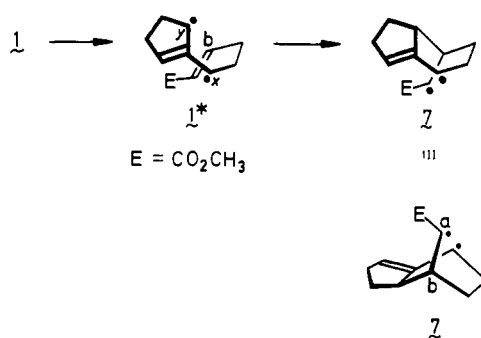


Scheme III



have maintained the diylophile stereochemistry.^{2b,d}

In a similar fashion, it was determined that minor product **5** also possesses the same ring system and that it is isomeric with **2** about the ester-bearing carbon. Finally, the minor product **4** was subjected to the same sequence and the resulting hydrocarbon was compared with and seen to be different from that derived from **6**. However, comparison with the hydrocarbon derived from catalytic hydrogenation of *endo*-dicyclopentadiene established that **4** possesses the same basic skeleton as **5** but differs in that the five-membered ring is endocyclic in compound **4**.

Inspection of the ¹H NMR spectrum of the second major component **3** indicates the presence of three vinyl protons corresponding to the four sp² hybridized carbons which are evident in the CMR spectrum of **3**. Furthermore, the UV spectrum shows a maximum at 235 nm with an extinction coefficient of ca. 8000. Clearly, this material contains a conjugated diene unit. The nature of the carbon skeleton, but not the stereochemistry, at the relevant stereocenters in **3** was determined unambiguously by following the sequence of reactions outlined in Scheme II. In particular, both **3** and the previously characterized bicyclo[4.3.0]nonan-2-one⁶ are convertible to the same materials.

The chemistry of the diyl derived from diazene **1** differs markedly from that of any other we have examined. The nature of the products, especially the presence of stereoisomers and product **3**, suggests that they are formed in a nonconcerted reaction. In fact, their formation can most simply be rationalized by applying some of the ground rules that are typically associated with the closure of a monoradical onto an alkene;⁷ that is, given the option of closing between C_y and C_b to form a six-membered ring (6-exo, trig closure) or between C_x and C_b to form the significantly more strained four-membered ring (4-exo, trig closure), the literature clearly indicates that the former is kinetically preferred. Furthermore, studies of the equilibrium between the 4-pentenyl radical and cyclobutylcarbinyl show that, while the reaction is reversible, the equilibrium lies far to the side of the open form.⁷ Since no linearly fused product was identified, one is forced to conclude either that, in this instance too, a 4-exo, trig closure does not occur or that it is reversible and eventually leads to **7**, the diyl derived from **1*** by 6-exo, trig closure. Carbon-carbon bond formation between the two odd-electron centers in **7** (Scheme III) with concomitant rotation about the C_a - C_b bond leads to **2** and without rotation to **4** and **5**, while an unprecedented (*in our experience with diyl chemistry*) hydrogen atom abstraction leads to diene **3**.

We are continuing our efforts to determine the fundamental factors that govern the course of the diyl trapping reaction and to apply the results of those investigations to the construction of structurally interesting and potentially useful natural products.

Acknowledgment. This investigation was supported by PHS Grant CA 21144, awarded by the National Cancer Institute,

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DHHS. We are grateful for their continued support of our research. Partial support from the Alfred P. Sloan Foundation in the form of a fellowship to R.D.L. is also gratefully acknowledged.

Supplementary Material Available: Full X-ray data and perspective views of the molecular structure for $\text{C}_{11}\text{H}_{14}\text{O}_2$ (16 pages). Ordering information is given on any current masthead page.

