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Supplementary Material Available: Tables of the refined anisotropic thermal parameters for all non-hydrogen atoms at 298 K and 120 K and the calculated H-atom fractional coordinates for β-$(ET)_2AuCl_2$ at 298 and 120 K (3 pages); listing of observed and calculated structure factors for β-$(ET)_2AuCl_2$ at 298 K and 120 K (28 pages). Ordering information is given on any current masthead page.

Tungsten and Molybdenum 2-Oxaallyl (η^1-(C)-Enolate) Complexes: Functional Group Transformations, Photochemical Aldol Reactions, and Alkyne/CO Migratory Insertion Reactions

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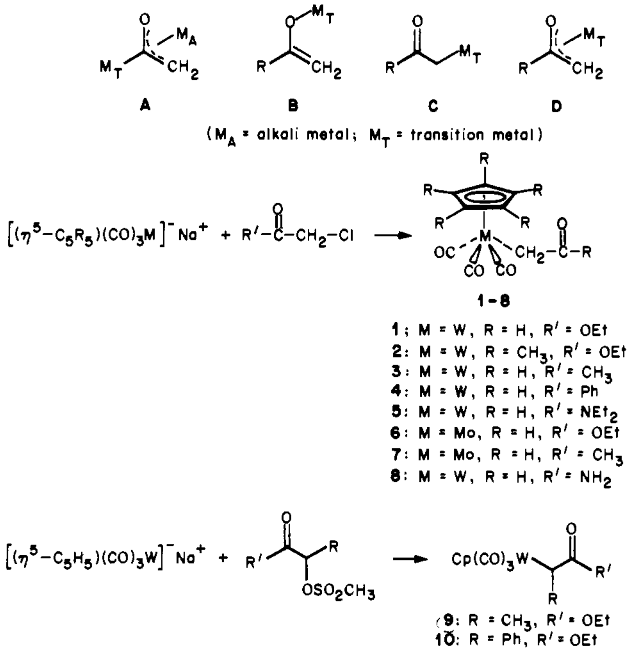
Abstract: Carbon bound tungsten and molybdenum 2-oxaalkyl (η^1-enolate) complexes **1–8** can be prepared easily by reaction of $C_5R_5(CO)_3M^- Na^+$ (R = H, CH_3; M = W, Mo) with α-chloro esters, ketones, and amides. Secondary tungsten enolates **9** and **10** were sucessfully prepared by using α-methanesulfonoxy esters. Organic carbonyl functional group transformations were carried out on $Cp(CO)_3W(CH_2CO_2Et)$ without M–C bond cleavage, leading to several new enolates including the novel organometallic acid chloride $Cp(CO)_3WCH_2COCl$ (**13**). Loss of CO from carbon bound enolates generated η^3-oxaallyl complexes **15–21**. These are stable in solution, but only one, $Cp(CO)_2WCH_2CONEt_2$ (**18**), can be isolated. The tungsten η^3-oxaallyl complexes undergo reaction with CO to regenerate the parent complexes and substitution reactions with various ligands (PPh_3, CH_3CN, C_5H_5N, $Ph_2PCH_2PPh_2$, and PhC≡CH) to give new isolable substituted η^1-enolate complexes. The primary tungsten enolates undergo photochemical aldol condensation with aldehydes to give aldolates **31**, **33**, **34**, and **36** and give combined CO/alkyne insertion products **44** and **46** with alkynes. Evidence is presented supporting the intermediacy of the η^3-oxaallyl complexes in the ligand substitution, aldol, and alkyne insertion reactions. In addition, crystal structures of the following complexes have been obtained: η^1-enolate $Cp(CO)_3WCH_2CO_2Et$ (**1**), η^3-oxaallyl $Cp(CO)_2WCH_2CONEt$ (**18**), bisalkyne complex $Cp(PhC{\equiv}CH)_2WCH_2CO_2Et$ (**49**), oxo/alkyne complex $Cp(PhC{\equiv}CH)(O)WCH_2CO_2Et$ (**50**), and CO/alkyne insertion product **44**.

The exploitation of highly ordered transition states in organic reactions to obtain predictable reactivity is an important goal of organic chemistry. The specific relative orientation of organic ligands located in the coordination sites of transition-metal centers provides a method for generating such ordered transition states, and this technique has been used increasingly in recent years to control stereochemistry in organic reactions.[1]

Partly because of the utility of the aldol reaction in constructing hydroxylated carbon chains, extensive studies have been carried out aimed at developing methods for executing this transformation with a high degree of stereoselectivity.[1] The techniques employed normally utilize a chiral group attached to the enolate reactant; transfer of chirality from the enolate to the newly formed stereocenter can then be achieved in some cases with very high degrees of selectivity. Many types of chiral enolates have been utilized, including those with organic chiral auxiliaries attached to the carbonyl group of the enolate,[2] as well as those with optically active ligands bound to main group metals coordinated to the enolate oxygen atoms.[3]

One group of enolates whose propensity to engage in aldol reaction shas been little examined is the group of so-called "late" transition-metal enolates (i.e., those utilizing transition metals lying to the right of group V (Group 5, see ref 73) in the periodic table) in which the metal is bound to the potentially reactive carbon atom (type C in Scheme I). None of the complexes in this class have been shown to engage in aldol chemistry. In this paper we describe

Scheme I



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(1) Heathcock, C. H. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 3.

(2) (a) Heathcock, C. H. *Asymmetric Reactions and Processes in Chemistry*; Eliel, E. L., Otsuka, S., Eds.; American Chemical Society: Washington, DC, 1982. (b) Evans, D. A. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 3.

(3) Iwasawa, N.; Mukaiyams, T. *Chem. Lett.* **1982**, 1441.

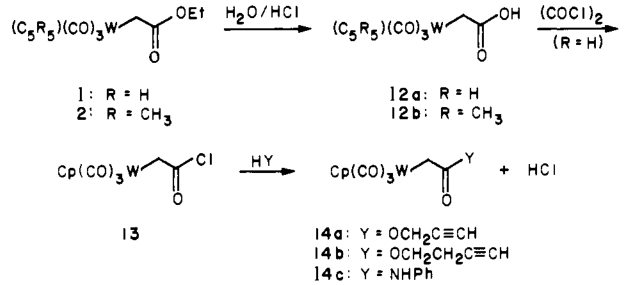
0002-7863/87/1509-2022$01.50/0

the synthesis and characterization (in several cases, by X-ray diffraction) of several group VI (6)[73] carbon bound organotransition-metal enolates. Exploration of their chemistry has revealed some novel reactions, including aldol condensation via unique oxaallyl complex intermediates. Some of the results reported in this paper have been communicated in preliminary form.[4]

Results and Discussion

Synthesis. Several different types of organotransition-metal enolates have been described (cf. Scheme I); reactions of some of these have led to important contributions to organic synthesis. Enolates of type A have been generated in situ by deprotonation of metal-acyl complexes of cobalt[5] and iron.[6] Enolates of type B have been generated by reactions involving complexes of zirconium,[7] titanium,[8] platinum,[9] palladium,[10] molybdenum,[11] thorium,[12] and uranium.[12] Enolates of type C have been synthesized or invoked as reaction intermediates for molybdenum,[13] manganese,[14] cobalt,[15] iron,[13] tungsten,[13,16] rhenium,[17] nickel,[18] palladium,[10,19] platinum,[20] rhodium,[21,22] copper,[23] zinc,[24] and mercury.[25]

Scheme II



With few exceptions,[7,13,16] compounds in this class were obtained via indirect methods (3–4 steps), and/or obtained in poor yields (5–30%), and/or found to be both air sensitive and thermally unstable. In analogous alkyl organometallic compounds, carbon–metal bond strength usually increases as one descends a column in the periodic chart.[26] We thus set out to obtain type C enolates of greater stability by using tungsten and molybdenum.

The well-known nucleophilic anionic metal salts (η^5-C_5R_5)-$(CO)_3MNa$[27] (M = Mo, W) normally can be readily alkylated by using alkyl iodides and bromides R–X, leading to complexes of general structure $(C_5R_5)(CO)_3M$–R. In contrast, treatment of these anions with α-bromo ketones or α-bromo esters led only to metal–halogen exchange, resulting in metal bromide $(C_5R_5)(CO)_3M$–X and, presumably, the free enolate.[28] Fortunately, chlorocarbonyl compounds were better behaved. Thus, on treatment of the preformed anions with $ClCH_2COR$ (R = CH_3, Ph, OCH_2CH_3, $N(CH_2CH_3)_2$ (method A)) we obtained the desired products **1–8** (Scheme I). These materials were isolated in 50–80% yields and were fully characterized by spectroscopic and elemental analysis techniques. These conditions had previously been used by R. B. King and co-workers[13a] in the preparation of the molybdenum–carbon bound ester enolate **7** and by M. L. H. Green and co-workers[13c] in the preparation of **8**. The tungsten and molybdenum enolates are conveniently prepared on a larger scale by treating $W(CO)_6$ or $Mo(CO)_6$ with NaCp and then adding the α-chlorocarbonyl compound to the generated metal anion in a one-pot procedure (method B).

The use of chlorides in the above alkylations was successful only for primary halides. Addition of the metal anions to secondary α-chloro esters once again gave only metal–halogen exchange. However, treatment of $Cp(CO)_3WNa$ with α-methanesulfonoxy esters (obtained by treatment of α-hydroxycarbonyl compounds with methanesulfonyl chloride) led smoothly to the desired secondary tungsten enolates **9** and **10**. The α-methyl-substituted tungsten enolate was obtained after refluxing 7 h in THF, while the α-phenyl-substituted compound **10** was obtained after stirring 16 h at room temperature. Tungsten enolates **1–10** are light sensitive, air stable crystalline compounds, while the molybdenum enolates are slightly more sensitive.

Several other potential approaches to the tungsten and molybdenum enolates described above were screened but were largely unsuccessful. For example, direct reaction of lithium enolates with $Cp(CO)_3WCl$ did not lead to W–C bond formation. Another route based on reaction of $Cp(CO)_3W$–F with enol silanes was abandoned because we were unable to generate the tungsten fluoride by reaction of the $Cp(CO)_3WCl$ with tris(dimethylamino)sulfonium dimethyltrifluorosiliconate (TASF);[29] attempted

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(4) Doney, J. J.; Bergman, R. G.; Heathcock, C. *J. Am. Chem. Soc.* **1985**, *107*, 3724.

(5) Theopold, K. H.; Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 5250.

(6) (a) Liebeskind, L. S.; Walker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441. (b) Davies, S. G.; Dordor, I. M.; Walker, J. C.; Warner, P. *Tetrahedron Lett.* **1984**, *25*, 2709.

(7) (a) Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, 3975. (b) Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1980**, 4607.

(8) (a) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503. (b) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 1664. (c) Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855.

(9) Dall'Antonia, P.; Graziani, M.; Lenarda, M. *J. Organomet. Chem.* **1980**, *186*, 131.

(10) Ito, Y.; Nakatsuka, M.; Kise, N. Saegusa, T. *Tetrahedron Lett.* **1980**, *21*, 2873.

(11) Hirao, T.; Fujihara, Y.; Tsuno, S.; Ohshiro, Y.; Agawa, T. *Chem. Lett.* **1984**, 367.

(12) (a) Manriquez, J.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 7112. (b) Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 3484.

(13) (a) King, R. B.; Bisnette, M. B.; Fronzaylia, A. *J. Organomet. Chem.* **1966**, *5*, 341. (b) Ishaq, M. *J. Organomet. Chem.* **1968**, *12*, 414. (c) Ariyaratne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swainwick, M. G. *J. Chem. Soc. A* **1969**, 1309. (d) Crawford, E. J.; Lambert, C.; Menard, K. P.; Cutler, A. R. *J. Am. Chem. Soc.* **1985**, *107*, 3130. (e) Hillis, J.; Ishag, M.; Gorewit, B.; Tsutsui, M. *J. Organomet. Chem.* **1976**, *116*, 91. (f) Mitsudo, T.; Watanabe, Y.; Sasaki, T.; Nakanishi, H.; Yamashita, M.; Takegami, Y. *Tetrahedron Lett.* **1975**, *36*, 3163. (g) Akaita, M.; Kondon, A.; Yoshihiko, M. *J. Chem. Soc., Chem. Commun.* **1986**, *16*, 1296.

(14) Engelbrecht, J.; Greiser, T.; Weiss, E. *J. Organomet. Chem.* **1981**, *204*, 79.

(15) (a) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1962**, *84*, 2499. (b) Galamb, V.; Palyi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1981**, *209*, 183.

(16) Sieber, W. J.; Wolfgruber, M.; Kreissl, F. R.; Orama, O. *J. Organomet. Chem.* **1984**, *270*, C41.

(17) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157.

(18) Hirao, T.; Nagata, S.; Yamana, Y.; Agawa, T. *Tetrahedron Lett.* **1985**, *26* (*41*), 5061.

(19) (a) Bertani, R.; Castellani, C. B.; Crociani, B. *J. Organomet. Chem.* **1984**, *269*, C15. (b) Yanase, N.; Nakakamura, Y.; Kawaguchi, S. *Chem. Lett.* **1979**, 591. Yanase, N.; Nakamura, Y.; Kawaguchi, S. *Inorg. Chem.* **1980**, *19*, 1575. (c) Hirao, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *Chem. Lett.* **1982**, 1997. (d) Wanat, R. A.; Collum, D. B. *Organometallics* **1986**, *5*, 120.

(20) (a) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3030. (b) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans. 1* **1976**, 993. (c) Nizova, G. V.; Serdobov, M. V.; Nikitaev, A. T.; Shul'pin, G. B. *J. Organomet. Chem.* **1984**, *275*, 139.

(21) Tulip, Dr. T. DuPont, personal communication.

(22) (a) Milstein, D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3773. (b) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221.

(23) Posner, G. H.; Lentz, C. M. *J. Am. Chem. Soc.* **1979**, *101*, 934.

(24) Shirner, R. L. *Org. React.* **1942**, *1*, 1.

(25) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1982**, 2323. House, H. O. *J. Org. Chem.* **1973**, *38*, 514.

(26) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; Chapter 2.

(27) (a) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263. (b) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. (c) Patil, H. R. H.; Graham, W. A. G. *Inorg. Chem.* **1966**, *5*, 1401. (d) Hayter, R. G. *Inorg. Chem.* **1963**, *5*, 1031.

(28) We observe only ethyl acetate or ketone in these reactions; the source of the new hydrogen in these molecules has not been determined.

(29) (a) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598. (b) Middleton, W. J. U.S. Patent 3940402, 1976.

Table I. Selected Intramolecular Distances for **1**[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
W1	C1	2.359 (4)	C26	C27	1.481 (6)
W1	C2	2.319 (4)	C27	O9	1.193 (5)
W1	C3	2.295 (4)	C27	O10	1.349 (5)
W1	C4	2.294 (4)	O10	C28	1.467 (5)
W1	C5	2.363 (4)	C28	C29	1.482 (7)
W1	CP1[b]	1.998			
			C11	O1	1.134 (5)
W1	C6	2.321 (4)	C12	O2	1.123 (5)
W1	C11	1.978 (5)	C13	O3	1.148 (5)
W1	C12	1.991 (4)	C16	O6	1.122 (5)
W1	C13	1.972 (5)	C17	O7	1.148 (5)
			C18	O8	1.146 (5)
W2	C21	2.305 (4)			
W2	C22	2.298 (4)	C1	C2	1.372 (7)
W2	C23	2.331 (5)	C2	C3	1.402 (7)
W2	C24	2.357 (4)	C3	C4	1.417 (7)
W2	C25	2.349 (4)	C4	C5	1.372 (7)
W2	CP2[b]	2.006	C5	C1	1.436 (7)
W2	C26	2.315 (4)	C21	C22	1.419 (8)
W2	C16	2.016 (5)	C22	C23	1.393 (7)
W2	C17	1.996 (5)	C23	C24	1.374 (7)
W2	C18	1.982 (5)	C24	C25	1.392 (7)
			C25	C21	1.367 (7)
C6	C7	1.441 (6)			
C7	O4	1.206 (5)			
C7	O5	1.350 (5)			
O5	C8	1.463 (5)			
C8	C9	1.459 (8)			

[a] esd's are in parentheses. [b] CP is the centroid of the cyclopentadiene ring.

generation of a TAS enolate and addition to $Cp(CO)_3WCl$ resulted in an unidentified black precipitate. Finally, treatment of $[Cp(CO)_3W^+BF_4^-]$[30] with several alkali metal enolates under various conditions gave only complicated mixtures. Heating the trimethylsilyl enol ether of acetophenone and $Cp(CO)_3W^+BF_4^-$ led to no reaction.

Reactions at the Tungsten Enolate Carbonyl Group. The stability of the tungsten–carbon bond in tungsten ester enolates, first suggested several years ago by the work of Green and his group,[13c] has allowed us to purify and handle these materials very conveniently and carry out a wide range of organic transformations on the organic carbonyl group. For example, treatment of tungsten ester **1** or amide **8** with aqueous HCl gave the tungsten-substituted acetic acid derivative $Cp(CO)_3W–CH_2CO_2H$ (**12a**). The analogous pentamethyl derivative $Cp^*(CO)_3WCH_2CO_2H$ (**12b**) was also prepared in this manner. In many cases the enolates may be purified by chromatography on silica gel in air; in solution, however, they decompose over several hours to days. The ester and ketone enolates decompose most rapidly, whereas the carboxylic acid can be recrystallized in air with little or no observed decomposition. Recrystallizations performed under N_2 in the absence of light show no decomposition.

In view of the stability of these transition-metal enolates, we wished to determine whether the W–C bond would survive standard transformations directed at the carbonyl group. Treatment of the tungsten-substituted carboxylic acid **12a** with oxallyl chloride in benzene successfully delivered the acid chloride $Cp(CO)_3W–CH_2COCl$ (**14**). An iron-substituted acetyl chloride was prepared recently but has not been fully characterized.[13g] Acid chloride **14** is isolable (71% yield) and has been fully characterized by spectroscopic and analytical techniques. It exhibits terminal M–CO stretching absorptions in the solution infrared at 2030 and 1950 cm⁻¹ and an acid chloride carbonyl stretch at 1775 cm⁻¹. Its ^1H and ^{13}C NMR spectra are consistent with the proposed structure (see Experimental Section). The presence of a W–C linkage is confirmed by the $^{183}W–^1H$ coupling observed at the methylene group. Treatment of the acid chloride **14** with alcohols and primary and secondary amines leads to the corresponding tungsten esters and amides in good yield (Scheme II).

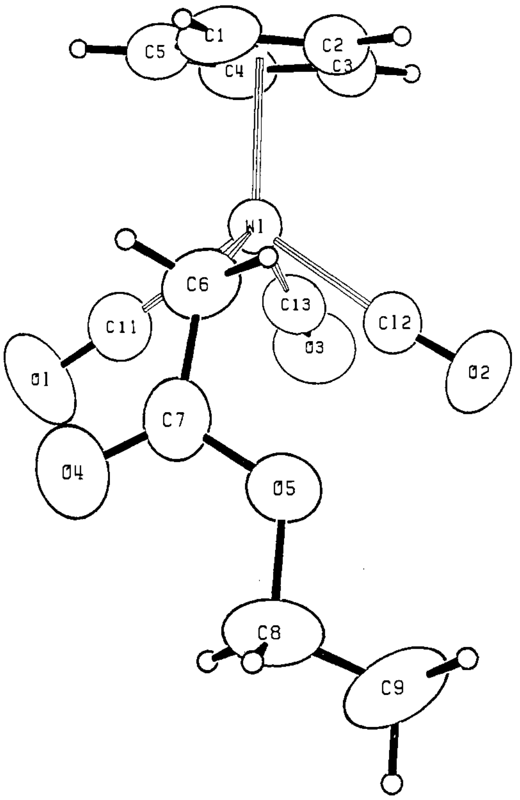
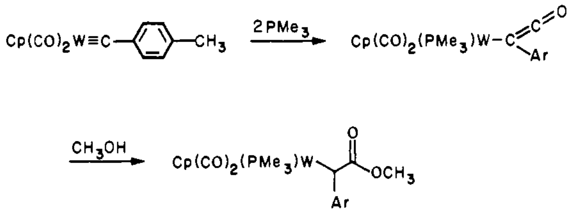


Figure 1. ORTEP diagram of tungsten enolate **1** with 50% probability thermal ellipsoids. The diagram shows the numbering scheme used in the tables.

Scheme III



Structure Elucidation. Several lines of spectroscopic evidence (Table III) support the carbon–metal bound enolate structure for complexes **1–10**. For example, examination of the ^{183}W satellite peaks (natural abundance = 14%) in the ^1H NMR spectrum reveals that the W–C–H coupling constants range from 5.3 Hz in the tungsten ester to 6.7 Hz in the tungsten ketone. These are consistent with literature values for analogous tungsten–alkyl complexes.[31] The ^{13}C NMR shifts for the metal-bound carbon atoms (occurring from 10 to −17 ppm) characteristically appeared 20–35 ppm upfield from the shifts for the free ketone, ester, or amide. The organic carbonyl stretching absorptions in the enolates are shifted to slightly lower frequency (compared to organic carbonyls) and ranged from 1673–1700 cm⁻¹ for the ester ligands, through 1643–1668 cm⁻¹ for the ketones, to 1586–1665 cm⁻¹ for the carboxamides.

