133 (20)
W(2)–C(6)	2.193 (13)	W(1)–CNT(1)	2.01 (1)
W(2)–C(7)	2.219 (15)	W(2)–CNT(2)	1.99 (1)
(b) Bond Angles, deg			
(av) C(6)–W(1,2)–C(7)	62.2 (5)	O(5)–C(5)–C(7)	130.7 (12)
(av) W(1)–C(6,7)–W(2)	83.7 (4)	O(5)–C(5)–C(6)	131.7 (11)
C(6)–C(5)–C(7)	98 (1)	W(1)–C(6)–C(5)	87.7 (8)
(av) CNT(1,2)–W(1,2)–W(2,1)	155.5 (7)	W(2)–C(6)–C(5)	89.2 (8)
(av) CNT–W(1,2)–C(7,6)	116.4 (7)	W(1)–C(7)–C(5)	87.2 (8)
(av) CNT–W(1,2)–C(6,7)	109.8 (7)	W(2)–C(7)–C(5)	88.0 (8)
W(1)–C(6)–C(36)	130.2 (10)	W(2)–C(6)–C(36)	128.5 (11)
W(1)–C(7)–C(26)	129.5 (11)	W(2)–C(7)–C(26)	130.7 (10)
C(5)–C(7)–C(26)	123.7 (12)	C(5)–C(6)–C(36)	123.5 (12)

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)°

two Pt atoms.[14] The latter was also supported by ^{13}C NMR data. The Pt centers in **9** are coordinatively unsaturated, and such interaction is not unexpected. In contrast, the C–C distances within the μ-TolCC{O}CTol ligand in **2** are not consistent with an η^3-allyl structure, and the long W(1)–C(5) (2.64 (2) Å) and W(2)–C(5) (2.65 (2) Å) distances imply little or no interaction of the central carbon with the coordinatively saturated W centers. The hybridization of carbon C(5) in **2** should thus be sp^2 as with typical ketonic organic carbonyls, but the C(6)–C(5)–C(7) angle of 98° is significantly less than the optimum 120° sp^2 angle and indicates some strain within the core of the molecule. A similar 99 (1)° angle was observed in **9**. Note also that the ν(CO) stretch of 1568 cm^{-1} associated with carbonyl C(5)O(5) is much lower than those found in typical organic carbonyls.

Discussion

The electronic absorption spectrum of **1** in *n*-pentane shows an intense band at λ 325 nm (ϵ = 10730 L mol^{-1} cm^{-1}) which can logically be assigned to a tungsten-to-carbyne CT transition, on the basis of previous studies by Bocarsly et al.[3] and calculations by Fenske and co-workers.[15] We suggest that the reactions described herein proceed via initial formation of such a tungsten-to-carbyne CT excited state, in which rapid migration of a coordinated carbon monoxide ligand to the carbyne carbon occurs to give the coordinatively unsaturated η^2-ketenyl intermediate shown in Scheme I. The increased electron density at this carbon in the excited state presumably facilitates such a process. Complex **2** could form by coordination of the W≡CR bond of a second equivalent of **1** to intermediate **10** to give **11**, followed by coupling of the carbyne and ketenyl ligands and then addition of CO to give the final product **2**. Coordination of a second equivalent of **1** to **10** has considerable precedence in Stone's numerous syntheses of binuclear μ-carbyne complexes via addition of **1** to unsaturated metal centers.[16] Alternatively, complex **2** may form by initial addition of CO to **10** to form the saturated η^2-ketenyl complex **12**, which could then react with complex **1**. The observation that the yield of **2** is far higher when the reaction is conducted in the presence of added CO may argue for the second pathway via **12**, but it could also be rationalized that the coordinatively unsaturated complex formed from ketenyl–carbyne coupling in **11** does not yield the final product **2** unless it is trapped by added CO. Addition of PPh$_3$ or dppe to the presumed intermediate **10** would, respectively, give the η^2-ketenyl product **5** and the precursor **13** to the dppe complex **7**, Scheme I.