Tetranuclear Carbido-tungsten and Nitridomolybdenum Clusters Supported by Alkoxide Ligands: $\text{W}_4(\text{C})(\text{O}-i\text{-Pr})_{12}(\text{NMe})$ and $\text{Mo}_4(\text{N})_2(\text{O}-i\text{-Pr})_{12}$

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We report here our discovery of the first examples of carbido and nitrido clusters of tungsten and molybdenum supported by alkoxide ligands.¹

The reaction between $\text{W}_2(\text{NMe}_2)_6(\text{M}\equiv\text{M})$ and *i*-PrOH (>>6 equiv) in hexane at room temperature has been shown to yield $\text{W}_4(\text{H})_2(\text{O}-i\text{-Pr})_{14}$ ² by way of an intermediate, $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{HNMe}_2)_2$,³ which is the major product at short reaction times (<1 h). However, a persistent impurity in preparations of $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{HNMe}_2)_2$ is a black crystalline compound, $\text{W}_4(\text{C})(\text{NMe})(\text{O}-i\text{-Pr})_{12}$ (**I**), which is formed in ca. 5–10% yield based on tungsten.⁴ Compound **I** does not react with *i*-PrOH to give $\text{W}_4(\text{H})_2(\text{O}-i\text{-Pr})_{14}$ and appears to be formed competitively with $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{HNMe}_2)_2$ during the alcoholysis of $\text{W}_2(\text{NMe}_2)_6$ since we have been unable to convert pure samples of $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{HNMe}_2)_2$ to **I**. Compound **I** is presumably formed by degradation of a NMe_2 ligand, possibly by way of a $(\mu\text{-CH}_2)\text{NMe}$ ligand as recently noted in reactions of NMe_2 ligands at the W_2^{6+} center.⁵ Our formulation of **I** as the carbido cluster $\text{W}_4(\text{C})(\text{NMe})(\text{O}-i\text{-Pr})_{12}$ is based on elemental analyses, a single-crystal X-ray study, the appearance of the molecular ion cluster in the low-resolution electron impact mass spectrum, and NMR spectroscopy which reveals the presence of 12 different *O*-*i*-Pr ligands, the NMe group, and the carbido carbon: $\delta(\text{W}_4(\text{C}))$ 366.8 relative to Me_4Si .⁶ We have not, using natural abundance ¹³C samples with $\text{Cr}(\text{acac})_3$, been able to resolve any of the satellite spectrum which is expected due to coupling to four different ¹⁸³W nuclei (¹⁸³W, $I = 1/2$, natural abundance = 14.5%).

(1) For recent reviews of carbido, nitrido, and alkoxide chemistry, see ref 1a, 1b, and 1c, respectively: (a) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1. Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203. (b) Dehnicke, K.; Strahle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413. Gladfelter, W. L. In "Organometallic Compounds: Synthesis, Structure and Theory"; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1983; p 281. (c) Bradley, D. C.; Mehrota, R. C.; Gaur, P. D. "Metal Alkoxides"; Academic Press: New York, 1978. Mehrota, R. C.; Martin, R. L. *J. Organomet. Chem.* **1982**, *239*, 159.

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(3) Chetcuti, M. J.; Chisholm, M. H.; Huffman, J. C.; Leonelli, J. *J. Am. Chem. Soc.* **1983**, *105*, 292.

(4) Note the use of dry and oxygen-free atmospheres (N_2) and solvents. Pure crystalline samples of **I** were separated from $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{HNMe}_2)_2$ by hand in a Vacuum Atmospheres Dri-Box.

(5) Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 152.

(6) Crystal data (i) for $\text{W}_4(\text{O}-i\text{-Pr})_{12}(\text{NMe})(\text{C})$ at -165°C : $a = 19.379$ (1) Å, $b = 12.516$ (1) Å, $c = 11.883$ (1) Å, $\alpha = 119.37$ (6)°, $\beta = 84.98$ (5)°, $\gamma = 98.79$ (5)°, $Z = 2$, $d_{\text{calcd}} = 1.988$ g cm⁻³, and space group *P1*. Final residuals are $R(F) = 0.054$ and $R_w(F) = 0.046$. (ii) for $\text{Mo}_4(\text{N})_2(\text{O}-i\text{-Pr})_{12}$ at -160°C : $a = 11.338$ (3) Å, $b = 12.568$ (3) Å, $c = 11.348$ (3) Å, $\alpha = 95.84$ (2)°, $\beta = 119.55$ (1)°, $\gamma = 67.81$ (2)°, $Z = 1$, $d_{\text{calcd}} = 1.437$ g cm⁻³, and space group *P1*. Final residuals are $R(F) = 0.019$ and $R_w(F) = 0.024$.