Crystals of complex **1** were obtained by slow evaporation of an ether solution of the material at −40 °C. The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. Details of the structure determination, including positional parameters and structure factors, were deposited in the Cambridge data files following publication of the communication describing the preliminary results of this work.[4] The unit cell was found to be triclinic, and selected bond lengths and angles are given in Tables I and II of this paper. An ORTEP drawing of the structure of **1** is shown in Figure 1. The complex

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(30) Beck, W.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214.

(31) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570.

Table II. Selected Intramolecular Angles for 1[a]

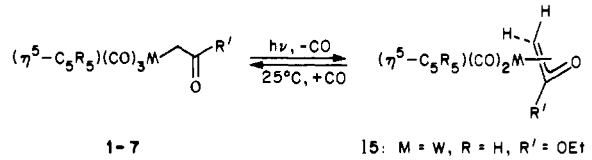
atom 1	atom 2	atom 3	angle
CP1	W1	C6	109.51
CP1	W1	C11	125.76
CP1	W1	C12	123.56
CP1	W1	C13	114.44
C6	W1	C11	77.24 (16)
C6	W1	C12	77.71 (17)
C6	W1	C13	136.05 (16)
C11	W1	C12	110.58 (17)
C11	W1	C13	78.24 (18)
C12	W1	C13	77.59 (19)
W1	C6	C7	118.3 (3)
C6	C7	O4	125.9 (4)
C6	C7	O5	113.0 (4)
O4	C7	O5	121.1 (4)
C7	O5	C8	118.1 (4)
O5	C8	C9	107.9 (5)
W1	C11	O1	177.2 (4)
W1	C12	O2	175.2 (4)
W1	C13	O3	179.4 (4)
C5	C1	C2	108.2 (4)
C1	C2	C3	109.0 (4)
C2	C3	C4	106.5 (4)
C3	C4	C5	109.6 (4)
C4	C5	C1	106.7 (4)
C25	C21	C22	109.1 (4)
C21	C22	C23	106.1 (5)
C22	C23	C24	108.5 (5)
C23	C24	C25	109.0 (4)
C24	C25	C21	107.3 (4)
CP2	W2	C26	110.65
CP2	W2	C17	127.00
CP2	W2	C18	125.40
CP2	W2	C16	117.47
D26	W2	C17	79.18 (15)
C26	W2	C18	73.38 (16)
C26	W2	C16	131.75 (16)
C17	W2	C18	107.50 (18)
C17	W2	C16	75.20 (17)
C18	W2	C16	76.36 (19)
W2	C26	C27	113.8 (3)
C26	C27	O9	126.6 (4)
C26	C27	O10	110.8 (3)
O9	C27	O10	122.6 (4)
C27	O10	C28	116.1 (3)
O10	C28	C29	107.3 (4)
W2	C17	O7	176.5 (4)
W2	C18	O8	177.6 (4)
W2	C16	O6	178.0 (4)

[a] esd's are in parentheses.

exhibits the expected four-legged piano stool geomery; the carbonyl oxygen is not coordinated to the metal center. An X-ray structure of a methyl ester similar to compound **10** has been obtained recently by Kreissl et al.[16] and was prepared by the unusual route outlined in Scheme III.

At this point, a brief discussion of the term "enolate" as applied to compounds such as **1** is in order, particularly in view of the extreme resistance of the carbon-metal bond in **1** to protonolysis (vida supra). In this regard, the term is used as a generic one, implying simply that there is an association of the metal with the oxaallyl unit. However, the physical properties of **1** and related compounds do reveal that the carbon-metal bonding electrons interact extensively with the carbonyl π-orbital. For example, the ester C═O stretching absorptions in ester **1**, ketone **3**, and amide **5** occur at 1691, 1668, and 1605 cm^{-1}, respectively. Each of these absorptions is shifted about 40 cm^{-1} toward lower energy, relative to the normal carbonyl counterparts.[32] Confirmation of this interaction is seen in the crystal structure of **1**. First, the orientation of the carbon–tungsten bond is optimum for overlap of the C–W bonding electrons with the C═O π-orbital. Second, although the C═O bond length of 1.206 Å is in the range normally observed for an ester carbonyl group (ca. 1.21 Å), that for the (C═O)—C bond (1.441 Å) is significantly shorter than the normal ester value of 1.48–1.51 Å.[33]

Scheme IV



1-7

15: M = W, R = H, R' = OEt
16: M = W, R = H, R' = CH_3
17: M = W, R = H, R' = Ph
18: M = W, R = H, R' = NEt_2
19: M = Mo, R = H, R' = OEt
20: M = Mo, R = H, R' = CH_3
21: M = W, R = CH_3, R' = OEt

Additional X-ray structures have been reported for enolates of type C having molybdenum,[13c] iron,[13c] cobalt,[15b] manganese,[14] platinum,[20a] and iridium[22] centers.

Conversion of Enolates to Oxaallyl Complexes. Ultraviolet irradiation (200-W Hanovia lamp, 6–25 °C) of several of the tungsten enolates described above results in the loss of 1 equiv of CO (measured quantitatively by Toepler pumping). Spectroscopic monitoring of this reaction (sealed NMR tube) demonstrates that the irradiation generates a new class of complexes with properties substantially different from those of the starting materials. These data (see Scheme IV and the discussion below) are consistent with the formation of η^3-oxaallyl complexes **15–21**. Variable amounts of W–C bond cleavage occur in a parallel reaction (e.g., to give ethyl acetate and $[Cp(CO)_3W]_2$ (**11**)) in the case of **1**. However, photolysis at low temperature and use of an uranium glass filter (transparent at $\lambda > 360$ nm) decreased the amount of this side reaction to ≤5%. Low temperatures also improve the extent of conversion. For example, irradiation of a solution of **1** at −30 °C quantitatively gives **15**, whereas irradiation for the same period of time at 6 °C gives incomplete conversion (65–70%).

In order to generate solutions of **15** in large quantities, an Ace photochemical reactor was used. By purging the reaction solution with nitrogen gas to liberate CO from the reaction vessel, high conversion of **1** to **15** was accomplished in diethyl ether, benzene, and toluene. Alternatively, treatment of **1** with trimethylamine-*N*-oxide (Me_3NO) cleanly removed one CO ligand and generated **15** without the use of light.[34]

Attempts to isolate **15** by lyophylization of C_6D_6 or **21** by crystallization from toluene/pentane at −40 °C resulted in decomposition to ethyl acetate and $[Cp(CO)_3W]_2$. However, R_2N-substituted oxaallyl complex **18** (best prepared by reaction of tungsten amide **5** with Me_3NO in acetonitrile) has been isolated as a crystalline solid. This compound was characterized spectroscopically and by elemental analysis. In addition, crystals of **18** suitable for X-ray analysis were obtained from toluene/hexane at −40 °C (see below).

In contrast to the many π-allyl complexes known, complexes containing the η^3-oxaallyl ligand are rare. Tulip[21] has isolated and obtained a single-crystal X-ray structure of $(Et_3P)Rh(\eta^3\text{-}CH_2C(O)Ph)$; however, the chemistry of this compound has not been investigated in detail. Three X-ray studies of complexes with chelating ligands containing the η^3-oxaallyl part structure have

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[32] Nakanishi, K.; Solomon, P. H. *Infrared Absorption Spectroscopy*, 2nd ed.; Holden-Day: San Francisco, 1977.

[33] See, inter alia: Mathieson, A. M.; Welsh, H. *Acta Crystallogr.* **1965**, *18*, 953. Vloon, W. J.; Hottentot, D.; Overbeek, A. R.; Stam, C. H. *Acta Crystallogr.* **1979**, *35*, 119. Huisgen, T.; Ott, H. *Tetrahedron* **1959**, *6*, 253.

[34] Trimethylamine oxide removes metal bound carbonyl ligands which exhibit IR stretching frequencies greater than 2000 cm^{-1}. (a) Luh, T.-Y. *Coord. Chem. Rev.* **1984**, *60*, 255. (b) Albers, M. O.; Coville, N. J. *Ibid.* **1984**, *53*, 227. (c) Blumer, D. S.; Barnett, K. W.; Brown, T. L. *J. Organomet. Chem.* **1979**, *173*, 71. Luh, T.-Y.; Wong, G. S. *J. Organomet. Chem.* **1985**, *287*, 231.

Table III. Spectroscopic Data on Organotransition Metal Enolates $(\eta^5\text{-}C_5R_5)(CO)_2(L)M\text{–}CH(R'')LCOR'$

compd	M	R	L	R″	R′	^{1}H NMR (α-proton resonance) (J_{JW}) (Hz)	^{13}C NMR (α-carbon resonance) (C_6D_6)	IR (organic carbonyl) (solvent)
1	W	H	CO	H	Et	2.09 (5.3)	−14.82	1691 (THF)
2	W	Me	CO	H	OEt	1.61 (6.9)	−5.50	1696 (C_6D_6)
3	W	H	CO	H	Me	2.22 (6.7)	−1.02	1668 (THF)
4	W	H	CO	H	Ph	2.83 (6.3)	−7.64	1643 (Et_2O)
5	W	H	CO	H	NEt_2	2.06 (4.7)	−16.71	1605 (toluene)
6	Mo	H	CO	H	OEt	1.84	−3.94	1687 (THF)
7	Mo	H	CO	H	CH_3	1.98	8.54	1658 (THF)
8[g]	W	H	CO	H	NH_2	1.83[a]	−11.21[d]	1649 (CH_2Cl_2)
9	W	H	CO	Me	OEt	3.06 (5.5)	−0.75	1700 (Et_2O)
10	W	H	CO	Ph	OEt	4.26 (6.5)	10.43	1698 (Et_2O)
12a	W	H	CO	H	OH	2.04 (5.4)		1649 (KBr)
12b	W	CH_3	CO	H	OH	1.57[a]	−5.66[f]	1699 (THF)
13	W	H	CO	H	Cl	2.29 (5.8)	−2.43[e]	1775 (C_6D_6)
14a	W	H	CO	H	$OCH_2C{\equiv}CH$	2.04 (5.4)	−15.68[f]	1617 (C_6D_6)
14b	W	H	CO	H	$OCH_2CH_2C{\equiv}CH$	2.02 (5.4)	15.32	1694 (C_6D_6)
14c	W	H	CO	H	N(H)Ph	2.14 (4.7)[b]	−9.67[b]	1665 (THF)
22a	W	H	PMe_3	H	NEt_2	1.50,[a] 1.60 (J_{PH} = 8) for both	−10.21 (J_{PC} = 13.0)[f]	1593 (KBr), 1586 (CH_2Cl_2)
22b	W	H	PMe_3	H	NEt_2	2.39[a] (J_{PH} = 4.9)	−15.00 (J_{PC} = 8.2)[f]	1593 (KBr), 1586 (CH_2Cl_2)
23	W	H	PPh_3	H	NEt_2	2.53[a] (J_{PH} = 4.0)	−13.96 (J_{PC} = 7.6)[f]	1598 (KBr), 1586 (CH_2Cl_2)
24	W	H	PPh_3	H	OEt	1.94,[a] 1.59 (J_{PH} = 9.5) for both	−5.84 (J_{PC} = 12.5)	1678 (THF)
25	W	H	PPh_3	H	OEt	2.56[a] (J_{PH} = 3.5)	−12.54 (J_{PC} = 10)	1680 (THF)
26	W	H	CD_3CN	H	OEt	1.72 (6.4), 1.83 (7.4)[c]	−1.72[c]	1675 (CD_3CN)
27	W	H	C_5H_5N	H	OEt	1.96 (9.5), 2.14 (7.0)	7.54	1673 (KBr)
29	W	H	DPPM	H	OEt	2.04,[a] 1.77 (8.0) (J_{PH} = 8.5)	6.35 (J_{PC} = 12)	1690 (Et_2O)
30	W	H	DPPM	H	OEt	2.53[a] (J_{PH} = 3.7)	−12.25 (J_{PC} = 6.5)	1683 (C_6D_6)

[a] Unable to resolve J_{WH}. [b] THF-d_8. [c] CD_3CN. [d] Acetone-d_6. [e] Toluene-d_8. [f] CD_2Cl_2. [g] Ariyarathne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishag, M.; Prout, C. K.; Swainwick, M. G. *J. Chem. Soc. A* **1969**, 1309. All ^{1}H and ^{13}C NMR spectra were measured in C_6D_6 unless otherwise noted.

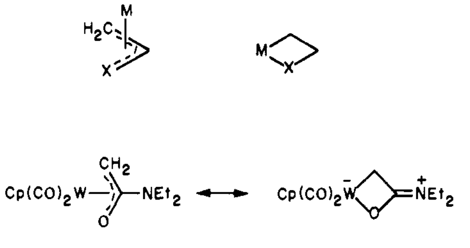
been published.[35] Saegusa and co-workers[36] have obtained evidence for a palladium η^3-oxaallyl intermediate which is believed to undergo olefin insertion, If β-hydrogens are present, β-elimination occurs, leading to α,β-unsaturated carbonyl compounds. The intermediacy of transition-metal η^3-oxaallyl species has been suggested in certain reactions of iron,[37] ruthenium,[38] cobalt,[39] and copper[24] complexes.

Supporting an expected increase in electron density at the metal center, the IR spectrum of each η^3-oxaallyl complex shows the two metal–carbonyl stretches shifted to lower energy relative to the corresponding η^1-enolate. In addition, **21**, the η^5-C_5Me_5 analogue of **15**, has CO stretching absorptions 14 cm^{-1} lower in energy, as a result of the additional electron donation provided by the pentamethylcyclopentadienyl ligand.

In the ^{1}H NMR spectrum, the η^3-oxaallyl complexes exhibit two methylene patterns. One is the AB pattern due to the syn and anti protons of the oxaallyl methylene group. The other is the doublet of quartets observed for the methylene hydrogens of the ester ethyl group, which are also diastereotopic. Tungsten satellites are observed for the oxaallyl methylene hydrogens. The chemical shift difference for these syn and anti hydrogens (Δδ) ranges from 0.3 to 2.1 ppm. The η^5-C_5Me_5 analogue displays the largest Δδ, perhaps due to the steric environment created by the η^5-C_5Me_5 methyl groups.

In the ^{13}C NMR spectra of the oxaallyl complexes, the resonance due to the carbon atom attached to the metal center (C-1) is shifted downfield from the region normally associated with sp^3 tungsten bound carbons (+4–17 ppm). The central oxaallyl carbon (C-2) is shifted upfield from the normal range of the enolate carbonyl carbon. Furthermore, the coupling constants J_{CH} at C-1 range from 143 to 158 Hz. This may be compared with the usual range of J_{CH} for the carbons of η^3-allyl groups which is ≈ 155–168 Hz.[40]

Scheme V



The ^{13}C NMR spectra correlate qualitatively with reactivity; the downfield shift (relative to η^1-enolate) is smaller in the unreactive oxaallyls than in the reactive ones. In addition, the relatively reactive oxaallyl complex **15** exhibits higher J_{CH} values than its less reactive analogue **18**. The fact that CH coupling constants normally correlate with hybridization suggests that the terminal oxaallyl carbon in the reactive complexes are sp^2-like, whereas the hybridization in the less reactive complexes tend toward sp^3—that is, they may have a certain amount of metallacyclic character (Scheme V),

Crystals of complex **18** were obtained from THF/hexane at −40 °C. X-ray data on a single crystal were collected under the conditions summarized in Table IV. The unit cell was found to be monoclinic, with the lattice parameters listed in Table IV. Structure refinement is described in the Experimental Section; selected bond lengths and angles are listed in Tables V and VI.

An ORTEP diagram of $Cp(CO)_2WCH_2CONEt_2$ (Figure 2) illustrates the distorted four-legged piano stool structure of the molecule. Both the Cp ring and the amide–enolate ligand are asymmetrically bonded to tungsten. The W–C(Cp) distances vary from 2.277 to 2.406 Å, corresponding either to a tilt of the Cp away from the amide–enolate ligand by 4.5° or a slip of the

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(35) (a) Holmgren, J. S.; Shapley, J. R.; Wilson, S. R.; Pennington, W. T. *J. Am. Chem. Soc.* **1986**, *108* (3), 508. Bennett, M. A.; Watt, R. *J. Chem. Soc., Chem. Commun.* **1971**, 95. (b) Bennett, M. A.; Robertson, G. B.; Watt, R.; Whimp, P. O. *Ibid.* **1971**, 752. (c) Robertson, G. B.; Whimp, P. O. *Inorg. Chem.* **1973**, 1740. (d) Beirsack, H.; Herrman, W. A. *J. Organomet. Chem.* **1980**, *194*, 317.

(36) (a) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011. (b) Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494.

(37) Alper, H.; Keung, E. C. H. *J. Org. Chem.* **1972**, *37*, 2566.

(38) Prince, R. H.; Raspin, K. A. *J. Chem. Soc.* A **1969**, 612.

(39) Goetz, R. W.; Orchin, M. *J. Am. Chem. Soc.* **1963**, *85*, 2782.

(40) Cp*(PMe$_3$)Ir(H)(η^3-allyl) has J_{CH} = 160 Hz (McGhee, W. D.; Bergman, R. G., unpublished results). Published coupling constants for iron allyl compounds range between 155 and 168 Hz: Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981; p 201.

Table IV, Summary of Crystallographic Data

compd	**18**	44	49	**50**
formula	$C_{13}H_{17}NO_3W$	$C_{20}H_{18}O_5W$	$C_{25}H_{23}O_2W$	$C_{17}H_{18}O_3W$
formula wt	419.14	522.2	540.32	454.18
cryst system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P1$	$P2_1/n$	$P2_1/a$
cell dimensns (25°)				
a, Å	9.8216 (11)	9.1061 (6)	7.7514 (11)	6.6634 (10)
b, Å	8.1050 (7)	9.9740 (8)	14.5061 (11)	16.605 (3)
c, Å	17.6904 (22)	11.2946 (6)	18.5385 (15)	14.106 (2)
α, deg		75.407 (5)		90
β, deg	99.963 (10)	89.099 (5)	90.216 (10)	97.500 (12)
γ, deg		69.202 (6)		90
V, Å^3	1387.0 (5)	925.0 (1)	2084.5 (6)	1547.4 (8)
Z	4	2	4	4
d_{calcd}, g/cm^{-1} (25 °C)	2.01	1.88	1.72	1.95
cryst dimensns, mm	0.22 × 0.23 × 0.24	0.13 × 0.20 × 0.34	0.27 × 0.32 × 0.34	0.06 × 0.15 × 0.31
radiation, Å	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
temp of colln, °C	25 °C	25 °C	25 °C	25 °C
data collctn method	2–2θ scan	2–2θ scan	θ–2θ scan	θ–2θ scan
scan speed, deg/min	0.78–6.7	0.6–6.7	0.6–6.7	0.72–6.7
scan range, $\Delta\theta$ deg	0.65 + 0.347 tan θ	0.5 + 0.347 tan θ	0.5 + 0.347 tan θ	0.60 + 0.35 tan θ
no. of reflctns collctd	2078	2405	3086	2160
total unique data	1805	2285	2720	1879
no. of variables	172	236	262	194
$R = \sum\lvert\lvert F_o\rvert - \lvert F_o\rvert\rvert/\lvert F_o\rvert$	1.36%	1.33%	1.53%	1.44%
$R_w = [\sum w_i\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2/w_i\lvert F_o\rvert^2]^{1/2}$	1.86%	1.89%	2.37%	1.91%
GOF	1.351	1.394	1.294	1.51

Table V, Selected Intramolecular Distances for **18**[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
W	O1	2.180 (2)	C1	C2	1.435 (5)
W	C1	2.273 (3)	C1	H1A	0.96 (3)
W	C2	2.459 (3)	C1	H1B	0.95 (3)
			C2	O1	1.302 (4)
W	C7	1.939 (4)	C2	N	1.333 (4)
W	C8	1.930 (4)	N	C3	1.473 (4)
W	C9	2.277 (3)	N	C5	1.458 (4)
W	C10	2.326 (3)	C3	C4	1.515 (5)
W	C11	2.406 (4)	C5	C6	1.508 (5)
W	C12	2.386 (3)	C7	O2	1.165 (4)
W	C13	2.292 (4)	C8	O3	1.174 (4)
W	CP	2.010			
			C9	C10	1.416 (5)
			C10	C11	1.388 (5)
			C11	C12	1.392 (5)
			C12	C13	1.408 (5)
			C13	C9	1.412 (5)

[a] esd's are in parentheses.

Table VI, Selected Intramolecular Angles for **18**[a]

atom 1	atom 2	atom 3	angle
CP	W	O1	114.92
CP	W	C1	118.14
CP	W	C2	134.57
CP	W	C7	121.79
CP	W	C8	120.31
O1	W	C7	86.03 (11)
C7	W	C8	74.35 (13)
C8	W	C1	83.01 (13)
C1	W	O1	61.89 (10)
O1	W	C8	123.75 (13)
C1	W	C7	119.53 (15)
W	C7	O2	175.8 (3)
W	C8	O3	178.3 (3)
W	O1	C2	85.95 (16)
W	C1	C2	79.59 (19)
W	C2	N	137.19 (23)
W	C1	H1A	125.0 (19)
W	C1	H1B	105.1 (21)
C2	C1	H1A	115.4 (19)
C2	C1	H1B	109.3 (20)
H1A	C1	H1B	116.5 (28)
C1	C2	O1	113.6 (3)
C1	C2	N	126.7 (3)
O1	C2	N	119.2 (3)
C2	N	C3	119.9 (3)
C2	N	C5	121.5 (3)
C3	N	C5	117.9 (3)
N	C3	C4	112.7 (3)
N	C5	C6	113.7 (3)
C10	C9	C13	107.4 (3)
C9	C10	C11	107.4 (3)
C10	C11	C12	109.8 (3)
C11	C12	C13	107.2 (3)
C9	C13	C12	108.1 (3)

[a] esd's are in parentheses.

tungsten away from the amide–enolate group toward C9 by about 0.15 Å.