The results described herein may be of relevance to the earlier reported photolysis of [Cl(CO)$_4$W≡CTol] in the presence of acetylacetone (Hacac) to give a complex with a hydroxyalkyne ligand, eq 1.[4] Our results indicate that this latter reaction proceeds via photoinduced carbonylation of the carbyne ligand to form the η^2-ketenyl intermediate **14** shown in Scheme II. Protonation of the η^2-ketenyl ligand by Hacac followed by coordination of the acac$^-$ anion would give the observed product. Precedent for the former reaction comes from Stone and co-workers' demonstrated formation of a hydroxyalkyne ligand via protonation of the η^2-ketenyl ligand in Cp(CO)(PMe$_3$)W(η^2-TolCCO).[17]

Experimental Section

The complex Cp(CO)$_2$W≡CTol was prepared by the literature procedure.[18] Solvents were dried by stirring over Na/benzo-

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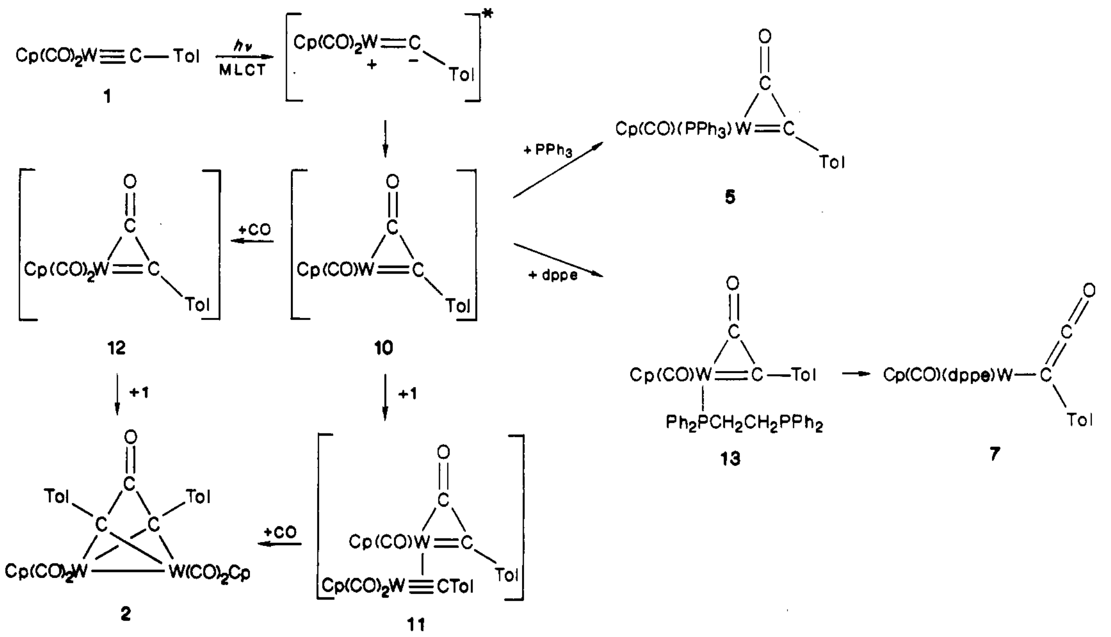
(15) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 489.

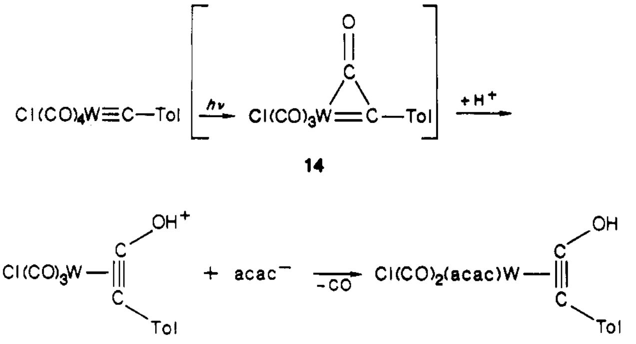
(16) Stone, F. G. A. In *Inorganic Chemistry towards the 21st Century*; Chisholm, M., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, DC 1983; p 383.

(17) Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Stone, F. G. A. *J. Organomet. Chem.* **1983**, *258*, C37.

Scheme I



Scheme II



phenone (pentane, Tetrahydrofuran (THF), toluene) or CaH_2 (CH_2Cl_2) and were freshly distilled prior to use. All manipulations were preformed by using standard Schlenk techniques. IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the transmittance mode, NMR spectra were obtained on a Brucker WP 200 FT NMR spectrometer, and electron impact (EI) mass spectra were recorded on an AEI-MS9 mass spectrometer. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY. Photolyses were conducted in Pyrex Schlenk glassware with broad-band irradiation from a 450-W medium pressure Hg lamp (Hanovia). Low-temperature photolyses were done by irradiation through an unsilvered Pyrex Dewar, filled with ice or cooled propan-2-ol, in which the reaction flask was suspended.