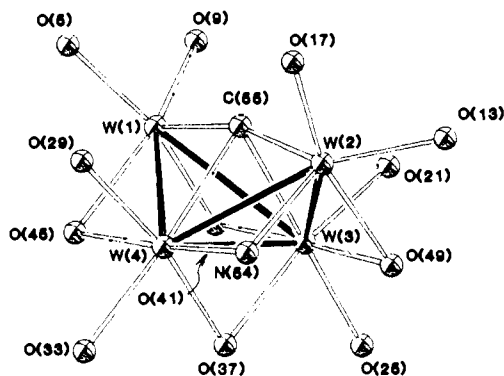
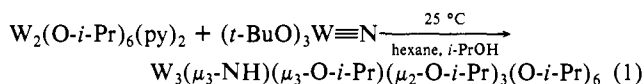


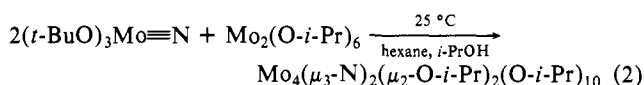
Figure 1. Ball and stick view of the central W_4CNO_{12} skeleton of the $W_4(C)(NMe)(O-i-Pr)_{12}$ molecule. Selected bond distances (Å) and angles (deg): $W(1)-W(3) = 2.799$ (2), $W(1)-W(4) = 2.814$ (2), $W(2)-W(3) = 2.822$ (1), $W(2)-W(4) = 2.747$ (2), $W(3)-W(4) = 2.795$ (2), $W(1)-C(55) = 1.914$ (14), $W(2)-C(55) = 1.956$ (15), $W(3)-C(55) = 2.251$ (14), $W(4)-C(55) = 2.241$ (14), $W(2)-N(54) = 1.922$ (13), $W(4)-N(54) = 1.984$ (12), $W-O(\text{terminal}) = 1.90$ (3) (av) $W-O(\text{bridging}) = 2.03$ (3) (av); $W(1)-C(55)-W(2) = 163.5$ (8), $W(3)-C(55)-W(4) = 77.0$ (4), $W(1)-C(55)-W(3) = 84.0$ (5), $W(1)-C(55)-W(4) = 84.9$ (5), $W(2)-C(55)-W(3) = 83.9$ (5), $W(2)-C(55)-W(4) = 81.5$ (5), $W(3)-W(1)-W(4) = 59.7$ (1), $W(3)-W(2)-W(4) = 60.2$ (1), $W(1)-W(3)-W(2) = 85.9$ (1), $W(1)-W(3)-W(4) = 60.4$ (1), $W(2)-W(3)-W(4) = 58.6$ (1), $W(1)-W(4)-W(2) = 87.1$ (1), $W(1)-W(4)-W(3) = 59.9$ (1), $W(2)-W(4)-W(3) = 61.2$ (1).

The W_4CNO_{12} skeleton of I is shown in Figure 1. The molecule bears a striking resemblance to the well-known "iron-butterfly" $Fe_4(\mu-C)(CO)_{13}$.⁷ If, for the sake of electron counting, charge is partitioned between the metal atoms and the ligands as C^{4-} , NMe^{2-} , and OR^- , then the tetranuclear center is formally W_4^{18+} having only 6 electrons for M-M cluster bonding. Although this is only a formalism and there is a mixing of metal-ligand and metal-metal bonding, the five W-W bonding distances, 2.78 Å (averaged), within the W_4 butterfly are notably longer than in the 12-electron cluster M_4 -butterflies such as $Mo_4Br_4(O-i-Pr)_8$ and $Mo_4Br_3(O-i-Pr)_9$, where the Mo-Mo bonding distances average 2.50 Å.⁸

Following our discovery of the formation of the imido-capped tritungsten compound $W_3(\mu_3-NH)(\mu_3-O-i-Pr)(\mu_2-O-i-Pr)_3(O-i-Pr)_6$ according to (1); we attempted a related reaction between



$(t-BuO)_3Mo \equiv N$ and $Mo_2(O-i-Pr)_6$. Although there is spectroscopic evidence for the formation of some $Mo_3(\mu_3-NH)(\mu_3-O-i-Pr)(\mu_2-O-i-Pr)_3(O-i-Pr)_6$, the major product was a relatively insoluble green compound, $Mo_4(\mu_3-N)_2(\mu_2-O-i-Pr)_2(O-i-Pr)_{10}$ (II).⁶ By changing the stoichiometry to that shown in eq 2, II may be



isolated in ca. 60% yield based on Mo after recrystallization from hot hexane.