C1 and O1 are clearly coordinated to the metal with bond distances of 2.273 (3) and 2.180 (2) Å, respectively. Whether C2 is bonded to tungsten or just lies nearby because it is bonded to C1 and O1 is less obvious. On the one hand, the distance between W and C2 of 2.459 (3) Å is only 0.05 Å longer than the largest W–C(Cp) distance. In general, however, the central carbon of η^3-allyl complexes is closer to the metal atom than is the terminal carbon.[41] Only a few structures are known for η^3-oxaallyl complexes, and these also exhibit a closer central carbon.[21,35] The η^3-azaallyl complex $Cp(CO)_2Mo(CH_2CHNH)$ shows a central carbon (Mo–C = 2.262 (3) Å) which is 0.072 Å further from the tungsten than from the terminal carbon (Mo–C = 2.334 (3) Å).[42]

The angle between the plane of the amide–enolate ligand and the W–C1–O1 coordination plane is 125.5°. This large dihedral angle and the long W–C2 distance are compatible with a significant contribution from the metallacycle resonance structure shown in Scheme V. The dihedral angle in cyclobutane is 150° whereas known metallacycles range from 180° (planar) to 150°.[43]

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[41] (a) Fenn, R. H.; Graham, A. J. *J. Organomet. Chem.* **1972**, *37*, 137; **1970**, *25*, 173. (b) Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Freidrich, P.; Bejenke, V.; Neugebauer, D. *J. Organomet. Chem.* **1978**, *145*, 329. (c) Allen, S. R.; Baker, P. K.; Barner, S. G.; Bottrill, M.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1983**, 927.

[42] Green, M.; Mercer, R. J.; Merton, C. E.; Orper, A. G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 422.

[43] (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980, pp 514–518. (b) Ephritikhine, M.; Green, M. L. H.; Mackinzie, R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 619. (c) Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; Mackinzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131. (d) Fajaram, J.; Ibers, J. A.; Collman, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 829.

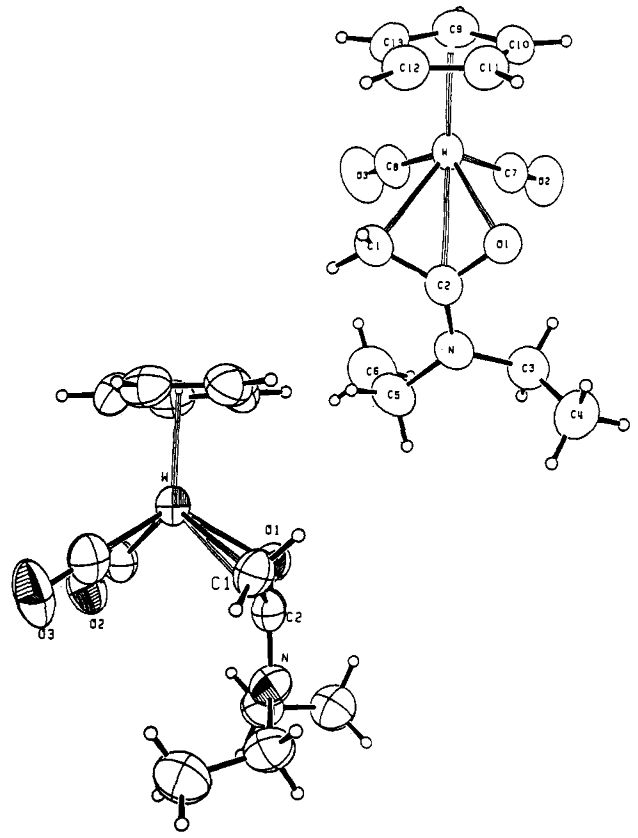


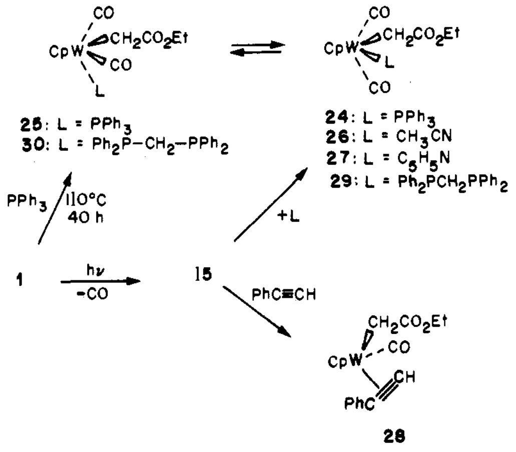
Figure 2. Two views of 18 showing the pseudometallocyclic structure.

The angle between the plane of the amide–enolate ligand and the Cp plane is about 90°.

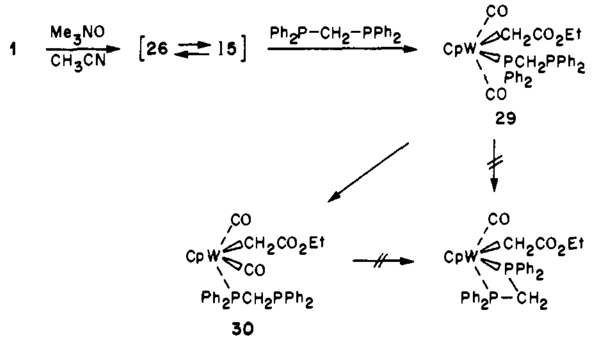
It seems likely that the presence of an NEt_2 group at C-2 reinforces this picture of the structure. In contrast to the structure of Seebach's lithium amide enolate dimer,[44] which displays a pyramidal dimethylamino group, the nitrogen of the amide–enolate ligand is planar with the ethyl groups bent away from the tungsten atom. This planarity and the length of the N–C2 bond suggests that the resonance form with a partial negative charge on tungsten and partial positive charge on nitrogen, as shown in Scheme V, contributes substantially to the structure, further reinforcing the metallacyclic character of this complex. In addition, a high barrier to rotation about the C2–N bond must exist since distinct signals due to the anisochronous pair of ethyl groups are observed in the ^1H and ^{13}C NMR spectra. The C2–N bond length of 1.333 (4) suggests that it is intermediate between a single and double bond. In comparison, the two C–N bond lengths in the lithium–amide enolate dimer are 1.435 (7) and 1.427 (5) Å.[44] The C–N bond lengths in enamines normally range between 1.380 and 1.426 Å.[44] Compound **18** is substantially less reactive than the alkoxy-substituted oxaallyl complex **15**, see below, and does not undergo insertion reactions with either benzaldehyde or alkynes. Monosubstitution with PMe_3 or PPh_3 can be induced to give cis and trans mixtures of $Cp(PR_3)(CO)_2WCH_2CONEt_2$ (R = Me (**22**), Ph (**23**)), but relatively high temperatures are required (see Experimental Section).

Addition of Dative Ligands to the Oxaallyl Complex 15. As mentioned above, solutions of oxaallyl complex **15** were generated on a preparative scale from tungsten ether **1** by using an Ace photochemical reactor and nitrogen gas purge (Scheme IV). To provide confirmatory chemical evidence for the structure of this unisolable material, it was treated with various dative ligands (Scheme VI). The reaction of **15** with CO, which regenerates η^1-tungsten enolate **1**, was discussed above. Treatment of solutions of **15** with PPh_3 leads initially to **24**, the cis phosphine-substituted analogue of **1**, in 82% isolated yield. Thermal conversion of the cis phosphine complex **24** (7.5×10^{-2} M) to a mixture containing 80% trans phosphine complex **25** and 20% cis phosphine complex **24** was accomplished by heating to 60 °C in C_6D_6 for 1 h. The trans phosphine complex **25** could be prepared directly from the tungsten ester enolate **1**, but this required heating the enolate in toluene at 110 °C for 40 h to achieve 50% conversion. Presumably the slow rate of this reaction is due to the difficulty of thermal CO dissociation from **1**.

Scheme VI



Scheme VII



If either of the stereoisomeric phosphine complexes **24** or **25** is irradiated, loss of PPh_3 to regenerate oxaallyl complex **15** is the major reaction path, judging from monitoring these reactions by ^1H NMR spectroscopy at early conversion. Peaks are also present in the ^1H NMR spectrum that are consistent with formation of a small amount of the phosphine-substituted oxaallyl complex.

Oxaallyl complex **15** may also be trapped with other dative ligands. Treatment with pyridine gives the cis pyridine-substituted enolate **27**, which can be isolated in 35% yield and fully characterized. Upon addition of phenylacetylene to solutions of **15**, a second equivalent of CO is liberated, and the monocarbonyl alkyne-substituted enolate **28** is isolated in 58% yield. Reactions of **15** and its η^1-enolate relatives with alkynes are discussed more extensively in a later section of this paper.

Solutions of the acetonitrile complex **26** were generated independently by treatment of the tungsten ethyl ester **1** with Me_3NO in acetonitrile. Attempts to use this material to introduce the potentially chelating phosphine ligand (diphenylphosphino)methane (DPPM) into the coordination sphere of the metal were unsuccessful in acetonitrile solvent. However, when an acetonitrile-d_3 solution of $Cp(CO)_2(CD_3CN)WCH_2CO_2Et$ was diluted with C_6D_6, monitoring by ^1H NMR showed that the weakly bound acetonitrile ligand had dissociated partly, generating a mixture of acetonitrile complex and tungsten oxaallyl complex **15**. Treatment of this solution with DPPM then led rapidly to a new substitution product (35% yield) which spectral data indicated was the η^1-cis DPPM tungsten enolate complex **29** (Scheme VII). This material isomerized thermally to a mixture of **29** (14%) and the more stable trans compound **30** (86%). However, no conditions

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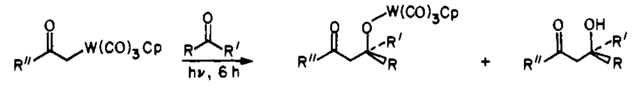
[44] Bauer, W.; Laube, T.; Seebach, D. *Chem. Ber.* **1985**, *118(2)*, 764.

Scheme VIII



R = H, R′ = Ph, R″ = OEt:	31		
R = H, R′ = *i*-Pr, R″ = OEt:	33		
R = CH$_3$, R′ = Ph, R″ = OEt:	34	+	35
R = H, R′ = Ph, R″ = CH$_3$:	36	+	37

could be found under which either the η^1-cis or η^1-trans DPPM complex could be converted to the η^2-chelate thermally, photochemically, or chemically (e,g,, with Me$_3$NO),

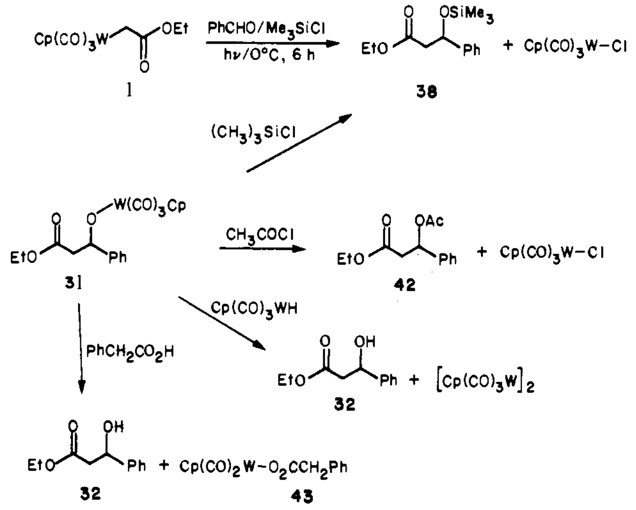
Aldol Reactions of Tungsten Enolate 1. Upon photolysis of tungsten enolate **1** and benzaldehyde for 5–6 h at 5 °C in C$_6$D$_6$, by using a uranium glass filter and a 200 W Hanovia Hg vapor lamp in a closed reaction vessel (standard conditions), tungsten aldolate **31** was generated in 90–95% yield by NMR (Scheme VIII). This product is one of the few known cyclopentadienyl tungsten tricarbonyl alkoxide complexes. It is thermally unstable, air sensitive, and has so far resisted isolation. However, its assignment as **31** is supported firmly by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy as well as by its chemical transformations (see below). The ^{1}H NMR spectrum of complex **31** is similar to that of the corresponding free aldol EtO–CO–CH$_2$–CH(OH)Ph (**32**), except for the singlet at δ 4.95 due to the Cp group, the lack of an O–H proton, and a substantial upfield shift of the benzylic proton ($\Delta\delta$ = 0.35 ppm). The linear (nonchelating) form of complex **31** is established by the presence of three ^{13}C NMR resonances at δ = 237,1, 224,1, and 226,8 due to the diastereotropic metal bound carbonyl groups as well as three metal carbonyl IR peaks,

In a reaction analogous to that observed with benzaldehyde, photolysis of **1** with isobutyraldehyde gave solutions containing tungsten aldolate **33** in 87% yield by NMR. Once again, this material was too sensitive to isolate. The corresponding reaction with acetophenone resulted in a mixture of **34** and the free aldol **35** (5;3 ratio) in 78% combined yield (NMR). After standing at room temperature for several days in C$_6$D$_6$, **34** disappeared while the free aldol increased to 47% of the mixture. Similarly, irradiation of tungsten ketone enolate **3** in the presence of benzaldehyde gave a mixture of **36** and **37** (3;1, respectively) by NMR, which accounted for a 60–65% combined yield (Scheme VIII), All the tungsten aldolates appear to decompose this way in solution (although at different rates); this is consistent with a decomposition route involving metal–oxygen bond cleavage followed by hydrogen atom or proton transfer from a second molecule of metal bound aldolate.

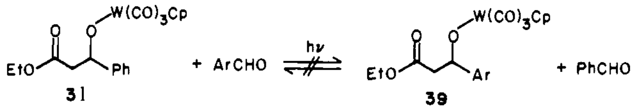
It seems reasonable to assume that the mechanism of the aldol reaction involves oxaallyl complex **15** as the critical intermediate. We propose that after photochemical generation of **15**, it reacts with aldehyde, giving a transient η^1-enolate with benzaldehyde complexed to the tungsten center. The η^1-enolate group can then migrate to the aldehyde carbon atom, generating an aldolate, The first aldolate formed may also have its ester carbonyl ligand coordinated to the tungsten center; presumably this species reacts rapidly with CO to give the observed tricarbonyl aldolate **31**.

A few experiments were carried out aimed at testing the broad outlines of this proposed mechanism. The tungsten ester **1** does not react with benzaldehyde even on prolonged heating at 110 °C in C$_6$D$_6$; thus irradiation is required to activate the complex toward reaction with benzaldehyde. We have made some attempts to determine the competency of intermediate **15** by generating it in the absence of benzaldehyde and then adding the aldehyde in a second step. Unfortunately, the rapid CO-induced reconversion of **15** to **1** has made the results of these experiments somewhat difficult to interpret. In one experiment, oxaallyl complex **15** was generated photochemically in a sealed NMR tube. As might be expected, upon addition of benzaldehyde and warming, **1** was regenerated cleanly because of the CO still present in the tube. In order to circumvent this problem, in a second experiment a solution of **15** was generated photochemically, and the extruded CO was removed under vacuum. Benzaldehyde was

Scheme IX



Scheme X



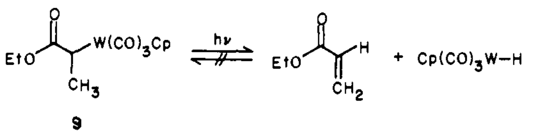
then added, and the solution was allowed to stand in the dark for 3 h. After this time, NMR analysis showed a 21% yield of free aldol **32**, along with 29% remaining **15**, 21% starting enolate **1**, and 14% ethyl acetate; the remainder of the material had decomposed, The low yield of **32** and the absence of the sensitive tungsten aldolate **31** are undoubtedly due to the deficiency of CO in the system. We presume that the dicarbonyl (perhaps ester carbonyl-coordinated) analogue of aldolate **31** forms in this experiment but undergoes rapid decomposition (along with some conversion to free aldol), because essentially no CO is available to convert it to its more stable tricarbonyltungsten relative **31**, Thus, experiments do not tell us rigorously whether **15** is the sole intermediate in the conversion of **1** to **31**, but they at least demonstrate that oxaallyl complex **15** is capable of undergoing the aldol reaction.

The sensitivity of the tungsten aldolates toward decomposition emphasized the need to find conditions to trap the initial aldol condensation products in situ before M–O bond cleavage occurs. As indicated above, aldolate **31** can be generated reproducibly in high yield, The reactivity of solutions of **31** was investigated with a variety of potential cleaving reagents. Reaction of **31** with acetic anhydride or triethylsilane resulted in complex mixtures, while *tert*-butyldimethylsilyl chloride gave no reaction. As outlined in Scheme IX, however, preliminary NMR experiments indicated the reactions of acetyl chloride, trimethylsilyl chloride, phenyl acetic acid, and Cp(CO)$_3$W–H with **31** gave high conversions to the desired cleavage products in hours at room temperature. Irradiation of a mixture of **1**, benzaldehyde, and trimethylsilyl chloride for 6 h at 5 °C gave Cp(CO)$_3$WCl (85%) and trimethylsilyl ether **38** (47%), Analysis of the reaction mixture by ^{1}H NMR spectroscopy showed that ether **38** is formed in 84% yield; some of the silyl ether appears to be destroyed in the workup, as only 47% of **38** was isolated after chromatography.

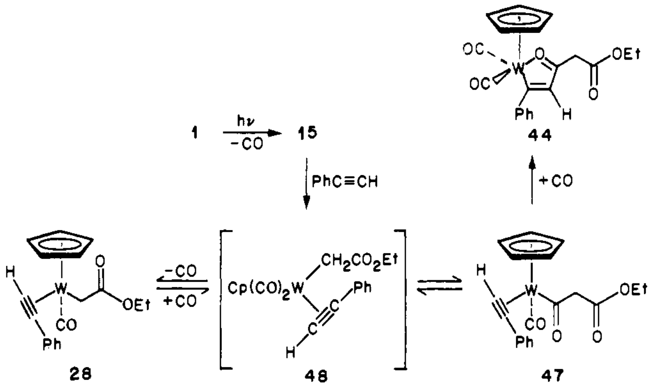
A few other experiments designed to examine the chemistry of tungsten aldolate **31** have been carried out, Irradiation of **31** in the presence of *p*-methoxybenzaldehyde resulted in no exchange of aldehydes to give substituted aldol **39** (Scheme X), providing evidence that the tungsten aldolate does not undergo reversion to enolate and aldehyde under standard photochemical conditions. The reverse reaction of **39** and benzaldehyde does not yield **31** under standard photochemical conditions either. Upon heating ethyl (α-trimethylsilyl)acetate with **31** no reaction was observed.

In order to examine the possibility of carrying out the oxaallyl-forming and aldol reactions with secondary enolates, irradiation of methyl-substituted complex **9** (Scheme XI) was examined.

Scheme XI



Scheme XII



Unfortunately, these reactions were frustrated by an increased propensity for W–C bond cleavage. Although some of the oxaallyl complex was formed, β-elimination to give ethyl acrylate and $Cp(CO)_3W{-}H$ was the major reaction pathway. In another experiment, $Cp(CO)_3WH$ and ethyl acrylate did not give enolate **9** by reinsertion either thermally or photochemically. Furthermore, when **9** was irradiated with PhCHO, no evidence for aldol-type condensations was observed.

Alkyne Insertion of Tungsten Enolates. Aldol condensations are typically thought of as reactions between a nucleophilic (enolate) and electrophilic (carbonyl compound) partner. From the foregoing discussion it is clear that the tungsten enolates fit this model. However, coordination at transition-metal centers often facilitates reactions between much less intrinsically activated reactants. The most well-known examples are migratory insertion reactions, in which new bonds are formed between metal bound alkyl groups and coordinated ligands such as CO, alkenes, and alkynes.

We investigated the possibility of carrying out such insertion chemistry with tungsten enolates, since it is difficult to add alkali metal enolates to unactivated organic multiple bonds. We began by looking for alkyne reactions. Insertion of alkynes into conventional metal–carbon bonds has been studied in detail for alkyl and acyl complexes of W,[45] Mo,[45] Ru,[46] Ir,[47] Mn,[48] Fe,[49] Ni,[50] and Pd.[51] Generally, the products result from insertion of CO to yield an acyl group that sequentially inserts the alkyne. This has been observed on irradiation of $Cp(CO)_3W{-}CH_3$ and $Cp(CO)_3W{-}CH_2CH_3$ with CO, the alkyl complexes most closely related to the enolates under discussion here.[45b] Although it is rare, several cases are known in which an alkyne inserts into a metal–carbon bond without prior CO insertion. For example, reaction of pentacarbonyl(methyl)manganese and hexafluorobutyne gives the insertion product $(CO)_5Mn[(F_3C)C{=}C(CF_3)(CH_3)]$,[48] and the reaction of $(acac)(Ph_3P)NiMe$ and diphenylacetylene gives $(acac)(Ph_3P)NiC(Ph){=}C(Ph)Me$.[50a] Furthermore, the propensity for carbon monoxide insertion (or, at least, the stability of the inserted products) is reduced in cases where the migrating group carries an electron-withdrawing substituent.[13d] For example, insertion of CO into the enolate moiety has been observed by Palyi[52] in the reaction of $(CO)_4CoCH_2CO_2CH_2CH_3$ with triphenylphosphine, but the product cobalt 1,3-acyl ester is thermally unstable and was not fully characterized,

Table VII. Selected Intramolecular Distances for 44[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
W	O1	2.108 (2)	C1	C2	1.385 (4)
W	C7	2.148 (2)	C1	C6	1.402 (4)
W	C14	1.972 (3)	C2	C3	1.357 (5)
W	C15	1.984 (3)	C3	C4	1.373 (5)
			C4	C5	1.397 (4)
W	C16	2.308 (3)	C5	C6	1.390 (4)
W	C17	2.291 (3)	C6	C7	1.482 (3)
W	C18	2.335 (3)	C7	C8	1.386 (4)
W	C19	2.367 (3)	C8	C9	1.378 (4)
W	C20	2.358 (3)	C9	O1	1.290 (3)
W	CP	2.003	C9	C10	1.505 (4)
C14	O4	1.146 (3)	C10	C11	1.510 (4)
C15	O5	1.144 (3)	C11	O2	1.335 (4)
			C11	O3	1.175 (4)
			O2	C12	1.461 (5)
			C12	C13	1.446 (6)
			C16	C17	1.418 (4)
			C17	C18	1.401 (4)
			C18	C19	1.398 (4)
			C19	C20	1.408 (4)
			C20	C16	1.393 (4)

[a] esd's are in parentheses.