Preparation of $[Cp(CO)_2W]_2(\mu\text{-}TolCC\{O\}CTol)$ (2). A cold (0 °C) pentane (20 mL) solution of $Cp(CO)_2W{\equiv}CTol$ (0.2 g, 0.5 mmol) was irradiated with Pyrex-filtered UV light under a constant purge of CO gas. After 2 h, the resultant orange precipitate was filtered off and washed with pentane (20 mL), followed by recrystallization from CH_2Cl_2/pentane to give **2** as a red crystalline solid (0.13 g, 63%). Additional product was obtained by concentrating the mother liquors and continuing the photolysis under CO. **2**: IR (CH_2Cl_2) ν(CO) 2020 (s), 1977 (m), 1935 (m), 1568 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (6 H, s, Me), 5.04 (10 H, s, Cp), 7.02 (4 H, d, J = 8 Hz, Tol), 7.57 (4 H, d, J = 8 Hz, Tol); ^{13}C NMR (C_6D_6) δ 21.0 (Me), 78.0 (*C*Tol, $J_{^{13}C-^{183}W}$ = 40 Hz), 91.2 (Cp), 128.3, 128.8, 128.9, 133.5 (Tol), 177.3 (TolC*C*{O}CTol), 215.5 (CO, $J_{^{13}C-^{183}W}$ = 149 Hz); MS, m/z 844 (M^+), 816 ($M^+ - CO$), 788 ($M^+ - 2CO$), 760 ($M^+ - 3CO$). Anal. Calcd: C, 44.07; H, 2.84. Found: C, 43.97; H, 2.95.

Preparation of $Cp(CO)(PPh_3)W(\eta^2\text{-}TolCCO)$ (5). A cold (0 °C) Et_2O (15 mL) solution of **1** (0.1 g, 0.25 mmol) and PPh_3 (0.2 g, 0.75 mmol) was irradiated with Pyrex-filtered UV light for 45 min. Removal of the mother liquors gave **5** as a purple crystalline solid (0.17 g, 60%). Additional product was obtained by concentration of the mother liquors and continued photolysis. This species was previously characterized in ref 11.

Preparation of $Cp(CO)_2(PPh_3)W(\eta^1\text{-}TolCCO)$ (6). A cold (−30 °C) CH_2Cl_2 (20 mL) solution of **5** (0.20 g, 0.30 mmol) was purged with carbon monoxide (1 atm) for 10 h. The resulting orange solution was reduced in volume in vacuo at −10 °C and treated with *n*-hexane (20 mL) to give complex **6** as a pale orange solid (0.18 g, 86%). Complex **6** slowly reacts under N_2 at room temperature to give **5** and CO, both in the solid state or in solution, and a satisfactory elemental analysis was not obtained. **6**: IR (CH_2Cl_2) ν(CCO) 2035 (s) cm^{-1}, ν(CO) 1946 (s), 1856 (s) cm^{-1}; ^{31}P NMR (acetone-d_6, −10 °C) δ 33.8 (J_{P-W} = 188 Hz); $^{13}C\{^1H\}$ NMR (acetone-d_6, −10 °C) δ 13.4 (*C*CO), 20.7 (CH_3), 93.0 (Cp), 128–134 (Tol), 158.2 (C*C*O), 224.8, 224.9, 225.2 (CO); ^1H NMR (acetone-d_6, −10 °C) δ 2.23 (s, CH_3), 5.20 (d, J_{H-P} = 2 Hz, Cp).

Thermal Reaction of 1 with dppe. A CH_2Cl_2 (15 mL) solution of $Cp(CO)_2W{\equiv}CTol$ (0.1 g, 0.25 mmol) and dppe (0.2 g, 0.5 mmol) was allowed to stand at 0 °C in the dark for 7 h. Spectroscopic analysis showed only the presence of $Cp(CO)(dppe)W(\eta^1\text{-}TolCCO)$ (**7**) along with a small amount of unreacted **1**. **7**: IR (CH_2Cl_2) ν(CCO) 2020 (vs) cm^{-1}, ν(CO) 1819 (m) cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 54.4 (J_{P-W} = 232 Hz), 51.1 (J_{P-W} = 296); ^1H NMR ($CDCl_3$) δ 7.44–7.10 (m, dppe), 6.63–6.36 (m, Tol), 5.13 (s, Cp), 2.43 (s, $CH_3C_6H_5$).