A view of the centrosymmetric molecule $Mo_4(\mu_3-N)_2(\mu_2-O-i-Pr)_2(O-i-Pr)_{10}$ is shown in Figure 2. Coordination about nitrogen is T-shaped¹⁰ while that about each molybdenum atom corresponds closely to a trigonal bipyramid. There are two short Mo-N

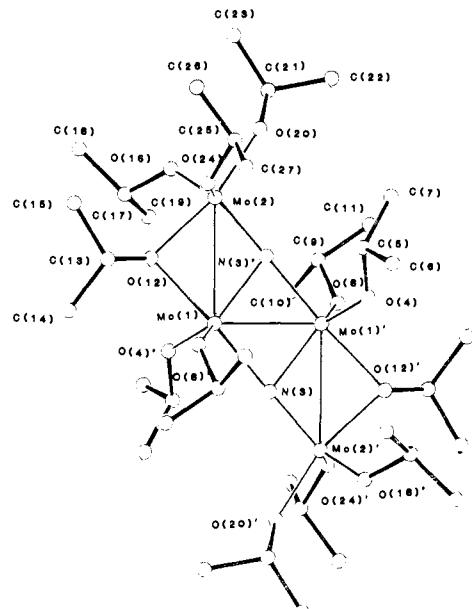
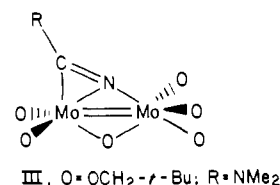
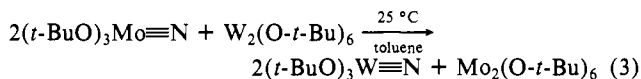


Figure 2. ORTEP view of the centrosymmetric $Mo_4(\mu_3-N)_2(\mu_2-O-i-Pr)_2(O-i-Pr)_{10}$ molecule showing the number scheme for the atoms. The two nitrogen atoms and four oxygen atoms, O(12), O(12)', O(20), and O(20)', all lie within 0.1 Å of the plane containing the four Mo atoms. Selected bond distances (Å) and angles (deg): $Mo(1)-Mo(1') = 2.552$ (1), $Mo(1)-Mo(2) = 2.918$ (1), $Mo(1)-N(3) = 1.996$ (2), $Mo(1)-N(3) = 2.034$ (2), $Mo(2)-N(3') = 1.841$ (2), $Mo-O(\text{terminal}) = 1.92$ (1) (av), $Mo(1)-O(12) = 2.139$ (2), $Mo(2)-O(12) = 2.058$ (2); $Mo(1)-Mo(1)-Mo(2) = 89.84$ (3), $Mo(1)-N(3)-Mo(1) = 78.58$ (7), $Mo(1)-N(3)-Mo(2) = 174.83$ (11).

distances, 1.84 Å (equatorial bonds), and four longer distances ca. 2.00 Å (two equatorial and two axial bonds) corresponding formally to Mo-N double and single bonds, respectively.¹¹ If the ligands are assigned charge N^{3-} and OR^- then the tetranuclear center is Mo_4^{18+} and six electrons are available for M-M bonding. The Mo-Mo distances, two long, 2.92 Å, and one short, 2.55 Å, taken together with the alternating short and long Mo-N distances are suggestive of partial oxidative addition of two (d^0) $Mo \equiv N$ units across a $(Mo \equiv Mo)^{6+}$ center. This bears a striking analogy with the reactions between $Me_2NC \equiv N$ and $Mo_2(OR)_6$ compounds which yield 1:1 adducts $Mo_2(OR)_6(NCNMe_2)$ having the structure depicted by III.¹²



In view of the current interest in metathesis reactions involving the $(M \equiv M)^{6+}$ unit in $M_2(OR)_6$ compounds ($M = Mo, W$) and alkynes and nitriles,¹²⁻¹⁴ it is interesting (i) to speculate that II may represent the thermodynamically favored product in the hypothetical reaction between dinitrogen and $Mo_2(O-i-Pr)_6$ (2 equiv) and (ii) to note that the reaction between $(t-BuO)_3Mo \equiv N$ (2 equiv) and $W_2(O-t-Bu)_6$ proceeds according to eq 3.