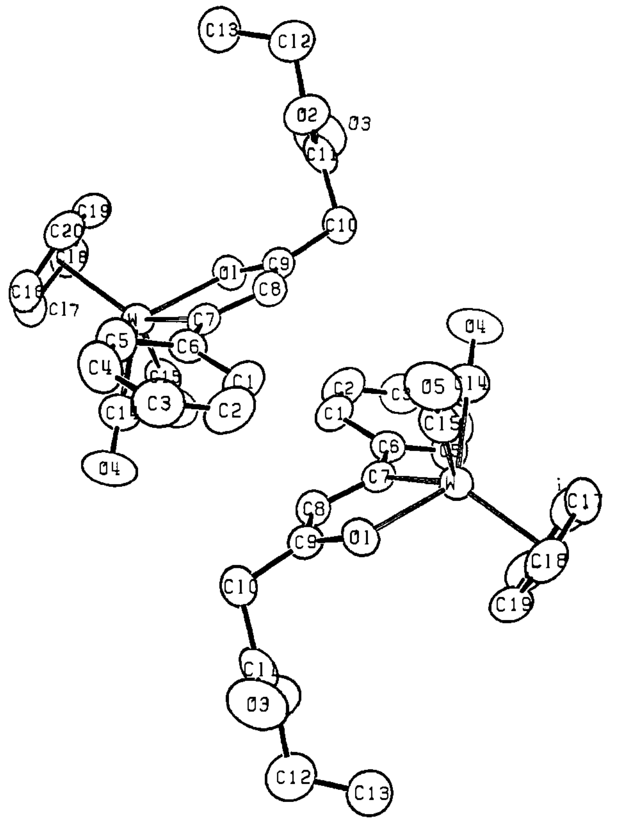


Figure 3. Perspective ORTEP diagram of 44 showing the close packing of the molecules across the inversion center at (0, 0, 1/2).

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(45) (a) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055. (b) Alt, H. G.; Engelhardt, H. E.; Thewalt, U.; Riede, J. *J. Organomet. Chem.* **1985**, *288*, 149–163; 165–177, and references therein. (c) Davidson, J. L.; Shiralian, M.; Muir, L. M.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1984**, 2167. (d) Davidson, J. L.; Vasapollo, G.; Muir, L. M.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1982**, 1025. (e) Green, M.; Nyatha, J. Z.; Scott, C.; Stone, F. G. A.; Welch, A. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1978**, 1067.

(46) (a) Blackmore, T.; Bruce, M. T.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 106. (b) Smart, L. E. *J. Chem. Soc., Dalton Trans.* **1976**, 390.

(47) Corrigan, P. A.; Dickson, R. S. *Aust. J. Chem.* **1979**, *32*, 2147.

(48) Booth, B. L.; Hargreaves, R. G. *J. Chem. Soc. A*, **1970**, 308.

(49) Bottrill, M.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 292.

(50) (a) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002. (b) Carmona, E.; Gutierrez-Puebla, E.; Monge, A.; Marin, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1984**, *3*, 1438.

(51) (a) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93. (b) Maitlis, P. M.; Taylor, S. H.; Mann, B. E. *J. Organomet. Chem.* **1978**, *145*, 255. (c) Norton, J. R.; Murray, T. F. *J. Am. Chem. Soc.* **1979**, *101*, 4107.

(52) Galamb, V.; Palyi, G.; Furmanova, M. G.; Struchov, Y. T. *J. Organomet. Chem.* **1981**, *209*, 183.

Table VIII. Selected Intramolecular Angles for 44[a]

atom 1	atom 2	atom 3	angle
CP	W	O1	113.42
CP	W	C7	123.59
CP	W	C14	116.23
CP	W	C15	116.94
O1	W	C7	74.40 (8)
O1	W	C14	130.25 (10)
O1	W	C15	79.80 (9)
C7	W	C14	76.35 (10)
C7	W	C15	119.38 (10)
C14	W	C15	80.73 (11)
W	C14	O4	179.1 (3)
W	C15	O5	177.5 (3)
W	C7	C6	128.59 (18)
W	C7	C8	114.29 (18)
C6	C7	C8	117.1 (2)
C7	C8	C9	115.3 (2)
C8	C9	O1	117.7 (2)
C9	O1	W	118.19 (16)
C8	C9	C10	125.9 (3)
C9	C10	C11	110.7 (2)
C10	C11	O2	110.1 (3)
C10	C11	O3	125.3 (3)
O2	C11	O3	124.5 (3)
C11	O2	C12	117.7 (3)
O2	C12	C13	112.3 (3)
C2	C1	C6	120.4 (3)
C1	C2	C3	121.3 (3)
C2	C3	C4	119.5 (3)
C3	C4	C5	120.4 (3)
C4	C5	C6	120.7 (3)
C1	C6	C5	117.7 (2)
C1	C6	C7	119.9 (2)
C5	C6	C7	122.4 (2)
C20	C16	C17	107.9 (3)
C16	C17	C18	107.8 (3)
C17	C18	C19	108.0 (3)
C18	C19	C20	108.3 (3)
C19	C20	C16	108.0 (3)

[a] esd's are in parentheses.

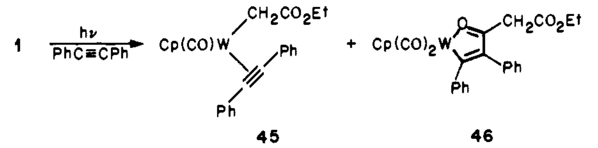
A route to an iron 1,3-acyl ester was investigated by Davies,[53] but this product is also unstable.

To look for insertion in our system, we irradiated a benzene-d_6 solution of phenylacetylene and tungsten enolate **1** in a sealed NMR tube. This reaction led to two major products observed by ^{1}H NMR (Scheme XII); the alkyne-substituted enolate **28** (42%; identified earlier in the reaction of oxaallyl complex **15** with PhC≡CH) formed by displacement of two molecules of CO and the insertion product **44** (42%). Allowing this mixture to stand under CO converted **28** to **44** (78% yield by NMR), which was isolated in 62% yield. Oxametallacycle **44**, in analogy to the reactions of Cp(CO)$_2$W–R with alkynes observed by Alt[45b] and Davidson,[45c–e] is the result of a combined CO and alkyne insertion. The product contains a chelating ligand in which the inserted carbonyl group is coordinated to the tungsten atom.

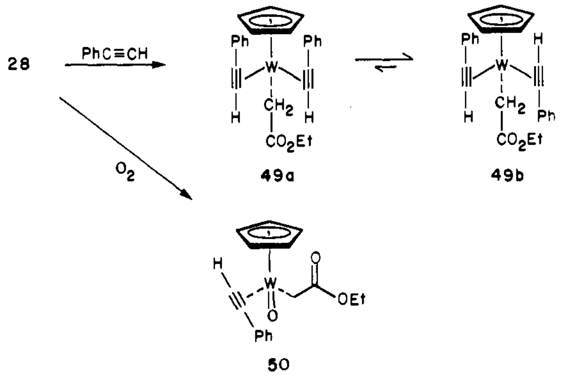
Crystallization of the insertion product **44** from hexamethyldisiloxane/THF gave red polyhedral crystals suitable for X-ray diffraction. X-ray data were obtained under the conditions summarized in Table IV. The unit cell was found to be triclinic, with the lattice parameters listed in Table IV. Structure refinement is described in the Experimental Section; selected bond lengths and angles are given in Tables VII and VIII.

An ORTEP diagram of **44** is shown in Figure 3. The insertion product is a single regioisomer, formed by migration of the carbonylated enolate group to the unsubstituted carbon of the alkyne. The stereochemistry about the double bond is that formed by stereoselective cis insertion of the alkyne. No trace of a second stereo- or regioisomer was detected by ^{1}H NMR analysis of crude reaction mixtures. The crystalline structure consists of separated distorted four-legged piano stool molecules tightly packed in the triclinic unit cell, with numerous intermolecular contacts between 3,5 and 3.9 Å. The shortest nonbonding C–C distance of 3.31 Å between C1 and C9 can be regarded as a somewhat short van der Waals contact between two sp^2 hybridized carbons; it does not significantly distort the molecules.

Scheme XIII



Scheme XIV



The chelating ligand seems extensively delocalized, as C7–C8 and C8–C9 are essentially the same length (1.386 (4) and 1.378 (4) Å, respectively) and C9–O1 is intermediate between a single and double bond length at 1.290 (3) Å. In addition, the W–C7 bond length (2.148 (2) Å) is significantly shorter than a normal W–C single bond. The Cp ring and carbonyl ligands are normal.

As mentioned earlier, alkyne complex **28** was obtained in 58% yield by addition of phenylacetylene to a solution of the oxaallyl compound **15**. Its IR spectrum shows a single metal carbonyl band at 1932 cm^{-1} and an ester carbonyl absorption band at 1685 cm^{-1}. The acetylenic proton appears at δ 12.40 ppm, an indication of the formal four-electron-donating character of the alkyne ligand in this complex.[54]

As shown in Scheme XIII, irradiation of **1** with diphenylacetylene in benzene-d_6 leads primarily to the double CO replacement product **45** in 82% yield. The spectral properties of **45** are similar to those of **28**. We assume the geometry of the tungsten atom in **28** and **45** is similar to that in Cp(CO)(CF$_3$C≡CF$_3$)MoSC$_6$F$_5$,[55] which approximates an octahedron with three facial sites occupied by the cyclopentadienyl ligand. Taking the W–CO bond as a reference, the alkyne bond is parallel to the W–CO axis, and the enolate group is perpendicular to the W–CO axis. A small amount (6%; presumably because diphenylacetylene is more encumbered sterically) of the chelated insertion product **46** was also formed in the irradiation; the two products were separated by flash chromatography on silica gel under N$_2$ and fully characterized. The isolated yield of **46** can be increased to 42% by conducting the reaction under an excess of CO. However, the insertion reaction is still quite slow at room temperature, requiring 20 days with 2.2 equiv CO.

Proposed Mechanism of the CO/Alkyne Insertion Reaction. Additional information about the course of the CO/alkyne insertion reaction was obtained by carrying out the irradiations at low temperature. Our results are summarized in Scheme XII. Tungsten enolate **1** in toluene-d_8 solution containing 1.2 equiv of phenylacetylene was irradiated in a sealed NMR tube at −78 °C. The tube was periodically transferred to the probe of an NMR spectrometer precooled to the same temperature, and reaction was

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(53) Davies, S. G.; Watts, O.; Aktogu, N.; Felkin, H. *J. Organomet. Chem.* **1983**, *243*, C51.

(54) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 1532.

(55) Howard, J. A. K.; Stansfield, R. F. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 246.

Table IX. Selected Intramolecular Distances for **49**[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
W	C1	2.253 (3)	C10	H10	1.00 (3)
W	C10	2.052 (3)	C10	C11	1.272 (5)
W	C11	2.074 (3)	C11	C12	1.463 (4)
W	C18	2.042 (3)	C12	C13	1.386 (4)
W	C19	2.055 (3)	C12	C17	1.388 (4)
W	C5	2.376 (4)	C13	C14	1.382 (5)
W	C6	2.393 (3)	C14	C15	1.371 (5)
W	C7	2.366 (4)	C15	C16	1.373 (5)
W	C8	2.348 (3)	C16	C17	1.373 (6)
W	C9	2.353 (3)	C18	H18	0.81 (3)
W	CP	2.050	C18	C19	1.287 (5)
C1	C2	1.471 (5)	C19	C20	1.455 (4)
C2	O1	1.202 (4)	C20	C21	1.387 (4)
C2	O2	1.357 (4)	C20	C25	1.388 (4)
O2	C3	1.447 (4)	C21	C22	1.377 (5)
C3	C4	1.486 (6)	C22	C23	1.372 (6)
			C23	C24	1.371 (5)
			C24	C25	1.361 (4)
			C5	C6	1.375 (5)
			C6	C7	1.396 (6)
			C7	C8	1.408 (5)
			C8	C9	1.398 (5)
			C9	C5	1.381 (5)

[a] esd's are in parentheses.

monitored by ^1H NMR spectrometry. After a 30-min photolysis period the following organometallic compounds were observed by ^1H NMR at −75 °C: oxaallyl **15**, coordinated monocarbonyl phenylacetylene adduct **28**, insertion product **44**, starting material **1**, and a new compound. This new compound has a ^1H NMR resonance at δ 12.03 characteristic of an alkyne donating four electrons. The acetylenic proton resonance is distinctly different from the acetylene proton resonance of **28**. We propose that this material is **47**, the CO insertion product formed from the most likely (but apparently unobservable) initial single CO displacement product **48**. Intermediate **47** is thermally unstable at slightly higher temperature and is converted to **44** at −60 °C. Exact ratios of products in the low-temperature experiment could not be determined because of line broadening problems due to solvent viscosity, but we estimate that **47** comprised about 5% of the total tungsten containing products.

On the basis of these observations, we propose that the photochemical reaction proceeds by initial (and probably reversible) CO insertion into the tungsten enolate bond, migration of the 1,3-dicarbonyl ligand to the coordinated alkyne, chelation of the γ-carbonyl group, and recoordination of CO to give the isolated insertion product **44** (alternatively, the CO may recoordinate prior to alkyne insertion to reconvert the alkyne to a two-electron donor). In a second pathway, loss of CO from proposed intermediate **48** gives the isolable compound **28**.

Some further chemistry of monocarbonyl alkyne complex **28** was also investigated. In support of the pathways proposed in Scheme XII, in the absence of light reaction of **28** with CO gives insertion product **44**, presumably via **48** and **47**. Thermally **28** reacts with additional phenylacetylene to give a new complex **49** containing two alkyne ligands (Scheme XIV). Yellow crystals of this material were obtained from THF/hexane at −40 °C, and a study of its structure was carried out by X-ray diffraction. X-ray data were obtained under the conditions summarized in Table IV. The unit cell was found to be monoclinic, with the lattice parameters listed in Table IV. Refinement of the structure is described in the Experimental Section.

An ORTEP diagram of $Cp(PhCCH)_2WCH_2CO_2Et$ is shown in Figure 4; the material is the bis(alkyne) enolate complex **49**. Selected bond lengths and angles are compiled in Tables IX and X. Structurally this bis(alkyne) enolate complex is similar to $Cp(alkyne)_2WX$ complexes studied by Davidson[56] and Stone (X = Cl,[57] X = SR[58]). The alkyne carbons are nearly equidistant from the tungsten atom; the metal is pseudo-tetrahedrally coor-

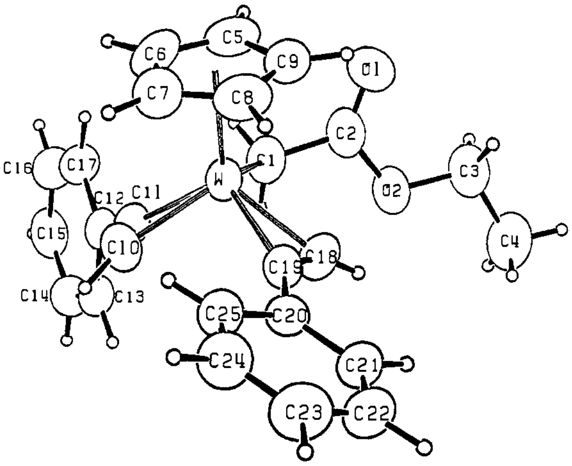

Figure 4. ORTEP diagram of **49** showing the orientation of the phenyl groups.

Table X. Selected Intramolecular Angles for **49**[a]

atom 1	atom 2	atom 3	angle
CP	W	C1	109.37
CP	W	C10	112.63
CP	W	C11	120.88
CP	W	C18	127.30
CP	W	C19	112.04
C1	W	C10	114.68 (13)
C1	W	C11	79.69 (12)
C1	W	C18	81.46 (13)
C1	W	C19	117.97 (12)
C11	W	C18	111.75 (13)
C10	W	C19	88.99 (14)
W	C1	C2	114.3 (2)
C1	C2	O1	127.7 (3)
C1	C2	O2	111.1 (3)
O1	C2	O2	121.2 (3)
C2	O2	C3	116.5 (3)
O2	C3	C4	107.9 (3)
W	C10	H10	149.6 (20)
H10	C10	C11	135.8 (21)
W	C11	C12	144.8 (2)
C10	C11	C12	144.1 (3)
C11	C12	C13	122.2 (3)
C11	C12	C17	120.0 (3)
C13	C12	C17	117.8 (3)
C12	C13	C14	121.1 (3)
C13	C14	C15	119.7 (3)
C14	C15	C16	120.2 (3)
C15	C16	C17	119.9 (3)
C12	C17	C16	121.3 (3)
W	C18	H18	149.9 (24)
H18	C18	C19	137.7 (24)
W	C19	C20	146.2 (2)
C18	C19	C20	142.7 (3)
C19	C20	C21	120.2 (3)
C19	C20	C25	121.8 (3)
C21	C20	C25	117.9 (3)
C20	C21	C22	120.3 (3)
C21	C22	C23	120.6 (3)
C22	C23	C24	119.4 (3)
C23	C24	C25	120.4 (3)
C20	C25	C24	121.4 (3)
C6	C5	C9	109.1 (4)
C5	C6	C7	108.2 (3)
C6	C7	C8	107.4 (3)
C7	C8	C9	107.5 (3)
C5	C9	C8	107.8 (3)

[a] esd's are in parentheses.

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(56) Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1975**, 2531.

Table XI. Selected Intramolecular Distances for **50**[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
W	O3	1.714 (2)	C6	H6	0.86 (3)
			C6	C7	1.270 (4)
W	C6	2.066 (3)	C7	C8	1.465 (4)
W	C7	2.070 (3)	C8	C9	1.381 (4)
W	C14	2.211 (3)	C9	C10	1.390 (5)
W	CP1	2.084	C10	C11	1.378 (5)
W	C1	2.406 (4)	C11	C12	1.374 (5)
W	C2	2.386 (4)	C12	C13	1.375 (5)
W	C3	2.358 (4)	C13	C8	1.395 (5)
W	C4	2.411 (4)	C14	C15	1.463 (5)
W	C5	2.433 (4)	C15	O1	1.208 (4)
			C15	O2	1.339 (5)
			O2	C16	1.450 (5)
			C16	C17	1.420 (6)
			C1	C2	1.377 (6)
			C1	C5	1.401 (6)
			C2	C3	1.401 (5)
			C3	C4	1.416 (6)
			C4	C5	1.394 (15)

[a] esd's are in parentheses.

dinated. The structure shows that all four alkyne carbons are approximately equidistant from the tungsten at 2.05 Å (av). The carbon–carbon bond distances of the phenylacetylene ligands are intermediate between a double and triple bond length, at 1.287 (5) and 1.272 (5) Å. The phenyl group proximal to the enolate ligand is tilted approximately 75° from the W–C10–C11 plane while the distal phenyl group is essentially coplanar with the W–C18–C19 plane. The cyclopentadienyl ring is η^5-coordinated with a slight tilt away from the proximal phenyl ring. The enolate is planar as expected and coordinated via C1 with a normal sp^3-like WCC angle of 114° and bond length of 2.253 (3) Å. The corresponding bond length in Cp(CO)$_3$WCH$_2$CO$_2$Et (**1**) is 2.321 (4) Å.