Photoinduced Reaction of 1 with dppe. A cold (0 °C) CH_2Cl_2 (15 mL) solution of $Cp(CO)_2W{\equiv}CTol$ (0.1 g, 0.25 mmol) and dppe (0.15 g, 0.38 mmol) was irradiated with Pyrex-filtered UV light for 45 min. Spectroscopic analysis showed only the presence of $Cp(CO)(dppe)W(\eta^1\text{-}TolCCO)$ (**7**) along with excess dppe and a small amount of unreacted **1**. This mixture in CH_2Cl_2 was chromatographed on Kieselgel 60 (Merck) at −35 °C. The initial yellow orange band of **7** rapidly turned red during elution with an acetone/CH_2Cl_2 mixture (1/10, v/v). Removal of solvent from the red band followed by recrystallization from CH_2Cl_2/pentane gave analytically pure $[Cp(CO)W(\eta^2\text{-}TolCCO)]_2(\mu\text{-}dppe)$ (**8**) as a purple-red solid mixture of two diastereomers (A/B, 1:2.3). **8**: MS (EI), m/z 1158 ($M^+ - 2CO$), 1102 ($M^+ - 4CO$); IR (CH_2Cl_2) ν(CCO) 1684 (m) cm^{-1}, ν(CO) 1889 (s) cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 33.9 (J_{P-W} = 416 Hz, A), δ 33.2 (J_{P-W} = 416 Hz, B); ^1H NMR ($CDCl_3$) δ 8.11–7.43 (m, Tol, A), 7.67–7.10 (m, Tol, B), 7.25–7.22 (m, dppe, A), 6.99–6.95 (m, dppe, B), 5.45 (s, Cp, B), 5.50 (s, Cp,

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(18) Fischer, E. O.; Lindner, F. R. K.; Kreissl, F. R. *J. Organomet. Chem.* 1976, *112*, C27.

A), 2.34 (s, $CH_3C_6H_4$, B), 2.45 (s, $CH_3C_6H_4$, A); ^{13}C NMR ($CDCl_3$) δ 223.2 (WCO, B), 222.2 (WCO, A), 205.3 (*C*CO, A + B), 198.2 (*C*CO, A), 198.0 (*C*CO, B), 138.8–137.0 (Tol, A + B), 133.2–126.9 (dppe, A + B), 94.4 (Cp, B), 94.2 (Cp, A), 21.8 (Tol, A), 21.5 (Tol, B), 29.5 (t, J_{P-C} = 16 Hz, dppe, B), 27.9 (t, J_{P-C} = 16 Hz, dppe, A). Anal. Calcd: C, 55.37; H, 3.98. Found: C, 55.85; H, 4.01.

Conversion of 8 into 7. A CH_2Cl_2 solution of 8 (60 mg, 0.049 mmol) was treated with dppe (20 mg, 0.05 mmol) at room temperature to give an immediate color change from purple-red to orange-red. An IR spectrum showed that the mixture contained a 1:1 mixture of 7 and 8. Continued stirring at room temperature for 1 h showed no further changes in the IR spectrum so additional dppe (80 mg, 0.20 mmol) was added. An IR spectrum of the now orange solution showed only carbonyl bands attributable to 7.

Crystallographic Characterization of $[Cp(CO)_2W]_2(\mu\text{-}TolCC\{O\}CTol)$ (2). Table I provides the crystal parameters and details of the data collection and refinement processes. The data crystal was cleaved from a larger specimen grown from CH_2Cl_2/pentane. The unit-cell parameters were obtained from the angular settings of 25 reflections (26° $\leq 2\theta \leq$ 31°) which included Friedel-related sets to inspect optical and diffractometer alignment. The centosymmetric triclinic space group $P\bar{1}$ was indicated correct by the successful and computationally stable refinement of the structure. Delauney reduction indicated that no higher symmetry existed. Owing to the platelike crystal shape and evidence for large edge-effect intensity deviations, the empirical correction for absorption ignored those reflections making a glancing angle of $\leq$3° to the major face (001). Of the 216 ψ-scan reflections used, 12 were ignored, and 368 data were similarly discarded from the full data set. For the remaining 204 ψ-scan reflections R(int) was reduced from 10.7% to 1.6% with T(max)/T(min) = 0.68/0.36.

The W atoms were located by an autointerpreted Patterson synthesis. Subsequent difference Fourier synthesis provided the remaining non-hydrogen atoms. Hydrogen atoms were idealized (d(C–H) = 0.96 Å) and updated. All non-hydrogen atoms were refined anisotropically.

All software routines are contained in the SHELXTL (5.1) program library (Nicolet Corp., Madison, WI). Tables of complete bond lengths and angles, anisotropic thermal parameters, calculated hydrogen atom positions, and structure factors for 2 were provided as supplementary material to ref 9.