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Further studies are in progress.¹⁵

Supplementary Material Available: Fractional coordinates and stereoviews for I and II (4 pages). Ordering information is given on any current masthead page.

(15) We thank the Department of Energy, Office of Basic Sciences, Chemical Sciences Division, and the Wrubel Computing Center for support.

Synthesis, Structure, and C-C Bond-Forming Reactions of Carbon-Bound Molybdenum, Tungsten, and Rhenium Enolates. Detection of an η^3 -Oxaallyl Intermediate

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Received December 10, 1984

The generation and reactions of organotransition-metal enolates has recently led to several important contributions to organic synthesis. Enolates of type **1** (Scheme I) have been generated in situ by deprotonation of metal acyl complexes;¹ enolates of type **2** have been generated in situ by reactions involving complexes of early transition metals (e.g., Ti, Zr).² Both types have shown stereoselectivity in their aldol reactions with aldehydes.³

Several carbon-bound transition-metal enolates (type **3**) have also been generated and isolated. These have often been referred to in the literature as "substituted methyl", "acylmethyl", and "oxoalkyl" complexes, and surprisingly little is known about their chemistry.⁴ In particular, reactions with organic electrophiles such as aldehydes and nitriles have not been observed. We now wish to report (1) a general method for preparing carbon-bound transition-metal enolates, (2) the isolation and full characterization of several of these materials, (3) observation of photochemical aldol reactions for the tungsten and molybdenum complexes, (4) detection of an η^3 -enolate (i.e., an η^3 -oxaallyl complex) in one of the irradiations, and evidence that this is the critical intermediate

(1) (a) Theopold, K. H.; Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 5250. (b) Liebeskind, L. S.; Walker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441. (c) Davies, S. G.; Dordor, I. M.; Walker, J. C.; Warner, P. *Tetrahedron Lett.* **1984**, *25*, 2709.

(2) (a) Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, *21*, 3975. (b) Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1980**, *21*, 4607. (c) M. T.; Peter, R. *Tetrahedron Lett.* **1980**, *21*, 4691. (d) Grubbs, R. H.; Stille, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 1664. (e) Ho, S. C. H.; Strauss, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. *Ibid.* **1984**, *106*, 2210. (f) Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855. (g) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1978**, *100*, 7114. For an example of a late-transition-metal enolate which has also been assigned the O-bound structure, see: (h) Ito, Y.; Nakatsuka, M.; Kise, N.; Saegusa, T. *Tetrahedron Lett.* **1980**, *21*, 2873. We are grateful to a referee for calling this paper to our attention.

(3) For a general review of aldol stereoselectivity, see: Heathcock, C. H. "Asymmetric Syntheses"; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3.

(4) (a) King, R. B.; Bisnette, M. B.; Fronzaylia, A. *J. Organomet. Chem.* **1966**, *5*, 341. (b) Engelbrecht, J.; Greiser, T.; Weiss, E. *J. Organomet. Chem.* **1981**, *204*, 79. (c) Galamb, V.; Palyi, G. *J. Organomet. Chem.* **1981**, *209*, 183. (d) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1982**, *104*, 2323. (e) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221. (f) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157. (g) Nizova, G. V.; Serdobov, M. V.; Nititayev, A. T.; Shul'pin, G. B. *J. Organomet. Chem.* **1984**, *275*, 139. (h) Bertani, R.; Castellani, C. B.; Crociani, B. *Ibid.* **1984**, *269*, C15. (i) Ariyaratne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swanwick, M. G. *J. Chem. Soc. A* **1969**, 1309. (j) Hoff, C. D.; Ungváry, F.; King, R. B.; Markó, L. *J. Am. Chem. Soc.* **1985**, *107*, 666. Transition-metal enolates are also presumably involved as short-lived intermediates in several reported reactions of α -halocarbonyl compounds with low-valent complexes; see, e.g.: (k) Alper, H.; Des Roches, D. *J. Org. Chem.* **1976**, *41*, 806. (l) Yoshisato, E.; Tsutsumi, S. *J. Am. Chem. Soc.* **1968**, *90*, 4448; *Chem. Commun.* **1968**, 33.