On the basis of the 18-electron rule, the two alkyne ligands in **49** formally donate three electrons each to tungsten, a situation which has precedent in earlier studies when the alkynes are fluxional.[57,58] A variable temperature NMR study was conducted on this complex to determine which conformer predominates in solution. At low temperature two conformational isomers appear to be present (Scheme XIV). The major conformer (80%) displays inequivalent acetylenic protons, suggesting this is **49b**, the isomer present in the solid state. The other conformer (**49a**; 20%) exhibits magnetically equivalent acetylenic protons and probably has the phenyl rings of the alkyne distant from the enolate ligand. From the chemical shift differences and coalescence temperature we estimate that $\Delta G^{\ddagger}$ for the interconversion of these isomers is 12.6 kcal/mol at −4 °C. At room temperature, the average chemical shift of the acetylenic carbons of **49** is observed as a broad absorption centered at δ 169. At −70 °C the ^{13}C NMR spectrum shows distinct acetylenic carbons for the two conformers in the range δ 190.1–164.8. This is the appropriate range for alkynes donating three or four electrons to a metal center.[59]

Reaction of alkyne complex **28** with 1 equiv of oxygen gives a tungsten oxo complex, **50**. Spectral data indicate the presence of the alkyne and enolate moieties. The IR spectrum shows stretches at 1695 cm^{-1} due to the ester and/or coordinated alkyne[60] and at 946 cm^{-1} characteristic of the W=O vibration.[60,61] Tan monoclinic crystals of **50** were grown from toluene/hexane at −40 °C, and the structure was solved by X-ray diffraction. The lattice parameters and X-ray collection conditions are listed in Table IV. Selected bond lengths and angles are compiled in Tables XI and

Table XII. Selected Intramolecular Angles for **50**[a]

atom 1	atom 2	atom 3	angle
O3	W	C6	108.72 (13)
O3	W	C7	101.76 (11)
O3	W	C14	95.43 (12)
O3	W	CP1	121.2
C14	W	C6	82.44 (13)
C14	W	C7	118.16 (12)
C14	W	CP1	108.9
CP1	W	C6	126.6
CP1	W	C7	111.1
W	C6	H6	139.8 (20)
C7	C6	H6	147.8 (21)
W	C7	C8	144.5 (2)
C6	C7	C8	143.3 (3)
C7	C8	C9	121.0 (3)
C7	C8	C13	119.9 (3)
C13	C8	C9	119.0 (3)
C8	C9	C10	120.8 (3)
C9	C10	C11	119.2 (3)
C10	C11	C12	120.6 (3)
C11	C12	C13	120.3 (3)
C12	C13	C8	120.1 (3)
W	C14	C15	118.9 (2)
C14	C15	O1	125.9 (4)
C14	C15	O2	112.3 (3)
O1	C15	O2	121.8 (4)
C15	O2	C16	118.7 (3)
O2	C16	C17	111.9 (4)
C2	C1	C5	108.4 (4)
C1	C2	C3	108.5 (4)
C2	C3	C4	107.5 (4)
C3	C4	C5	107.3 (4)
C1	C5	C4	108.3 (4)

[a] esd's are in parentheses.

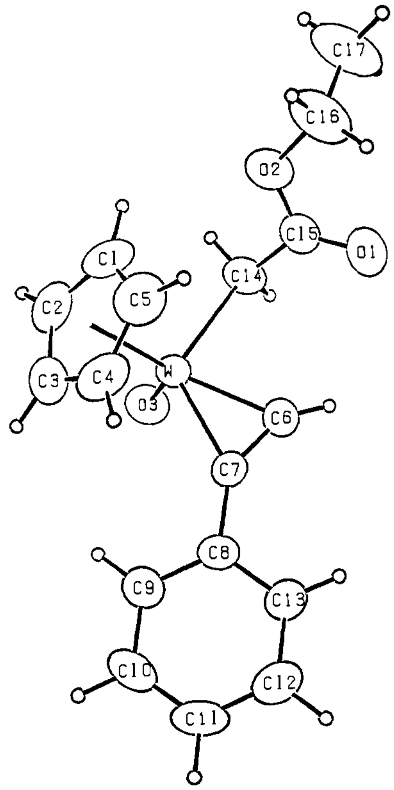

Figure 5. Perspective ORTEP diagram of **50** showing the orientation of the phenylacetylene ligand with respect to the enolate moiety and the numbering scheme. The refined hydrogen on C6 is H6.

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(57) (a) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 738. (b) Davidson J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1974**, 706.

(58) Davidson, J. L. *J. Organomet. Chem.* **1980**, *186*, C19.

(59) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

(60) Similar values have been reported for some of the few other alkyne–oxo complexes known. (a) Templeton, J. L.; Ward, B. C.; Chen, C. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1313. (b) Mayer, J. M.; Tulip, T. H. *J. Am. Chem. Soc.* **1984**, *106*, 3878.

(61) (a) Feinstein-Jaffe, I.; Gibson, D.; Lippard, S. J.; Schrock, R. R.; Spool, A. *J. Am. Chem. Soc.* **1984**, *106*, 6305. (b) Bokiy, N. G.; Gatilov, Y. V.; Struchkov, Y. T.; Ustynyuk, N. A. *J. Organomet. Chem.* **1973**, *54*, 213.

XII, with the atoms numbered according to the ORTEP diagram, Figure 5.

The structure is similar to the structure of $Cp(CF_3CCCF_3)(O)MoSC_6F_5$,[55] $Cp(PhCCPh)(O)WC_6H_6$,[61b] and the molybdenum fragment of the dimer $Cp(CO)_2RuMo(O)(PhCCPh)Cp$.[62] The phenyl group of the phenylacetylene ligand is oriented in the less sterically demanding position distal from the enolate ligand. As noted by Woodward[55] in the similar molybdenum complex, the axis of the alkyne ligand lies approximately parallel to the W–C14 bond. The dihedral angle of C14–W–C7–C6 is 3,00 (20)°. The tungsten oxygen bond length W–O3 at 1.714 (2) Å is comparable to related W=O double bonds.[61b,63] The ^{13}C resonances of the coordinated phenylacetylene (145.80 and 155.67 ppm) are shifted upfield compared to the acetylenic carbons in complex **28** (191,78 and 201.23 ppm). The acetylenic proton is also shifted upfield from the normal range of a four-electron-donating alkyne.[54] This phenomenon has been explained by donation of the oxygen lone-pair electrons on terminal oxo groups to the appropriate metal $d\pi$ orbitals, lowering the demand for electron donation from the alkyne ligand.[60a] The cyclopentadienyl ring and the enolate are coordinated normally except that the W–C14 bond length is slightly shortened (2.211 (3) Å) in comparison to the corresponding bonds in **1** and **49**. The alkyne carbon–carbon bond distance has lengthened upon coordination to 1.270 (4) Å.

Summary and Conclusions

A wide range of tungsten and molybdenum 2-oxaalkyl or η^1-enolate complexes (some having functional groups incompatible with alkali metal enolates) can be prepared by treatment of nucleophilic anionic metal complexes with organic chlorocarbonyl compounds. Many of these materials are air stable and relatively easy to handle; they can be isolated and characterized by spectroscopic and analytical techniques, and several conventional organic transformations have been performed on the enolate carbonyl functionality. Irradiation or treatment with trimethylamine-*N*-oxide induces CO loss, leading to η^3-enolates (oxaallyl complexes); few such complexes have been previously identified. Irradiation of the η^1-enolates in the presence of aldehydes leads to aldol condensation. The initial observable products of these condensations are O-bound (tricarbonyl)tungsten aldolates, which can be converted to organic aldol products with suitable reagents that cleave the M–O bond. We believe the oxaallyl complexes are formed as transient intermediates in the aldol reactions.

Reaction with substrates less electrophilic than aldehydes has also been investigated. Reaction with alkynes proceeds by initial CO insertion followed by migration of the carbonylated enolate group to the less hindered alkyne carbon atom and chelation of the inserted carbonyl to the metal center.

Secondary enolates (carrying substituents at the carbon atom bound to the metal) can be prepared, but the synthesis requires alkylation of metal anions with methanesulfonates rather than with chlorides. Unfortunately, the metal–carbon bonds in these materials are more labile than those of their primary analogues, and M–C cleavage occurs in preference to aldol chemistry. Studies on systems based on metals other than tungsten and molybdenum and on other ligands are now under way. These are aimed at (a) finding complexes in which aldol chemistry occurs more rapidly than simple M–C bond cleavage, (b) locating enolates in which direct reaction between the enolate group and nonelectrophilic substrates (e.g., alkynes, alkenes) occurs, and (c) developing methods for carrying out asymmetric aldol reactions.

Experimental Section

General Methods. All manipulations involving air sensitive materials were performed under nitrogen by using Schlenk or vacuum line techniques[64] or in a Vacuum Atmospheres 553-2 inert atmosphere glovebox equipped with a MO-40-1 inert gas purifier.

Air sensitive materials were exposed only to thoroughly dried and degassed solvents. Tetrahydrofuran (THF), diethyl ether, toluene, glyme, and benzene were distilled from sodium/benzophenone under a nitrogen atmosphere. Hexane, pentane, and acetonitrile were distilled from CaH_2 under a nitrogen atmosphere. THF-d_8, toluene-d_8, and benzene-d_6 were stirred over sodium/benzophenone and then transferred under vacuum prior to use. Acetone-d_6 was dried over molecular sieves. Acetonitrile-d_3 and methylene chloride-d_6 were dried over CaH_2 and vacuum transferred prior to use. Ethyl chloroacetate (Matheson, Coleman, and Bell), chloroacetone (Aldrich), benzaldehyde (Matheson, Coleman, and Bell), phenylacetylene (Aldrich), aniline (Mallinckrodt), and propargyl alcohol (Aldrich) were distilled prior to use and stored over 3Å molecular sieves. Trimethylamine-*N*-oxide (Aldrich) was sublimed. Triphenylphosphine (Mallinckrodt) was recrystallized from ethanol, and trimethylphosphine (Strem Chemicals) was dried over a sodium mirror and vacuum transferred before use. Other reagents were used as received. $Cp(CO)_3WNa$,[45a] NaCp,[65] $Cp(CO)_3WCl$,[66] $Cp(CO)_3WCH_2CONH_2$,[13c] and $Cp(CO)_3WH$[66] were prepared according to published procedures.

^1H NMR spectra were recorded with the UCB-250 (250-MHz), the BVX-300 (300-MHz), or an AM 500 Bruker (500-MHz) Fourier transform NMR instrument at the University of California, Berkeley (UCB) NMR facility and are reported in units of parts per million (δ) with residual protons in the solvent as an internal standard (benzene-d_6, 7.15; acetonitrile-d_3, 1.93; acetone-d_6, 2.04; methylene chloride-d_2, 5.32; THF-d_8, 3.58; toluene-d_8, 2.09 ppm). Significant ^1H NMR data are tabulated in order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), number of protons, and coupling constants in Hz. The ^{31}P NMR (121.5-MHz) spectra and ^{13}C NMR (75.5-MHz) spectra were recorded with the BVX-300 spectrometer unless otherwise indicated. All ^{13}C NMR spectra are referenced by using ^{13}C resonance of the solvent as an internal standard (acetonitrile-d_3, 1.30; acetone-d_6, 206.0; benzene-d_6, 128.0; toluene-d_8, 20.4). All ^{31}P NMR spectra were proton decoupled and are reported in units of parts per million (δ) downfield from 85% phosphoric acid (H_3PO_4). Solution infrared spectra were recorded in 0.1- or 0.025-mm NaCl cells with a Perkin-Elmer Model 283 or Perkin-Elmer 1550 Fourier transform infrared spectrophotometer. Ir data are reported as (solvent) cm^{-1} (intensity: s, strong; m, medium; w, weak), and are calibrated with polystyrene (1601 cm^{-1}). Electron-impact and chemical ionization mass spectra were recorded at the UCB mass spectral facility with an AEI MS12 (low-resolution) mass spectrometer and are reported as the most intense peak of the isotope envelope. Elemental analyses were performed by the Microanalytical Laboratory, operated by the College of Chemistry at UCB. Melting points were obtained with a Thomas Hoover capillary melting point apparatus and are uncorrected.

Standard photolyses were accomplished by using an Ace-Hanovia 200-W lamp in an immersion well. Sample tubes were immersed in a methanol bath maintained at 6 °C (unless otherwise noted) by an ethylene glycol mixture being circulated through a copper coil heat exchanger; larger scale reactions were conducted in an Ace photochemical apparatus. All photolysis experiments were done through a uranium glass filter (transparent at $\lambda > 350$ nm).

Flash column chromatographic separations by the method of Still, Kahn, and Mitra were carried out by using either silica gel or Alumina (activity II) under nitrogen pressure.[68]

The X-ray crystal structures were solved by Patterson methods and refined by standard least-squares and Fourier techniques. Peaks corresponding to the expected positions of most of the hydrogen atoms were found by difference Fourier techniques; hydrogens were included in the structure factor calculations in their expected positions but were not refined in least squares.[69]

η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)tricarbonyltungsten (1), (Method A). In a 100-mL, round-bottomed flask equipped with a stirring bar was placed $Cp(CO)_3WNa$ (1.49 g, 4.0 mmol) and THF (35 mL). To this solution was added ethyl chloroacetate (490 mg, 4.0 mmol) via syringe. The reaction mixture was allowed to stir at room temperature for 4 h, after which NaCl had precipitated. The solvent was removed under high vacuum, and the yellow-brown residue was extracted with 3 25-mL portions of hexane. After filtration the combined hexane portions were concentrated to 10 mL under vacuum. The concentrated solution was placed into a –40 °C freezer for 3 days, and 907 mg of long yellow

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(62) Drage, J. S.; Tilset, M.f Vollhardt, P. C.; Wiedman, T. W. *Organometallics* **1984**, *3*, 812.

(63) Legzdins, P.; Rettig, S.; Sanchez, L. *Organometallics* **1985**, *4*, 1470.

(64) Shriver, D. F. *The Manipulation of Air Sensitive Compounds*; McGraw-Hill: New York, 1969.

(65) Kraihanzel, C. S.; Lasee, M. L. *J. Am. Chem. Soc.* **1968**, *90*, 4701.

(66) Hoffman, N. W. *Inorg. Chim. Acta* **1983**, *88*, 59.

(67) Fischer, E. O. *Inorg. Synth.* **1963**, *7*, 136.

(68) Still, W. C.; Kahn, M.; Mitra, A. *J. Am. Chem. Soc.* **1978**, *100*, 2923.

(69) The atomic coordinates for this work will be available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this paper.

needles (54% yield based on $Cp(CO)_3WNa$) were collected by filtration. These crystals, mp 36–37 °C, were judged to be pure by NMR, IR, and elemental analysis: IR (THF) 2022 (s), 1930 (vs), 1691 (m), 1235 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 4.62 (s, 5 H), 4.05 (q, 2 H, J = 7 Hz), 2.09 (s, 2 H, J_{WH} = 5.3 Hz), 1.10 (t, 3 H, J = 7 Hz); $\{^1H\}^{13}C$ NMR (C_6D_6) δ −14.82, 14.71, 59.33, 91.94, 181.25, 217.06, 229.64 (s); MS (CI w/methane), *m/z* 421 (M + 1), 335 (base). Anal. Calcd for $C_{12}H_{12}O_5W$: C, 34.31; H, 2.88. Found: C, 34.42; H, 2.89.

η^5-Pentamethylcyclopentadienyl(2-ethoxy-2-oxoethyl)tricarbonyltungsten (2), In a drybox, $W(CO)_6$ (1.663 g, 4.725 mmol) and $(CH_3)_5C_5Li$ (Cp*Li, 0.799 g, 5.62 mmol) were weighed into a 50-mL "Airless" Kontes flask fitted with condenser, magnetic stirring bar, and septum. On a Schlenk line under positive argon pressure 1,2-dimethoxyethane (glyme) (30 mL) was added. The light orange slurry was heated at 85 °C for 5 days. The color of the solution darkened over this period. An IR spectrum of this solution showed that very little $W(CO)_6$ remained. Ethyl chloroacetate (0.40 mL, 5.2 mmol) was added to the orange solution at room temperature. After stirring 3 h an IR spectrum of the reaction solution showed that the $Cp^*(CO)_3W$ anion had been consumed. The glyme was stripped from the reaction solution leaving an orange brown solid. The product was extracted from the LiCl with diethyl ether (4 × 25 mL). The ether was removed under vacuum. The orange solid was dissolved in a small amount of benzene and submitted to a flash silica gel column. Elution with 1:9 benzene/hexane separated a yellow band (32 mg) and an orange band (52 mg). Elution with 1:9 diethyl ether/hexane brought off the yellow $Cp^*(CO)_3WCH_2CO_2CH_2CH_3$ (1.52 g, 65%). Recrystallization from THF/hexane gave large amber crystals (1.29 g, 55%), mp 129–130 °C: IR (C_6D_6) 2014 (s), 1928 (s), 1696 (w), 1329 (w), 812 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 1.15 (t, 3 H, J = 7.14 Hz), 1.48 (s, 15 H), 1.65 (s, 2 H, J_{WH} = 6.86 Hz), 4.17 (q, 2 H, J = 7.14 Hz); $\{^1H\}^{13}C$ NMR (C_6D_6) δ −5.50, 10.00, 14.61, 59.03, 103.45, 181.08, 222.50, 234.12; UV–vis (cyclohexane) 3×10^{-4} M λ_{323} ϵ = 2280, λ_{378} ϵ = 925, 2.4×10^{-5} M λ_{207} ϵ = 41 200; MS (CI w/methane), *m/z* 491 (M + 1), 405 (base). Anal. Calcd for $C_{17}H_{22}O_5W$: C, 41.65; H, 4.52. Found: C, 41.74; H, 4.58.

η^5-Cyclopentadienyl(2-oxopropyl)tricarbonyltungsten (3), In a 100-mL, round-bottomed flask equipped with a stirring bar was placed $Cp(CO)_3WNa$ (1.49 g, 4.0 mmol) and THF (35 mL). To this solution was added chloroacetone (0.38 g, 4.1 mmol) via syringe. The reaction mixture was allowed to stir at room temperature for 1.5 h after which NaCl had precipitated. The solvent was removed under high vacuum, and the orange-brown residue was extracted with 3 25-mL portions of hexane. After filtration the combined hexane portions were concentrated to 25 mL under vacuum, and the solution was placed into a −40 °C refrigerator for 16 h. By filtration 874 mg of yellow-orange crystals (56% yield based on $Cp(CO)_3WNa$) was collected, mp 52–54 °C; IR (THF) 2140 (m), 2072 (m), 2022 (vs), 1988 (vs), 1668 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 4.61 (s, 5 H), 2.22 (q, 2 H, J = 0.7, J_{WH} = 6.7 Hz); 2.03, (t, 3 H, J = 0.7 Hz); $\{^1H\}^{13}C$ NMR (C_6D_6) δ −1.02, 30.04, 92.56, 212.54, 218.21, 228.60 (s); MS (CI w/methane), *m/z* 391 (M + 1), 335 (base). Anal. Calcd for $C_{11}H_{10}O_4W$: C, 33.87; H, 2.58. Found: C, 33.69; H, 2.53.

General Procedure for Large Scale Synthesis of $Cp(CO)_3MCH_2C(O)R$ Where M = Mo, W and R = Me, OEt, Ph (Method B): η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)tricarbonyltungsten (1), Example Procedure, In a 250-mL, round-bottomed flask equipped with a stirring bar and reflux condenser were placed $W(CO)_6$ (17.6 g, 50 mmol) and THF (75 mL). To this solution was added NaCp (5.5 g, 62 mmol) in THF (25 mL) via cannula under positive pressure. After having been stirred 1 h at room temperature ($Mo(CO)_6$ reaction is slightly exothermic), the reaction mixture was heated at reflux for 3 days (the $Mo(CO)_6$ reaction was complete in less than 16 h). The reddish yellow reaction mixture was cooled to room temperature, and ethyl chloroacetate (6.85 mL, 64 mmol) was added dropwise via syringe while stirring. After having been stirred an additional 4 h at room temperature, the volatiles were removed under high vacuum to leave a dark yellow-brown oil. This material was repeatedly extracted with hexane (5 × 75 mL) until a dry powdery solid remained. After filtration the yellow solution was concentrated under vacuum to a volume of 50 mL. The cold solution was filtered, yielding 13.0 g of yellow crystalline solid. A second crop was obtained after further concentration and overnight storage at −40 °C yielding an additional 0.795 g of product (total yield = 66%). This material was identical with **1** prepared by method A and could be used in subsequent reactions without further purification.

η^5-Cyclopentadienyl(2-oxopropyl)tricarbonyltungsten (3), Method B yielded 11.86 g (61%) of material identical with **3** prepared by method A.

η^5-Cyclopentadienyl(2-phenyl-2-oxoethyl)tricarbonyltungsten (4), Method B yielded 14.0 g (60%) of a yellow-gold crystalline solid, mp 82–3 °C. The material was recrystallized from hexane at −40 °C: IR (Et_2O) 2040 (s), 1934 (vs), 1643 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 2.83 (s, 2 H), 4.70 (s, 5 H), 7.15 (m, 3 H), 7.92 (m, 2 H); $\{^1H\}^{13}C$ NMR (C_6D_6) δ −7.64, 92.53, 128.44, 128.65, 131.64, 139.66, 206.43, 218.02, 229.34. Anal. Calcd for $C_{16}H_{12}WO_4$: C, 42.50; H, 2.68. Found: C, 42.49; H, 2.81.

η^5-Cyclopentadienyl(2-(diethylamino)-2-oxoethyl)tricarbonyltungsten (5), In the drybox, $Cp(CO)_3W^-Na^+$ (0.293 g, 0.823 mmol) was weighed into a 25-mL Kontes "Airless" flask. THF (5.0 mL) and 2-chloro-*N*,*N*-diethylamide (0.010 mL, 0.73 mmol) were added to the reaction vessel, and the solution stirred 4 h. The reaction solution was concentrated to ~1 mL, and NaCl precipitated from the yellow solution. The NaCl was filtered off, and hexane was layered over the deep yellow solution. Upon chilling to −40 °C yellow crystals formed, 180 mg (49%), mp 89–91 °C. A second crop was collected, 47 mg, mp 88–89 °C (62% combined yield): IR (toluene) 2016 (s), 1923 (s), 1605 (m), 1276 (w) cm^{-1}; ^1H NMR (C_6H_6) δ 0.86 (t, 3 H, J = 7.06 Hz), 1.07 (t, 3 H, t = 7.03 Hz), 2.09 (s, 2 H), 2.92 (q, 2 H, J = 7.06 Hz), 3.30 (q, 2 H, J = 7.03 Hz), 5.00 (s, 5 H); $\{^1H\}^{13}C$ NMR (C_6D_6) δ −16.71 (J_{WC} = 34.6 Hz), 13.65, 14.29, 40.11, 43.44, 92.34, 179.29, 219.41 (J_{WC} = 155.6 Hz), 230.12; MS (CI w/methane), *m/z* 448 (M + 1), 390 (base); EI (70 eV), *m/z* 419 (M − 28), 306 (base). Anal. Calcd for $C_{14}H_{13}NO_4W$: C, 37.61; H, 3.83; N, 3.13. Found: C, 37.72; H, 3.79; N, 3.14.