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Registry No. 1, 60260-15-3; 2, 95029-84-8; 5, 102615-19-0; 6, 102615-20-3; 7, 111189-61-8; 8 (isomer 1), 111265-70-4; 8 (isomer 2), 111189-59-4; *trans*-$Cl(CO)_4W{\equiv}CTol$, 68480-95-5; *trans*-$Cl(CO)_2(TMEDA)W{\equiv}CTol$, 111189-60-7.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom positions for 2 (5 pages); a listing of structure factors for 2 (22 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Fluxional Properties of the Novel Tetranuclear Osmium Clusters $Os_4(CO)_n(PMe_3)$ (n = 15, 14, 13)[1]

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Addition of $Os(CO)_4(PMe_3)$ to $Os_3(CO)_{11}(CH_3CN)$ or to $Os_3(\mu\text{-}H)_2(CO)_{10}$ affords $Os_4(CO)_{15}(PMe_3)$ (1) as the major product. Treatment of 1 in CH_2Cl_2 with Me_3NO gives $Os_4(CO)_{14}(PMe_3)$ (2) which in turn can be converted to $Os_4(CO)_{13}(PMe_3)$ (3) by heating in hexane at 90 °C under vacuum or by UV irradiation in hexane. The structures of 1, 2, and 3 have been determined by X-ray crystallography: Compound 1 crystallizes in the space group $P\bar{1}$, with a = 12.473 (2) Å, b = 13.325 (2) Å, c = 17.547 (2) Å, α = 109.05 (1)°, β = 90.44 (1)°, γ = 94.60 (1)°, and Z = 4; R = 0.037 and R_w = 0.041 for 5172 observed reflections. Compound 2 crystallizes in the space group $P2_1/a$, with a = 13.525 (5) Å, b = 12.969 (6) Å, c = 14.825 (5) Å, β = 99.14 (3)°, and Z = 4; R = 0.039 and R_w = 0.048 for 2424 observed reflections. Compound 3 crystallizes in the space group $P2_1/c$, with a = 15.470 (2) Å, b = 10.193 (1) Å, c = 16.527 (2) Å, β = 113.45 (1)°, and Z = 4; R = 0.047 and R_w = 0.060 for 2060 observed reflections. In 1, the $Os(CO)_4(PMe_3)$ acts as a ligand to an $Os_3(CO)_{11}$ fragment via an unbridged dative Os–Os bond of lengths 2.939 (1) and 2.937 (1) Å for the two independent molecules in the unit cell. The Os–Os bond lengths within the Os_3 triangle are 2.849 (1) and 2.855 (1) Å (trans to the Os–Os dative bond), 2.923 (1) and 2.930 (1) Å (cis to the Os–Os dative bond), and 2.894 (1) and 2.894 (1) Å. In CD_2Cl_2/CH_2Cl_2, 1 is rigid at −67 °C by ^{13}C NMR spectroscopy. However, at ambient temperature all the carbonyl ligands of 1 undergo exchange. Cluster 2 has a planar Os_4 skeleton with two adjacent short Os–Os bonds (of lengths 2.779 (2) and 2.784 (2) Å) and two long Os–Os bonds (of lengths 2.982 (2) and 3.013 (2) Å); the diagonal Os–Os bond is normal at 2.935 (2) Å. The unusual structure of 2 is rationalized in terms of three-center–two-electron metal–metal bonds to give Os–Os bonds of orders 1.5 and 0.5 and achieves an 18-electron configuration for each osmium atom. The cluster is also fluxional in solution, even at −89 °C. A novel mechanism that involves cleavage of the weakest Os–Os bond is proposed to account for the nonrigidity. Cluster 3 has a tetrahedral framework with an $Os(CO)_4$, an $Os(CO)_3(PMe_3)$, and two $Os(CO)_3$ units; the Os–Os bond lengths range from 2.765 (1) to 2.869 (1) Å. Weak semibridging interactions are present for four of the carbonyl ligands. The cluster is highly fluxional, exhibiting a singlet for the carbonyl ligands in the ^{13}C NMR spectrum even at −120 °C in $CHFCl_2/CD_2Cl_2$. This is believed to be the first report of a 64-electron cluster that has been successively converted to a 62- and then to a 60-electron cluster.

One of the challenges of modern inorganic chemistry is the rational synthesis of transition-metal cluster compounds.[2,3] Several strategies have been adopted for this purpose. These include the reaction of a transition-metal