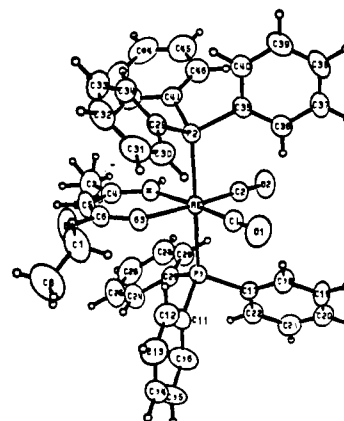
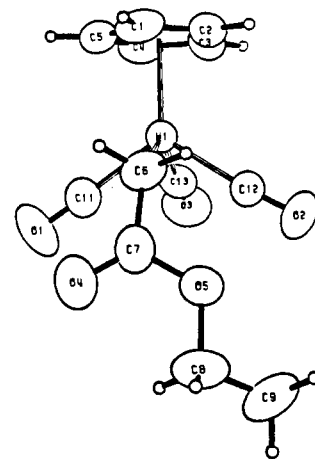


Figure 1. ORTEP structures of tungsten enolate **4a** and rhenium complex **11**.

in the aldol reaction, and (5) observation of a striking condensation reaction with acetonitrile in the case of rhenium ester enolate **9**.

Treatment of the carbonylmetallate salts⁵ Na[Cp(CO)₃M] (M = Mo, W) or Na[(CO)₅Re] with α -bromo ketones or esters leads only to halogen transfer (giving Cp(CO)₃MBr and (CO)₅ReBr, perhaps by radical processes) rather than alkylation, and no metal enolates are formed. In sharp contrast, alkylation with α -chloro carbonyl compounds⁴ⁱ leads successfully in all the cases illustrated in Scheme I to the enolates **4a-d** and **9**. These materials were isolated by crystallization from hexane and characterized fully by IR, ¹H and ¹³C NMR spectroscopy and by elemental analysis. In addition, crystals of the [(ethoxycarbonyl)methyl]tungsten complex **4a** suitable for X-ray analysis, mp 37–38 °C, were obtained by slow evaporation of an ether solution at –40 °C. Solution of the structure⁶ confirmed the carbon-bound enolate formulation,

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(6) Following are selected data for the two X-ray structures reported in this paper. Both 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. (a) For tungsten ester **4a**: space group *P1*; *a* = 8.8376 (10) Å, *b* = 10.9925 (15) Å, *c* = 13.9447 (21) Å, α = 88.482 (12)°, β = 79.956 (11)°, γ = 89.554 (10)°, *V* = 1333.7 (5) Å³; *D_c* = 2.092 g cm⁻³; μ_{calcd} ($\mu\text{o K}\alpha$) = 88.56 cm⁻¹. A total of 3476 unique reflections were collected; the final residuals for which 326 variables refined against the 3154 data for which $F^2 > 3\sigma F^2$ were *R* = 1.85%, *R_w* = 3.19%, and *GOF* = 1.85. For rhenium addition product (PPh₃)₂(CO)₂(C₆H₅NO₂)Re (**11**): space group *P2₁/c*; *a* = 9.5049 (15) Å, *b* = 24.3527 (34) Å, *c* = 18.6400 (30) Å; β = 116.488 (13)°, *V* = 3861.7 (22) Å³; *D_c* = 1.54 g cm⁻³; μ_{calcd} (Mo *K}\alpha*) = 33.12 cm⁻¹. A total of 5037 unique reflections were collected; the final residuals for which 469 variables refined against the 3570 data for which $F^2 > 3\sigma F^2$ were *R* = 1.69%, *R_w* = 2.00%, and *GOF* = 1.092. Full details of the structure determinations are being deposited with the Cambridge X-ray structure determination archives.