η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)tricarbonylmolybdenum (6), Method B yielded 12.06 g (73%) of crystalline solid, mp 32.5–33.5 °C (lit.[12a] mp 33–34 °C): IR (THF) 2030 (s), 1940 (s), 1687 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 4.68 (s, 5 H), 4.02 (q, 2 H, J = 7 Hz), 1.84 (s, 2 H), 1.09 (t, 3 H, J = 7 Hz); $\{^1H\}^{13}C$ NMR (C_6D_6) δ −3.94, 14.73, 59.32, 93.51, 181.02, 227.04, 240.63; MS (CI w/methane), *m/z* 333 (M + 1), 89 (base). Anal. Calcd for $C_{12}H_{12}O_5Mo$: C, 43.39; H, 3.64. Found: C, 43.13; H, 3.79.

η^5-Cyclopentadienyl(2-oxopropyl)tricarbonylmolybdenum (7), Method B yielded 4.30 g (29%) of a reddish crystalline solid, mp 28–29 °C: IR (THF) 2026 (s), 1978 (w), 1933 (s), 1658 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 4.62 (s, 5 H), 2.03 (s, 3 H), 1.98 (s, 2 H); $\{^1H\}^{13}C$ NMR (C_6D_6) δ 8.54, 30.13, 94.02, 211.91, 228.10, 239.74; MS (CI w/methane), *m/z* 303 (M + 1), 59 (base). Anal. Calcd for $C_{11}H_{10}O_4Mo$: C, 43.73; H, 3.34. Found: C, 43.44; H, 3.34.

η^5-Cyclopentadienyl(2-amino-2-oxoethyl)tricarbonyltungsten (8), Compound **8** was prepared by the method of Green and Prout.[13c] Spectral properties matched those in the literature, mp 149–151 °C: IR (CH_2Cl_2) 2022 (s), 1921 (s), 1649 (m), 1264 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.00 (s, 2 H), 5.2 (br s, 2 H), 5.56 (s, 5 H); ^1H NMR (C_6D_6) 1.83 (s, 2 H), 4.4 (br s, 1 H), 4.78 (s, 5 H), 4.8 (br s, 1 H); ^{13}C NMR (acetone-d_6) −11.2 (J_{WC} = 17 Hz), 93.60, 183.44, 219.22 (J_{WC} = 156 Hz), 231.48; MS (CI w/methane), *m/z* 392 (M + 1), 335 (base). Anal. Calcd for $C_{10}H_9NO_4W$: C, 30.71; H, 2.32; N, 3.59. Found: C, 30.58; H, 2.24; N, 3.53.

η^5-Cyclopentadienyl(1-methyl-2-ethoxy-2-oxoethyl)tricarbonyltungsten (9), The methanesulfonate (mesylate) of ethyl lactate was prepared by the method of Hillis and Ronald[70] and distilled before use. In a 5-mm NMR tube was placed the mesylate (47 mg, 0.24 mmol), $Cp(CO)_3WNa$ (160 mg, 0.45 mmol), and THF-d_8 (1 mL). The tube was capped and placed into a 78 °C oil bath for 8 h at which time all the starting mesylate was consumed. The solvent was removed, and the reaction mixture was extracted with pentane, filtered, and recrystallized from pentane giving 80 mg (77%) of **9**, mp 42–43 °C: IR (ether) 2050 (s), 1945 (vs), 1700 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 1.11 (t, 3 H, J = 7 Hz), 1.64 (d, 3 H, J = 7 Hz), 3.06 (q, 1 H, J = 7, $J_{W\text{-}H}$ = 5.5 Hz), 4.04 (q, 2 H, J = 7 Hz), 4.65 (s, 5 H); $\{^1H\}^{13}H$ NMR (C_6D_6) δ −0.75, 14.64, 24.23, 59.22, 88.51, 92.48, 183.04, 218.03, 219.12, 229.81. Anal. Calcd for $C_{13}H_{14}O_5W$: C, 35.97; H, 3.25. Found: C, 35.57; H, 3.15.

η^5-Cyclopentadienyl(1-phenyl-2-ethoxy-2-oxoethyl)tricarbonyltungsten (10), The mesylate of ethyl mandelate was prepared by the method of Hillis and Ronald[70] and distilled before use. In a 50-mL, round-bottomed flask was placed $Cp(CO)_3WNa$ (2.0 g, 5.62 mmol), the mesylate (1.45 g, 5.62 mmol), and THF (25 mL). After having been stirred at room temperature for 16 h under a N_2 atmosphere, the solvent was removed under vacuum. The reaction mixture was extracted with pentane, filtered, and recrystallized from pentane giving 2.56 g (92%) of yellow crystalline solid, mp 116–117 °C: IR (ether) 2040 (s), 1942 (s), 1698 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 1.07 (t, 3 H, J = 7 Hz), 4.03 (dq, 2 H, J = 7, 4.5 Hz), 4.26 (s, 1 H, $J_{W\text{-}H}$ = 6.5 Hz), 4.51 (s, 5 H), 6.94 (t, 1 H, J = 8 Hz), 7.15 (d, 2 H, J = 8 Hz), 7.58 (d, 2 H, J = 8 Hz); $\{^1H\}^{31}C$ NMR (C_6D_6) δ 10.43, 14.44, 59.52, 93.34, 124.83, 128.00, 128.14, 148.52, 179.60, 219.84, 229.83. Anal. Calcd for $C_{18}H_{16}O_5W$: C, 43.56; H, 3.25. Found: C, 43.32; H, 3.13.

η^5-Cyclopentadienyl(2-hydroxy-2-oxoethyl)tricarbonyltungsten (12a), Compound **12a** can be prepared by the method of Green and Prout[13c] from $Cp(CO)_3WCH_2CONH_2$ or alternatively from **1** as follows. In air,

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(70) Hillis, L. R.; Ronald, R. C. *J. Org. Chem.* **1981**, *46*, 3348.

$Cp(CO)_3WCH_2CO_2CH_2CH_3$ (0.254 g, 0.605 mmol) was weighed into a 25-mL, round-bottomed flask equipped with a magnetic stirring bar and a condenser. THF (10 mL) and HCl (2 mL, 12 M) were added, and the stirring solution was heated at 90 °C for 20 min. The yellow solution was allowed to cool, and H_2O (10 mL) was added which precipitated a small amount of $Cp(CO)_3WCH_2CO_2H$. The THF was removed with a rotatory evaporator to precipitate $Cp(CO)_3WCH_2CO_2H$. The yellow solid was filtered, washed with H_2O (10 mL), and dried under high vacuum, 0.237 g (100%), mp 203–204 °C (dec). Spectral properties matched those reported in the literature:[1b] IR (KBr) 2020 (s), 1936 (br s), 1914 (s), 1886 (s), 1649 (s), 1286 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 2.04 (s, 2 H, J_{WH} = 5.4 Hz), 4.56 (s, 5 H); ^1H NMR (CD_2Cl_2) δ 1.78 (s, 2 H), 5.08 (s, 5 H).

η^5-Pentamethylcyclopentadienyl(2-hydroxy-2-oxoethyl)tricarbonyltungsten (12b). By the foregoing procedure $(CH_3)_5C_5(CO)_3WCH_2CO_2H$ was prepared by hydrolysis of $(CH_3)_5C_5(CO)_3WCH_2CO_2Et$. After recrystallization from CH_2Cl_2–hexane, complex **12b**, mp 193–195 °C (with darkening), was obtained in 61% yield: IR (THF) 2014 (s), 1929 (s), 1699 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 1.57 (s, 2 H), 1.44 (s, 15 H); $\{^1H\}^{13}C$ NMR (CD_2Cl_2) δ −5.66, 10.55, 104.06, 188.66, 222.75, 233.43; MS (EI, 70 eV), m/z 434 (M^+), 334 (base). Anal. Calcd for $C_{14}H_{18}O_4W$: C, 38.70; H, 4.18. Found: C, 38.68; H, 3.99.

η^5-Cyclopentadienyl(2-chloro-2-oxoethyl)tricarbonyltungsten (13). $Cp(CO)_3WCH_2CO_2H$ (0.206 g, 0.525 mmol) was weighed into a 50-mL Kontes "Airless" flask equipped with a magnetic stirring bar and a rubber septum. The apparatus was evacuated and refilled with nitrogen 3 times before addition of 8 mL of benzene via syringe. Oxalyl chloride (60.0 μL, 0.688 mmol) was added dropwise to the stirring yellow solution. The yellow cloudy solution became transparent as $Cp(CO)_3WCH_2CO_2H$ dissolved. After having been stirred for 30 min, the solution was concentrated to ca. 1 mL under vacuum and then filtered under nitrogen. The remaining benzene was removed in vacuo, leaving 202 mg of a yellow solid. Recrystallization from toluene/pentane gave 153 mg (71%) of acid chloride **13**, mp 73–74 °C: IR (C_6H_6) 2030 (s), 1950 (s), 1775 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 4.46 (s, 5 H), 2.29 (s, 2 H, J_{WH} = 5.8 Hz); ^1H NMR (toluene-d_8) δ 2.25 (s, 2 H), 4.66 (s, 5 H); $\{^1H\}^{13}C$ NMR (toluene-d_8) δ −2.43, 92.27, 177.15, 216.96 (J_{WC} = 153 Hz), 227.63; MS (CI w/methane), m/z 409 (M − 1), 59 (base). Anal. Calcd for $C_{10}H_7ClO_4W$: C, 29.26; H, 1.72; Cl, 8.64. Found: C, 29.32; H, 1.87; Cl, 8.38.

η^5-Cyclopentadienyl[2-(prop-2-ynyloxy)-2-oxoethyl]tricarbonyltungsten (14a). Acid chloride **13** (~0.23 mmol in ether, 5 mL) and excess propargyl alcohol (0.50 mL, 0.963 mmol) were stirred 15 min in a 10-mL, round-bottomed flask under nitrogen. The ether was removed to obtain a golden viscous oil which was chromatographed in a drybox. The column was eluted with 1:10 diethyl ether/hexane and then with increasing concentrations of ether in hexane. Slightly impure $Cp(CO)_3WCH_2CO_2CH_2CCH$ (103 mg) obtained from the deep yellow solutions was dissolved in toluene and filtered to remove the $Cp(CO)_3WCH_2CO_2H$ (10 mg). Hexane was added to the deep yellow solution and it was cooled to −40 °C. Yellow crystals of $Cp(CO)_3WCH_2CO_2CH_2CCH$ were collected by filtration (80 mg, 89%), mp 41–42 °C. This compound is very light sensitive, especially when in solution: IR (C_6D_6) 2027 (s), 1934 (s), 1617 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 2.01 (t, 1 H, J = 2.4 Hz), 2.04 (s, 2 H, J_{WH} = 5.4 Hz), 4.48, (d, 2 H, ^4J = 2.4 Hz), 4.69 (s, 5 H); $\{^1H\}^{13}C$ NMR (C_6D_6) δ −15.68, 50.59, 74.09, 92.00, 180.28, 216.80, 229.44; MS (CI w/methane), m/e 431 (M + 1), 335 (base). Anal. Calcd for $C_{13}H_{10}O_5W$: C, 36.31; H, 2.34. Found: C, 36.22; H, 2.33.

η^5-Cyclopentadienyl[2-(but-3-ynyloxy)-2-oxoethyl]tricarbonyltungsten (14b). From the tungsten acid **12a** was prepared $Cp(CO)_3WCH_2CO_2CH_2CH_2CCH$ in 61% yield by the same procedure as for $Cp(CO)_3WCH_2CO_2CH_2CCH$, mp 44–46°C: IR (C_6D_6) 2014 (s), 1930 (vs), 1694 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 1.78 (t, 1 H, J = 2.64 Hz), 2.02 (s, 2 H), 2.28 (dt, 2 H, J = 2.64 Hz, 6.80 Hz), 4.03 (t, 2 H, J = 6.80 Hz), 4.70 (s, 5 H); $\{^1H\}^{13}C$ NMR (C_6D_6) δ −15.32 (J_{WC} = 34 Hz), 19.37, 61.57, 70.15, 81.10, 92.00, 180.93, 217.00, 229.52 (J_{WC} = 156 Hz); MS (CI w/methane), m/z 445 (M + 1), 375 (base). Anal. Calcd for $C_{14}H_{12}O_5W$: C, 37.86; H, 2.72. Found: C, 37.77; H, 2.72.

η^5-Cyclopentadienyl[2-(phenylamino)-2-oxoethyl]tricarbonyltungsten (14c). From the tungsten acid **12a** was prepared $Cp(CO)_3WCH_2CON(H)Ph$ in 69% yield by the same procedure as for $Cp(CO)_3WCH_2CO_2CH_2CCH$, mp 180–182 °C: IR (THF) 2017 (s), 1920 (s), 1665 (w) cm^{-1}; ^1H NMR (THF-d_8) δ 2.14 (s, 2 H), 5.73 (s, 5 H), 6.88 (m, 1 H), 7.16 (m, 2 H), 7.57 (m, 2 H), 8.16 (s, 1 H); $\{^1H\}^{13}C$ NMR (THF-d_8) δ −9.67 (J_{WC} = 33 Hz), 93.50, 122.75, 129.05, 141.21, 179.70, 219.29 (J_{WC} = 155 Hz), 230.56 (J_{WC} = 126 Hz); MS (CI w/methane), m/z 468 (M + 1), 136 (base). Anal. Calcd for $C_{16}H_{13}NO_4W$: C, 41.14; H, 2.80; N, 3.00. Found: C, 41.21; H, 2.76; N, 3.01.

Irradiation of 1–7 in C_6D_6 (Example Procedure with 1). In a 5-mm NMR tube was placed tungsten ester **1** (50 mg, 0.12 mmol) in 1 mL of C_6D_6. The tube was sealed under vacuum and irradiated for 3 h at 6 °C. Examination by ^1H NMR spectroscopy showed complex **15** (60%), ethyl acetate (5%), and starting **1** (35%). The following spectral data were deduced for complex **15**: IR (Et_2O) 1942 (s), 1847 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 0.86 (t, 3 H, J = 7 Hz), 2.85 (d, 1 H, J = 5.5, J_{WH} = 5.5 Hz), 3.49 (d, 1 H, J = 5.5, J_{WH} = 2.6 Hz), 3.68 (dq, 1 H, J = 7 Hz), 3.91 (dq, 1 H, J = 7 Hz), 4.92 (s, 5 H); $\{^1H\}^{13}C$ NMR (C_6D_6) δ 13.04 (J_{CH} = 150, 158 Hz), 14.32, 61.34, 94.43, 159.22, 240.01, 244.60.

Complex 16: ^1H NMR (C_6D_6) δ 4.90 (s, 5 H), 3.34 (d, 1 H, J = 1.3 Hz), 2.94 (d, 1 H, J = 1.3 Hz), 2.35 (s, 3 H); $\{^1H\}^{13}C$ NMR (C_6D_6) δ 21.64, 34.63, 93.71, 144.62, 233.44, 237.23.

Complex 17: ^1H NMR (C_6D_6) δ 2.98 (d, 1 H, J = 2 Hz), 4.07 (d, 1 H, J = 7 Hz), 4.90 (s, 5 H), 7.05 (m, 3 H), 7.84 (m, 2 H).

η^5-Cyclopentadienyl-η^3-(2-(diethylamino)-2-oxoethyl)dicarbonyltungsten (18). The best method for the preparation of **18** is as follows: In the drybox trimethylamine-N-oxide (71.8 mg, 0.956 mmol) in a 25-mL, round-bottomed flask was dissolved in acetonitrile (12 mL). A solution of $Cp(CO)_3WCH_2CONEt_2$ (323.2 mg, 0.7228 mmol, in 3 mL of CH_3CN) was added to the stirring solution of Me_3NO. The orange solution became dark red after several min. The reaction was shown to be complete by TLC (alumina, benzene eluant) after 45 min. The solvent was removed under vacuum, and the dark red solution was dissolved in THF and filtered. Hexane was layered over the THF solution. Chilling to −40 °C yielded 249 mg (82%) of dark red prisms, mp 122–123 °C. A second crop was obtained, 23 mg, giving a total yield of 90%. Recrystallization from toluene/hexane gave several air stable crystals which were suitable for X-ray crystallography: IR (C_6D_6) 1926 (s), 1826 (s), 1548 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 0.74 (t, 3 H, J = 7.17 Hz), 0.78 (t, 3 H, J = 7.17 Hz), 2.49 (d, 1 H, J = 7.4 H), 2.52 (m, 2 H), 2.77 (d, 1 H, J = 7.4 Hz), 2.80 (m, 2 H), 3.20 (m, 1 H), 5.12 (s, 5 H); ^1H NMR (toluene-d_8) δ 0.78 (t, 3 H, J = 7.1 Hz), 0.82 (t, 3 H, J = 7.1 Hz), 2.45 (d, 1 H, J = 7.5 Hz), 2.55 (m, 1 H), 2.62 (m, 1 H), 2.74 (d, 1 H, J = 7.5), 2.83 (m, 1 H), 3.18 (m, 1 H), 5.15 (s, 5 H); $\{^1H\}^{13}C$ NMR (C_6D_6) δ 4.07, 12.83, 13.62, 38.40, 40.77, 94.57, 163.20, 248.04, 250.43; coupled ^{13}C NMR (C_6D_6) δ 4.09 (J = 143.3, 143.1 Hz), 12.83 (J = 128.4 Hz), 13.63 (J = 126.1 Hz), 38.43 (J = 133.9 Hz), 40.79 (J = 139.4 Hz), 94.57 (^1J = 177.8 Hz, ^2J = 6.8 Hz), 163.17, 248.05, 150.45; MS (EI, 70 eV), m/z 419 (M^+), 306 (base). Anal. Calcd for $C_{13}H_{17}NO_3W$: C, 37.25; H, 4.09; N, 3.34. Found: C, 37.35; H, 4.14; N, 3.31.

Complex 19: ^1H NMR (C_6D_6) δ 4.89 (s, 5 H), 3.86 (dq, 1 H, J = 7.3 Hz), 3.58 (dq, 1 H, J = 7, 3 Hz), 3.31 (d, 1 H, J = 4.5 Hz), 2.67 (d, 1 H, J = 4.5 Hz), 0.87, (t, 3 H, J = 7 Hz).

Complex 20: ^1H NMR (C_6D_6) δ 4.90 (s, 5 H), 3.29 (s, 1 H), 2.74 (s, 1 H), 1.91 (s, 3 H).

Complex 21: In the drybox $C_5Me_5(CO)_3WCH_2CO_2CH_2CH_3$ (21.6 mg, 0.0441 mmol) was weighed into an NMR tube and dissolved in 0.6 mL of C_6D_6. The capped tube was irradiated for 1 h at −30 °C and shown to be completely converted to $Cp(CO)_2WCH_2COOCH_2CH_3$ by ^1H NMR spectroscopy: IR (C_6D_6) 1929 (s), 1833 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 0.86 (t, 3 H, J = 7.17 Hz), 1.66 (s, 15 H), 1.72 (d, 1 H, J = 5.24 Hz), 3.68 (m, 1 H), 3.72 (d, 1 H, J = 5.24 Hz), 3.92 (m, 1 H); $\{^1H\}^{13}C$ NMR (C_6D_6) δ 10.30, 10.59, 14.24, 60.99, 105.43, 158.83, 244.14, 246.75.

Preparation of *cis*- and *trans*-η^5-Cyclopentadienyl(2-(diethylamino)-2-oxoethyl)(trimethylphosphine)dicarbonyltungsten (22a) and (22b). $Cp(CO)_2WCH_2CON(CH_2CH_3)_2$ (72.4 mg, 0.173 mmol) and CD_2Cl_2 (0.64 mL) were placed in an NMR tube (Wilmad 505PS). The solution was freeze-pump-thawed 3 times before PMe_3 (0.184 mmol) was condensed into the tube. The tube was then sealed and allowed to remain at ambient temperature for 3 days. A ^1H NMR spectrum showed that the reaction was complete, yielding a mixture of cis and trans substituted products in a ratio of 1:3.8. The tube was opened under nitrogen, and the yellow solution was transfered to a 3-mL vial. Pentane diffusion into the solution induced crystallization of 71.3 mg (83.4%) of yellow crystals, 89–91 °C. A second crop of 10.0 mg was obtained giving a combined yield of 95.1%: IR (KBr) 1916 (s), 1826 (s), 1812 (s), 1593 (m) cm^{-1}; IR (CH_2Cl_2) 1922 (s), 1830 (s), 1586 (m); ^1H NMR (C_6D_6) cis isomer δ 0.95 (d, 9 H, J_{PH} = 8.8 Hz), 1.27 (t, 3 H, J = 7.00 Hz), 1.29 (t, 3 H, J = 6.88 Hz), 1.50 (dd, 1 H, J_{PH} = J = 8 Hz), 1.60 (dd, 1 H, J_{PH} = J = 8 Hz), 3.03 (m, 1 H), 3.15 (m, 1 H), 3.38 (m, 1 H), 3.89 (m, 1 H), 5.02 (s, 5 H); ^1H NMR (C_6D_6) trans isomer δ 1.03 (d, 9 H, J_{PH} = 9.24 Hz), 1.0 (2 t, 6 H), 2.39 (d, 2 H, J_{PH} = 4.86 Hz), 3.33 (q, 2 H, J = 7.0 Hz), 3.56 (q, 2 H, J = 6.86 Hz), 4.39 (d, 5 H, J_{PH} = 1.93 Hz); ^1H NMR (CD_2Cl_2) cis isomer δ 1.01 (t, 3 H, J = 7.0 Hz), 1.06 (t, 3 H, J = 7.0 Hz), 1.34 (dd, 1 H, J = 12.6, 9.8 Hz), 1.51 (dd, 1 H, J = 6.6, 9.9 Hz), 3.0 (m, 3 H), 3.55 (m, 1 H), 5.39 (s, 5 H); ^1H NMR (CD_2Cl_2) trans isomer δ 1.04 (t, 3 H, J = 7.0 Hz), 1.11 (t, 3 H, J = 7.0 Hz), 1.52 (d, 9 H, J_{PH} = 9.0 Hz), 3.17 (q, 2 H, J = 7.0 Hz), 3.27 (q, 2 H, J = 7.0 Hz), 5.19 (d, 5 H, J_{PH} = 1.97 Hz); $\{^1H\}^{13}C$ NMR (CD_2Cl_2) cis isomer δ −10.21 (J_{PC} = 8.15 Hz), 13.80, 14.39, 39.88, 43.56, 91.38, 182.76, CO's not observed; $\{^1\mathrm{H}\}^{13}\mathrm{C}$ NMR (CD$_2$Cl$_2$) trans isomer δ 15.00 (J_{PC} = 8.15 Hz), 20.92, 21.39, 39.64, 43.33, 90.30, 182.58, 232.18 (J_{PC} = 17.9 Hz); ^{31}P NMR (C$_6$D$_6$), cis isomers δ −19.50 (J_{WP} = 270.6 Hz); ^{31}P NMR (C$_6$D$_6$) trans isomer, δ −16.27 (J_{WP} = 207.8 Hz); MS (CI with methane), *m/z* 496 (M + 1), 381 (base). Anal. Calcd for C$_{16}$H$_{26}$PNO$_3$W: C, 38.81; H, 5.29; N, 2.83; P, 6.25. Found: C, 39.04; H, 5.44; N, 2.83; P, 6.06.

trans-η^5-Cyclopentadienyl(2-(diethylamino)-2-oxoethyl)(triphenylphosphine)dicarbonyltungsten (23), In the drybox, Cp(CO)$_2$WCH$_2$CONEt$_2$ (31.8 mg, 0.0759 mmol) and triphenylphosphine (20.8 mg, 0.0793 mmol) were weighted into an NMR tube. The solids were dissolved in C$_6$D$_6$ (0.50 mL), and the resulting dark red solution degassed by successive freeze–pump–thaw cycles. The reaction was monitored by ^{1}H NMR. The tube was heated at 65 °C for 9 days whereupon the desired product comprised 80% of the mixture. Of the remaining components, only starting material (10%) was positively identified. The solution was transfered to a 3-mL vial in the drybox, and pentane (∼1 mL) was layered over the orange solution. The next day the yellow crystals (33.0 mg, 66.0%, mp 191–194 °C) were filtered from the solution and rinsed with benzene. A second crop of impure (contaminated with Cp(CO)$_2$WCH$_2$CONEt$_2$) yellow-orange crystals (15.0 mg) was obtained by concentration of the filtrate. This material was recrystallized from toluene/pentane to give 8.7 mg of yellow crystals of complex **23** for a combined yield of 80% pure product: IR (KBr) 1932 (s), 1845 (s), 1598 (m) cm^{-1}; IR (CH$_2$Cl$_2$) 1928 (s), 1842 (vs), 1586 (m) cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 1.05 (t, 3 H, J = 7.04 Hz), 1.24 (t, 3 H, J = 7.04 Hz), 2.35 (d, 2 H, J_{PH} = 3.97 Hz), 3.29 (q, 2 H, J = 7.04 Hz), 3.53 (q, 2 H, J = 7.04 Hz), 4.96 (d, 5 H, J_{PH} = 1.57 Hz), 6.98 (m, 9 H), 7.47 (br s, 6 H); ^{1}H NMR (CD$_2$Cl$_2$) δ 1.05 (t, 3 H, J = 7.10 Hz), 1.16 (t, 3 H, J = 7.10 Hz), 2.05 (d, 2 H, J_{PH} = 3.75), 3.21 (q, 2 H, J = 7.10 Hz), 3.31 (q, 2 H, J = 7.10 Hz), 5.07 (d, 5 H, J_{PH} = 1.61 Hz), 7.42 (br s, 15 H); $\{^1\mathrm{H}\}^{13}\mathrm{C}$ NMR (CD$_2$Cl$_2$) δ −13.96 (J_{PC} = 7.6 Hz), 13.83, 14.46, 39.72, 43.46, 91.91, 128.63 ($\mathrm{J_{PC}}$ = 9.9 Hz), 130.62, 133.82 (J_{PC} = 10.5 Hz), 136.37 (J_{Pc} = 48.8 Hz), 181.84, 232.33 (J_{PC} = 19.2 Hz); ^{31}P NMR (C$_6$D$_6$) δ 51.6; MS (CI with methane), *m/z* 682 (M + 1), 185 (base). Anal. Calcd for C$_{31}$H$_{32}$NO$_3$PW: C, 54.64; H, 4.73; N, 2.06; P, 4.54; Found: C, 54.45; H, 4.69; N, 2.09; P, 4.21.

cis-η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)(triphenylphosphine)dicarbonyltungsten (24), Tungsten ester **1** (0.5 g, 1.2 mmol) and 200 mL of ether were placed into a 250-mL Ace photochemical reactor. While maintaining the in situ temperature below 6 °C and purging the solution with nitrogen gas, the contents were irradiated for 12 min with a 450-W Hanovia lamp. To the stirring reaction mixture at 6 °C was added via syringe a solution of triphenylphosphine (320 mg, 1.22 mmol) in 20 mL of ether. After allowing the reaction mixture to warm slowly to room temperature the contents of the reactor were cannulated into a Kontes "Airless" flask, and the solvent was removed under high vacuum. The residue was triturated with hexane (3 × 50 mL), resulting in 0.64 g (82%) of a solid product, mp 134–135 °C, which was collected by filtration: IR (THF) 1937 (s), 1854 (m), 1678 (w) cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 7.34 (m, 6 H), 6.98 (m, 9 H), 5.07 (s, 5 H), 4.17 (dq, 2 H, J = 7, J_{PH} = 0.7 Hz), 1.94 (dd, 1 H, J = J_{PH} = 9.5 Hz), 1.59 (dd, 1 H, J = J_{PH} = 9.5 Hz), 1.17 (t, 3 H, J = 7 Hz); ^{13}C NMR (C$_6$D$_6$) δ −5.84 (d, J = 12.5 Hz), 15.03, 58.74, 91.72, 128.61 (d, J = 9.5 Hz), 130.34, 133.90 (d, J = 10 Hz), 134.43 (d, J = 45 Hz), 183.01 (d, J = 9 Hz), 232.60 (d, J = 4.5 Hz), 247.07 (d, J = 20 Hz); ^{31}P NMR (C$_6$D$_6$) δ 35.2 (J_{PW} = 43.5); MS (CI with methane), *m/z* 655 (M + 1), 262 (base). Anal. Calcd for C$_{29}$H$_{27}$O$_4$PW: C, 53.23; H, 4.16; P, 4.73. Found: C, 53.09; H, 4.10; P, 4.34.

trans-η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)(triphenylphosphine)dicarbonyltungsten (25), A solution of **24** (40 mg, 0.06 mmol) in benzene (1 mL) was heated at 60 °C for 2 h. The solvent was removed, and the solid residue was triturated with hexane to obtain a yellow solid, mp 134–135 °C: IR (THF) 1942 (m), 1858 (s), 1680 (w) cm^{-1}; ^{1}H NMR (C$_6$D$_6$ at 60 °C) δ 7.45 (m, 6 H), 7.00, (m, 9 H), 4.79 (d, 5 H, J = 1.5 Hz), 4.22 (q, 2 H, J = 7 Hz), 2.56 (d, 2 H, J = 3.5 Hz), 1.20 (t, 3 H, J = 7 Hz); $\{^1\mathrm{H}\}^{13}\mathrm{C}$ NMR (C$_6$D$_6$ at 60 °C) δ −12.54 (d, J = 10 Hz), 14.98, 58.83, 91.84, 128.52 (d, J = 10.5 Hz), 130.34 (d, J = 2 Hz), 133.92 (d, J = 10 Hz), 136.91 (d, J = 48 Hz), 182.50, 229.04 (d, J = 18 Hz); ^{31}P NMR (C$_6$D$_6$) δ 40.6 (J_{PW} = 35 Hz); MS (CI with methane), *m/z* 655 (M + 1), 262 (base). Anal. Calcd for C$_{29}$H$_{27}$O$_4$PW: C, 53.23; H, 4.16. Found: C, 53.23; H, 3.86.

Preparation of a Solution of _cis_-η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)(trideuterioacetonitrile)dicarbonyltungsten (26), In an NMR tube were placed Cp(CO)$_3$WCH$_2$CO$_2$Et (25.9 mg, 0.062 mmol) and 0.50 mL of CD$_3$CN. The tube was capped with a rubber septum and wrapped with Parafilm. To remove the evolved CO, nitrogen was bubbled through the solution during the photolysis via a 20-gauge inlet needle and a 27-gauge outlet needle. The yellow solution was irradiated for 45 min, after which the conversion of the starting material to Cp(CO)$_2$(CD$_3$CN)WCH$_2$CO$_2$Et was >90% complete as shown by a ^{1}H NMR spectrum of the red-orange solution: IR (CD$_3$CN) 1933 (s), 1834 (s), 1675 (m) cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 5.49 (s, 5), 3.90 (m, 2 H), 1.83 (d, 1 H, J = 7.8, J_{WH} = 7.4 Hz), 1.72 (d, 1 H, J = 7.8, J_{WH} = 6.4 Hz), 1.16 (t, 3 H, J = 7.1 Hz); $\{^1\mathrm{H}\}^{13}\mathrm{C}$ NMR (CD$_3$CN) δ −1.72, 15.0, 58.8, 93.7, 182.9, 245.4, 255.8.

Alternatively, Cp(CO)$_2$(CH$_3$CN)WCH$_2$CO$_2$Et can be prepared by reaction of 1 mol equiv of trimethylamine-*N*-oxide with Cp(CO)$_3$WCH$_2$CO$_2$Et in acetonitrile.

cis-η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)(pyridine)dicarbonyltungsten (27), Tungsten ester **1** (0.765 g, 1.82 mmol), pyridine (0.75 mL, 9.27 mmol), and pentane (50 mL) were placed into a 50-mL photochemical reactor equipped with a uranium glass filter. The solution was irradiated for 30 min at 5 °C. An orange precipitate formed during photolysis and upon warming the reactor to room temperature. The precipitate was filtered from the reaction solution and dried under nitrogen. There was obtained 0.30 g (35%) of orange solid, mp 92–93 °C: IR (KBr) 1914 (s), 1808 (s), 1673 (m) cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 1.11 (t, 3 H, J = 7 Hz), 1.96 (d, 1 H, J = 10, J_{WH} = 9.5 Hz), 2.14 (d, 1 H, J = 10, J_{WH} = 7 Hz), 3.94 (dq, 1 H, J = 3.5, J = 7 Hz), 4.10 (dq, 1 H, J = 3.5, J = 7 Hz), 5.15 (s, 5 H), 6.17 (t, 2 H), 6.36 (t, 1 H), 8.15 (d, 2 H), $\{^1\mathrm{H}\}^{13}\mathrm{C}$ NMR (C$_6$D$_6$) δ 7.54, 14.92, 58.54, 93.83, 124.91, 135.64, 157.21, 182.50, 240.24, 260.63. Anal. Calcd for C$_{16}$H$_{17}$NO$_4$W: C, 40.78; H, 3.64; N, 2.97. Found: C, 40.59; H, 3.59; N, 2.77.

η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)(phenylacetylene)carbonyltungsten (28), In a drybox Cp(CO)$_3$WCH$_2$CO$_2$Et (0.421 g, 1.00 mmol) was placed in a 25-mL Kontes "Airless" flask and dissolved in benzene (15 mL). The flask was capped with a septum, removed from the dry box, and placed under nitrogen on a Schlenk line. The flask was irradiated 1 h while bubbling nitrogen through the solution via a needle. An IR spectrum of an aliquot of the dark red solution showed that the starting material was converted to oxaallyl complex **15**. Phenylacetylene (0.11 mL, 1.0 mmol) was added via syringe, and the solution was stirred 15 min. The solvent was removed under reduced pressure leaving a dark red oil. This material was submitted to flash chromatography on silica gel (1 × 20 cm column), eluting with benzene, to separate tungsten dimer **11** (26.7 mg, 11%) and starting material (63 mg, 15%). Elution with diethyl ether gave Cp(CO)(PhCCH)WCH$_2$CO$_2$Et (271.5 mg, 58%) as a dark red oil, which crystallized after being kept overnight at room temperature, mp 68–69 °C: IR (C$_6$D$_6$) 1932 (s), 1686 (m), 1242 (m) cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 12.40 (s, 1 H), 7.57 (m, 2 H), 7.25 (m, 3 H), 5.07 (s, 5 H), 4.01–4.18 (m, 2 H), 1.90 (d, 1 H, J = 9.5 Hz), 1.09 (d, 1 H, J = 9.5 Hz), 1.06 (t, 3 H, J = 7.0 Hz); $\{^1\mathrm{H}\}^{13}\mathrm{C}$ NMR (C$_6$D$_6$) δ 4.78 (J_{WC} = 4.6 Hz), 5.35, 14.91, 58.76, 93.27, 128.69, 129.22, 130.38, 132.50, 136.29, 183.71, 191.78 (J_{WC} = 15 Hz), 201.23, 233.11; MS (CI w/methane), *m/z* 467 (M − 1), 379 (base). Anal. Calcd for C$_{18}$H$_{18}$O$_3$W: C. 46.38; H, 3.89. Found: C, 46.51; H, 3.88.

cis-η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)(η^1-bis(diphenylphosphino)methane)dicarbonyltungsten (29), In a drybox, trimethylamine-*N*-oxide (14.0 mg, 0.19 mmol) and Cp(CO)$_3$WCH$_2$CO$_2$Et (80.8 mg, 0.19 mmol) were weighed into a 3-mL vial equipped with a micromagnetic stirring bar. Upon addition of acetonitrile (1.0 mL) bubbles of gas (presumably CO$_2$) were immediately evolved, and the color of the solution changed from yellow to orange. The capped vial was covered with aluminum foil to protect the solution from light. After stirring 45 min, approximately half of the acetonitrile was removed under vacuum, leaving a red-orange solution of Cp(CO)$_2$(CH$_3$CN)WCH$_2$CO$_2$Et.

A solution of bis(diphenylphosphino)methane (DPPM, 73.5 mg, 0.19 mmol) and 1.5 mL of benzene was added dropwise to the stirring solution. The solution was stirred for 9 h, and solvent was removed under vacuum. Extraction of the orange oil with diethyl ether and chilling (−40 °C) of the concentrated ether solution gave 51.0 mg (35%) of complex **29** as a microcrystalline yellow solid, mp 175–176 °C: IR (diethyl ether) 1946 (s), 1860 (s), 1690 (m) cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 7.53 (m, 2 H), 7.38 (m, 2 H), 7.25 (m, 2 H), 7.09 (m, 2 H), 6.93 (m, 12 H), 5.15 (s, 5 H), 4.18 (m, 2 H), 3.40 (m, 1 H), 3.38 (m, 1 H), 2.04 (dd, 1 H, J = 10.0, 8.4, J_{WH} = 4.6 Hz), 1.77 (dd, 1 H, J = 10.0, 8.5, J_{WH} = 8.0 Hz), 1.18 (t, 3 H, J = 7.1 Hz); $\{^1\mathrm{H}\}^{13}\mathrm{C}$ (C$_6$D$_6$) δ 6.35 (J_{PC} = 12 Hz), 33.34 (J = 30 Hz), 58.80, 91.71, 125.64, 128.28, 128.40, 128.51, 128.61, 128.68, 128.74, 128.81, 128.89, 129.27, 130.21, 130.30, 132.63, 132.79, 133.06, 133.14, 133.23, 133.66, 133.73, 183.17 (J_{PC} = 9.92 Hz); CO's not observed; $\{^1\mathrm{H}\}^{31}\mathrm{P}$ NMR (C$_6$D$_6$) δ −24.3 (d, J = 67 Hz), 22.6 (d, J_{PP} = 67, J_{WH} = 18 Hz).

trans-η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)(η^1-bis(diphenylphosphino)methane)dicarbonyltungsten (30), The cis complex **29** slowly isomerizes in benzene-d_6 solution at ambient temperature in 10 days to a mixture of the cis and the trans compounds in the ratio of 1:6.3. Purification by chromatography on silica gel (diethyl ether/benzene, 1:1) gave the trans compound **30**, mp 168–170 °C (60%): IR (C$_6$D$_6$) 1937 (s), 1847 (s), 1683 (m) cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 7.53 (m, 4 H), 7.27 (m, 4 H), 6.69 (m, 12 H), 4.69 (d, 5 H, J_{PH} = 1.75 Hz), 4.25 (q, 2 H, J = 7.1 Hz), 3.68 (dd, 2 H, $J_{PH\text{-substituted}}$ = 7.4, $J_{PH\text{-unsubstituted}}$ = 1.8 Hz), 2.53 (d, 2 H, $J_{PH\text{-substituted}}$ = 3.7 Hz), 1.24 (t, 3 H, J = 7.1 Hz); $\{^1H\}^{13}C$ NMR (C_6D_6) δ −12.25, 15.02, 34.62, 58.87, 91.81, 128.52, 128.67, 128.77, 128.83, 130.29, 132.92, 133.05, 133.19, 182.61, 230.60 (d, $J_{PC\text{ substituted}}$ = 6.5 Hz); $\{^1H\}^{31}P$ NMR (C_6D_6) δ −24.6 (d, J_{pp} = 56 Hz), 27.6 (d, J_{PP} = 56 Hz, J_{PW} = 225 Hz).

General Procedure for Generating Aldolates 31, 33, 34 and 36, in C_6D_6: Generation of η⁵-2,4-Cyclopentadien-1-yl(1-phenyl-3-ethoxy-3-oxopropoxy)tricarbonyltungsten (31). In a 5-mm NMR tube was placed tungsten ester **1** (20 mg, 0.05 mmol), C_6D_6 (1 mL), and benzaldehyde (5 mg, 0.05 mmol). The NMR tube was sealed and placed into the immersion well of a photolysis apparatus cooled to 3–5 °C and equipped with a 200-W Hanovia lamp and a uranium glass filter for 6 h. Examination of the ^1H NMR spectrum showed a new product which integrated as 90–95% of the reaction mixture (hexamethyldisiloxane as internal standard), with ethyl acetate and tungsten dimer (2–5% each) the only side products. The following NMR and IR spectra are of the major product, which we have assigned structure **31**: IR (C_6H_6) 2045 (s), 1950 (s), 1925 (s), 1735 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 0.96 (t, 3 H, J = 7 Hz), 2.32 (dd, 1 H, J = 15, 3.6 Hz), 2.59 (dd, 1 H, J = 15, 9.2 Hz), 3.96 (dq, 2 H, J = 1.3, 7 Hz), 4.76 (dd, 1 H, J = 3.6, 9.2 Hz), 4.95 (s, 5 H), 7.04 (m, 3 H), 7.26 (m, 2 H); $\{^1H\}^{13}C$ NMR (C_6D_6) δ 14.32, 48.54, 59.93, 87.54, 94.91, 126.80, 127.33, 128.56, 146.94, 172.01, 223.29, 224.14, 237.11; MS (CI with methane), m/z 526 (M + 1), 498 (M − CO), 105 (base).

η⁵-2,4-Cyclopentadien-1-yl(1-isopropyl-3-ethoxy-3-oxopropoxy)tricarbonyltungsten (33). The foregoing procedure was employed with isobutyraldehyde to give aldolate **33** in 87% yield based on ^1H NMR (hexamethyldisiloxane as internal standard): ^1H NMR (C_6D_6) δ 0.77 (d, 3 H, J = 7 Hz), 0.81 (d, 3 H, J = 7 Hz), 1.18 (t, 3 H, J = 7 Hz), 1.64 (d-heptet, 1 H, J = 4, 7 Hz), 2.06 (dd, 1 H, J = 4.0, 12 Hz), 2.17 (dd, 1 H, J = 8, 12 Hz), 3.65 (ddd, 1 H, J = 4, 4, 8 Hz), 4.00 (q, 2 H, J = 7 Hz), 4.98 (s, 5 H). The identity of **34** was further substantiated by cleavage with acetic acid and comparison of the resulting protiated aldol product with an authentic sample.[71]

Generation of η⁵-2,4-Cyclopentadien-1-yl(1-phenyl-1-methyl-3-ethoxy-3-oxopropoxy)tricarbonyltungsten (34). The foregoing procedure was employed with acetophenone to give aldolate **34** and the β-hydroxy ester **35** (5:3, respectively). The combined yields are initially 78% (hexamethyldisiloxane as internal standard), but at room temperature in solution **34** slowly cleaves to give a lower yield (47%) of **35**. Structure **35** is identical with an authentic sample,[71] and the structure of **34** is assigned on the basis of its ^1H NMR spectrum (C_6D_6): δ 0.92 (t, 3 H, J = 7 Hz), 1.64 (s, 3 H), 2.62 (d, 1 H, J = 13 Hz), 2.75 (d, 1 H, J = 13 Hz), 3.89 (q, 2 H, J = 7 Hz), 5.00 (s, 5 H), 7.26 (m, 3 H), 7.43 (m, 2 H).

Generation of η⁵-Cyclopentadienyl(1-phenyl-3-oxobutoxy)tricarbonytungsten (36). The foregoing procedure was employed with **3** and benzaldehyde to give **36**, β-hydroxy ketone **37**, and acetone (3:1:2, respectively). The combined aldol products account for 65% of the products (hexamethyldisiloxane as internal standard). Structure **37** is identical with an authentic sample,[71] and the structure of **36** is assigned on the basis of its ^1H NMR spectrum (C_6D_6): δ 1.70 (s, 3 H), 2.13 (dd, 1 H, J = 3.5, 14 Hz), 2.53 (dd, 1 H, J = 9, 14 Hz), 4.69 (dd, 1 H, J = 3.5, 9 Hz), 4.90 (s, 5 H), 7.25 (m, 5 H).

Reaction of a Solution of Tungsten Oxaallyl Complex 15 with Benzaldehyde. Tungsten ester **1** (35.0 mgm, 0.083 mmol) and hexamethyldisiloxane internal standard (1 μL) were dissolved in 0.35 mL of toluene-d_8 in a medium-walled NMR tube inside a drybox. The tube was fitted with a Cajon adaptor and subjected to 2 freeze-pump-thaw cycles to degas the yellow solution. The tube was irradiated at −30 °C for 1 h through a uranium glass filter. Carbon monoxide was removed from the resulting dark red solution by 2 freeze-pump-thaw cycles. At this point, the tube was taken back into the drybox, and the Cajon fitting was replaced with a Teflon cap which was then wrapped with Parafilm. Analysis by ^1H NMR showed a quantitative material balance; the starting enolate had been converted to 72% oxaallyl complex **15** and 10% ethyl acetate with 18% **1** remaining.

Benzaldehyde (15 μL, 0.15 mmol) was then added to the solution under nitrogen, and the tube was protected from light with aluminum foil. After 3 h at room temperature ^1H NMR analysis showed 21% starting complex **1**, 21% free aldol **32**, 29% oxaallyl complex **15**, and 14% ethyl acetate. After 1 day at room temperature the amount of aldol product had increased to 23%, the tungsten ester to 31%, and ethyl acetate to 18%. Insoluble crystals (identified by IR and melting point as $[Cp(CO)_3W]_2$, 5 mg, 9%) were filtered from the solution and rinsed with hexane. The hexane wash was combined with the filtrate; this precipitated 10 mg of unidentified dark red-brown tungsten-containing decomposition products.

Ethyl 3-[(Trimethylsilyl)oxy]-3-phenylpropanoate (38). In a 5-mm NMR tube was placed **1** (100 mg, 0.24 mmol), benzaldehyde (30 mg, 0.28 mmol), and TMSCl (50 mg, 0.46 mmol) in C_6D_6 (1 mL). The NMR tube was sealed and irradiated for 14 h at 6 °C and then heated to 60 °C for 2 h in a constant temperature bath. Examination by ^1H NMR spectroscopy showed one major product (**38**) which integrated as 84% of the reaction mixture. The crude reaction mixture was triturated with 3 × 25 mL of pentane, and the precipitate was collected by filtration. The solid (75 mg, 85%) was shown to be $CpW(CO)_3Cl$ by comparison with an authentic sample.[66] Pure **38** (31 mg, 47%) was isolated by flash chromatography (alumina III, ether/pentane, 1:1) in a drybox. The product was found to be identical with a sample prepared by silylation of ethyl 3-hydroxy-3-phenylpropanoate **32** having the following spectrum: ^1H NMR (C_6D_6) δ 0.08 (s, 9 H), 0.93 (t, 3 H, J = 7 Hz), 2.47 (dd, 1 H, J = 4, 15 Hz), 2.80 (dd, 1 H, J = 15, 9.6 Hz), 3.95 (m, 2 H), 5.30 (dd, 1 H, J = 4, 9.6 Hz), 7.07 (m, 3 H), 7.24 (m, 2 H).

Cleavage Reaction of 31 with Acetyl Chloride. In a 9-in. 5-mm NMR tube was placed **1** (100 mg, 0.24 mmol) and benzaldehyde (30 mg, 0.28 mmol) in C_6D_6 (2 mL). The NMR tube was capped and irradiated for 14 h at 6 °C, and then an excess of acetyl chloride (3×) was added. After 3 h at room temperature the conversion to $Cp(CO)_3WCl$[66] and the acetate **42** was 95% based on ^1H NMR (hexamethyldisiloxane as internal standard). The crude reaction mixture was triturated with 3 × 25 mL of pentane, and the precipitate was collected by filtration and was shown to be $Cp(CO)_3WCl$ (77 mg, 86%) by comparison with an authentic sample. Pure **42** (36 mg, 67%) was isolated by flash chromatography in a drybox (alumina III, Et_2O/pentane, 1:1). The acetate **42** was identical with that prepared by acetylation of **32** having the following spectrum: ^1H NMR (C_6D_6) δ 0.9 (t, 3 H, J = 7 Hz), 2.48 (dd, 1 H, J = 5, 15 Hz), 2.83 (dd, 1 H, J = 9, 15 Hz), 3.88 (dq, 2 H, J = 7, 0.5 Hz), 6.41 (dd, 1 H, J = 5, 9 Hz), 7.05 (m, 3 H), 7.23 (d, 2 H, J = 7 Hz).

Cleavage Reaction of 31 with Phenylacetic Acid.[72] To a solution of **31** prepared as described above was added phenylacetic acid (28 mg, 0.24 mmol). The reaction was complete in less than 10 min at room temperature, and the conversion to the β-hydroxy ester **32** and tungsten phenylacetate **43** was 95% (hexamethyldisiloxane as internal standard) based on ^1H NMR. The crude reaction mixture was triturated with 3 × 25 mL of pentane, and the precipitate was collected by filtration. The solid was assigned as the tungsten η²-phenylacetate **43** (67 mg, 60%) based on the following: IR (THF) 1953 (s), 1851 (s), 1603 (w), 1500 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 2.86 (s, 2 H), 5.17 (s, 5 H), 7.0 (m, 5 H); $\{^1H\}^{13}C$ NMR (C_6D_6) δ 45.46, 96.52, 127.33, 129.42, 129.66, 132.82, 186.94; MS (CI w/methane), m/z 440 (M^+), 412 (M − CO), 91 (base). Pure **32** (26 mg, 55%) was isolated by flash chromatography in a drybox (alumina III, Et_2O) and was found to be identical with an authentic sample.[71]

Cleavage Reaction of 31 with $Cp(CO)_3WH$. To a solution of **31** prepared as described above was added an excess of the tungsten hydride (3×). The reaction was complete after 12 h at room temperature, and the conversion to β-hydroxy ester **32** and the tungsten dimer **11** was 85% (hexamethyldisiloxane as internal standard). Aldol product **32** was identical with an authentic sample.[70]

Photolysis of Methyl-Substituted Enolate 9. In a 5-mm NMR tube was placed tungsten ester **9** (22 mg, 0.05 mmol) in C_6D_6 (1 mL). The NMR tube was sealed and irradiated at 3–5 °C for 6 h. Examination of the ^1H NMR spectrum showed two products whose spectral properties were identical with those of ethyl acrylate and $Cp(CO)_3WH$.

η⁵-Cyclopentadienyl(5-ethoxy-η²-3,5-dioxo-1-phenylpent-1-enyl)dicarbonyltungsten (44). Phenylacetylene (25.7 mg, 0.252 mmol) and $Cp(CO)_3WCH_2CO_2Et$ (57.4 mg, 0.137 mmol) were placed in an NMR tube. Benzene-d_6 (0.60 mL) was added, and the tube was sealed under vacuum after 3 freeze–pump–thaw cycles. Progress of the reaction was monitored by ^1H NMR spectroscopy. Irradiation of the tube for 195 min generated a mixture of compound **28** and insertion product 44. After 4 days at ambient temperature, compound **28** was converted to compound 44, 78% as determined by ^1H NMR spectroscopy. Removal of the benzene-d_6 under reduced pressure left a dark red oil. Crystallization

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(71) The authentic samples were prepared independently by the addition of the appropriate lithium enolates to the corresponding aldehyde or ketone by standard literature methods (ref 2a).

(72) Phenylacetic acid was used to generate a more crystalline product for easier isolation; acetic acid works equally well.

(73) In this paper the periodic group notation (in parentheses) is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

by vapor diffusion of pentane into a toluene solution of the crude product at −40 °C gave 44 mg (62%) of burgundy crystals of compound 44, mp 113–114 °C: IR (C_6H_6) 1969 (s), 1894 (s), 1818 (m), 1739 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.28 (m, 4 H), 6.98 (s, 1 H, J_{WH} = 3.2 Hz), 4.81 (s, 5 H), 3.87 (q, 2 H, J = 7.1 Hz), 3.48 (s, 2 H), 0.88 (t, 3 H, J = 7.1 Hz); {^{1}H}^{13}C NMR (C_6D_6) δ 14.05, 42.25, 60.87, 91.94, 126.35, 127.57, 128.51, 130.44, 154.87, 168.56, 191.27, 237.11, 254.56; {^{1}H}^{13}C NMR (acetone-d_6) δ 14.35, 42.63, 61.31, 93.28, 128.99, 128.02, 128.68, 130.54, 154.76, 169.05, 192.44, 238.93, 254.29; MS (EI, 70 eV), m/z 522 (M$^+$), 128 (base). Anal. Calcd for $C_{20}H_{18}O_5W$: C, 46.00; H, 3.47. Found: C, 45.98; H, 3.44.

η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)(diphenylacetylene)carbonyltungsten (45) and η^5-Cyclopentadienyl(5-ethoxy-η^2-3,5-dioxo-1-phenylpent-1-enyl)dicarbonyltungsten (46), In a drybox, an NMR tube was charged with diphenylacetylene (23.1 mg, 0.130 mmol), Cp(CO)$_3$WCH$_2$CO$_2$Et (46.4 mg, 0.110 mmol), and 0.6 mL of benzene-d_6. The solution was degassed by 3 freeze–pump–thaw cycles and sealed under vacuum. The tube was irradiated for 1 h at 25 °C. ^{1}H NMR spectroscopy of the dark red-brown solution showed compound **45** comprised 82% of the mixture, the remaining being compound **46**, tungsten dimer **11**, ethyl acetate, and diphenylacetylene. The solution from the NMR tube was subjected to flash column chromatography (0.5 × 5 cm) in a drybox. Elution with benzene developed a red band containing tungsten dimer **11** and diphenylacetylene and an orange red band containing compound **46** (5 mg, 6%). Elution with 1:9 THF/benzene developed a brown band containing compound **45** (55.5 mg, 82%).

Spectral data for compound **45**, mp 63–64 °C: IR (C_6D_6) 1931 (s), 1686 (m), 1240 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.20 (m, 2 H), 7.27 (m, 4 H), 7.66 (m, 4 H), 5.08 (s, 5 H), 4.18 (m, 1 H), 4.02 (m, 1 H), 2.07 (d, 1 H, J = 9.6, J_{WH} = 11.6 Hz), 1.37 (d, 1 H, J = 9.6, J_{WH} = 10.8 Hz), 1.06 (t, 3 H, J = 7.1 Hz); {^{1}H}^{13}C NMR (125.76 MHz, C_6D_6) δ 4.66, 14.87, 58.78, 93.36, 127.91, 128.53, 128.70, 128.92, 128.99, 129.67, 130.22, 138.16, 140.45, 183.88, 199.96, 203.15, 233.69; MS (CI w/ methane, 70 eV), m/z 543 (M + 1), 455 (base). Anal. Calcd for $C_{24}H_{22}O_3W$: C, 53.16; H, 4.09. Found: C, 53.44; H, 3.87.

Spectral data for compound **46**, mp 181–198 °C (dec): IR (C_6D_6) 1969 (s), 1894 (m), 1654 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.86 (t, 3 H, J = 7.15 Hz), 3.57 (s, 2 H), 3.86 (q, 2 H, J = 7.15 Hz), 4.86 (s, 5 H), 6.98 (m, 10 H); ^{1}H NMR (acetone-d_6) δ 1.18 (t, 3 H, J = 7.11 Hz), 3.55 (s, 2 H), 4.06 (q, 2 H, J = 7.11 Hz), 5.68 (s, 5 H), 6.83 (m, 2 H), 6.87 (m, 1 H), 6.93 (m, 2 H), 7.10 (m, 5 H); {^{1}H}^{13}C NMR (125.76 MHz, acetone-d_6) δ 14.33, 42.86, 61.26, 93.63, 125.14, 124.31, 126.75, 127.67, 128.29, 129.01, 131.74, 139.54, 144.11, 155.80, 169.15, 190.91, 238.64, 255.13; MS (EI, 70 eV), m/z 598 (M$^+$), 572 (base). Anal. Calcd for $C_{26}H_{22}O_5W$: C, 52.19; H, 3.71. Found: C, 52.35; H, 3.64.

The Diphenylacetylene Insertion Reaction under 2 equiv of CO, Tungsten ethyl ester (20.6 mg, 0.0490 mmol) and diphenylacetylene (9.2 mg, 0.0516 mmol) were weighed into a heavy-walled NMR tube (Wilmad 504PP) and dissolved in 0.76 mL of C_6D_6. The tube was attached to a Teflon high vacuum stopcock via a Cajon ultratorr fitting (3/8 in. to 1/4 in. reducing union, model no. 55-6-UT-6-4). After 3 freeze–pump–thaw cycles 0.11 mmol of CO (after correction for the vapor pressure of CO at −195 °C, 470 torr) was condensed into the tube, and the tube was sealed. After irradiation for 6 h the following amounts of compounds were present in the NMR tube as determined by ^{1}H NMR integration: 8% Cp(CO)$_3$WCH$_2$CO$_2$CH$_2$CH$_3$, 7% oxaallyl **15**, 42% Cp(CO)$_2$WC(Ph)C(Ph)COCH$_2$CO$_2$CH$_2$CH$_3$ (**40**), 2% Cp(CO)(PhCCPh)WCH$_2$CO$_2$CH$_2$CH$_3$ (**41**), and 41% [Cp(CO)$_3$W]$_2$.

η^5-Cyclopentadienyl(bis(phenylacetylene))(2-ethoxy-2-oxoethyl)tungsten (49), In a drybox, Cp(CO)(PhCCH)WCH$_2$CO$_2$Et (0.670 g, 1.44 mmol) and phenylacetylene (0.50 mL, 4.55 mmol) were dissolved in benzene (15 mL) in a 50-mL heavy-walled tube sealable by a vacuum stopcock. The solution was freeze–pump–thawed, sealed under vacuum, and then heated to 60 °C for 48 h. The benzene was removed under vacuum. The brown solid was chromatographed on alumina giving 545 mg (70%) of complex **49**, mp 94–96 °C: IR (CD_2Cl_2) 1675 (w), 1238 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.20 (t, 3 H, J = 7.10 Hz), 3.82 (br s, 2 H), 4.31 (q, 2 H, J = 7.10 Hz), 5.18 (s, 5 H), 7.30 (m, 6 H), 7.52 (br s, 4 H), 10.37 (br s, 2 H); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 1.30 (t, 3 H, J = 7.10 Hz), 3.45 (br s, 2 H), 4.16 (q, 2 H, J = 7.10 Hz), 5.58 (s, 5 H), 7.3–7.6 (m, 10 H), 10.3 (br s, 2 H); ^{1}H NMR (CD_2Cl_2, −70°C) major isomer δ 1.24 (t, 3 H, J = 7.10 Hz), 2.47 (d, 1 H, J = 8.45 Hz), 3.89 (d, 1 H, J = 8.45 Hz), 4.07 (q, 2 H, J = 7.10 Hz), 5.52 (s, 5 H), 7.07–7.66 (m, 8 H), 8.19 (d, 2 H, J = 6.91 Hz), 9.63 (s, 1 H), 11.44 (s, 1 H); ^{1}H NMR (CD_2Cl_2, −70 °C) minor isomer δ 1.24 (t, 3 H, J = 7.10 Hz), 3.47 (s, 2 H), 4.07 (q, 2 H, J = 7.10 Hz), 5.58 (s, 5 H), 7.07–7.66 (m, 8 H), 8.19 (d, 2 H, J = 6.91 Hz), 9.86 (s, 2 H); {^{1}H}^{13}C NMR (CD_2Cl_2, 20°C) 13.21 (J_{WC} = 41 Hz), 15.27, 58.84, 99.06, 128.75, 129.04, 130.48, 138.36, 169.79 (br), 184.67; {^{1}H}^{13}C NMR (CD_2Cl_2, −70 °C) δ 10.80, 13.17, 14.56, 14.62, 58.58, 97.44, 98.87, 110.31, 127.06, 127.74, 128.34, 128.77, 128.84, 130.15, 130.69, 132.26, 134.74, 136.74, 137.90, 164.83, 168.70, 171.41, 173.44, 184.21, 184.55, 186.23, 190.147; MS (EI, 70 eV), m/z 540 (M$^+$), 396 (base). Anal. Calcd for $C_{25}H_{24}O_2W$: C, 55.56; H, 4.48. Found: C, 55.64; H, 4.57.

η^5-Cyclopentadienyl(2-ethoxy-2-oxoethyl)(phenylacetylene)(oxo)tungsten carbonyl (50), In a drybox, Cp(PhCCH)(CO)WCH$_2$CO$_2$Et (53.2 mg, 0.114 mmol) was placed into an NMR tube and dissolved in C_6D_6 (0.54 mL). The red solution was freeze–pump–thawed 3 times, and oxygen (0.142 mmol, corrected for the vapor pressure of oxygen, 155 torr at 77 K) was condensed into the tube. The tube was sealed and allowed to remain at room temperature for 1 day. The reaction was shown to be complete by ^{1}H NMR spectroscopy. The solvent was removed from the crude reaction mixture leaving a brown tar, which was dissolved in benzene and chromatographed on alumina II in a drybox. Benzene eluted a yellow orange band. Elution with ether brought off 30.0 mg (57.9%) of Cp(PhCCH)(O)WCH$_2$COOCH$_2$CH$_3$. Recrystallization from toluene/hexane afforded tan crystals, 16.2 mg, mp 111–112 °C: IR (toluene) 1695 (m), 1456 (w), 1329 (m), 1242 (w), 1098 (w), 949 (m), 813 (w), 753 (w) cm^{-1}; IR (KBr) 1695 (s), 1242 (m), 1087 (m), 938 (s), 832 (w), 761 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.08 (t, 3 H, J = 7.10 Hz), 3.41 (d, 1 H, J = 9.16, J_{WH} = 6.4 Hz), 3.66 (d, 1 H, J = 9.16, J_{WH} = 4.8 Hz), 4.15 (m, 2 H), 5.53 (s, 5 H), 7.17 (m, 1 H), 7.27 (m, 2 H), 7.69 (m, 1 H), 9.30 (s, 1 H, J_{WH} = 8.6 Hz); ^{1}H NMR (acetone-d_6) δ 1.25 (t, 3 H, J = 7.11 Hz), 3.19 (d, 1 H, J = 9.17, J_{WH} = 6.03 Hz), 3.46 (d, 1 H, J = 9.19, J_{WH} = 6.52 Hz), 4.13 (q, 2 H, J = 7.11 Hz), 6.25 (s, 5 H), 7.56 (m, 1 H), 7.64 (m, 2 H), 7.97 (m, 3 H), 9.33 (s, 1 H, J_{WH} = 4.24 Hz); {^{1}H}^{13}C NMR (C_6D_6) δ 14.85, 19.79 (J_{WC} = 80 Hz), 59.29, 105.46, 129.05 (2C), 129.70, 132.09 (2C), 136.51, 145.80 (J_{WC} = 34 Hz), 155.67 (J_{WC} = 50 Hz), 180.20; {^{1}H}^{13}C NMR (acetone-d_6) δ 17.93, 22.23, 62.41, 109.52, 132.66 (2C), 133.47, 135.71 (2C), 139.56, 148.81, 159.41, 183.33; coupled ^{13}C NMR (acetone-d_6) δ 14.93 (J = S/N too large to accurately determine), 19.18 (J_{CHA} = 131.8, J_{CHB} = 136.0 Hz), 59.41 (J = S/N too large to accurately determine), 106.53 (^1J = 179.6, ^2J = 6.6 Hz), 129.61 (J = 160.3 Hz), 130.52 (J = 159.6 Hz), 132.76 (J = 151.8 Hz), 136.53, 145.77 (J = 206.9 Hz), 156.41, 180.38; MS (CI, 70 eV), m/z 455 (M + 1), 411 (base). Anal. Calcd for $C_{17}H_{18}O_3W$: C, 44.96; H, 3.99. Found: C, 45.15; H, 3.99.

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