$MPPh_3$ moiety in place of a hydride ligand leads to a more directed substitution.

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Supplementary Material Available: Tables of hydrogen atom positions (Table S1), anisotropic thermal parameters (Table S2), and bond lengths and angles (Table S3) (4 pages); a listing of observed and calculated structure factors (Table S4) (30 pages). Ordering information is given on any current masthead page.

Synthesis of [Alkenyl(dimethylamino)carbene]tungsten Complexes Using the Peterson Reaction: X-ray Crystal Structure of (*E*)-$(CO)_5W[C(NMe_2)CH{=}CH(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$

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Treatment of $(CO)_5W[C(NMe_2)CH_3]$ (1) with *n*-BuLi followed by Me_3SiCl produced $(CO)_5W[C(NMe_2)CH_2SiMe_3]$ (2) in 90% yield. $(CO)_5W[C(NMe_2)CHSiMe_3]Li$, which was formed in the reaction between 2 and *n*-BuLi, reacted with several nonenolizable aldehydes or ketones to afford moderate yields (45–61%) of the desired (alkenylaminocarbene)tungsten complexes $(CO)_5W[C(NMe_2)CH{=}CR^1R^2]$ (**3a–f**) (**a**, $R^1 = R^2 = H$; **b**, $R^1 = H$, R^2 = Ph; **c**, $R^1 = H$, R^2 = 2-furyl; **d**, $R^1 = H$, R^2 = *trans*-CH=CHPh; **e**, $R^1 = H$, $R^2 = (\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$; **f**, $R^1 = R^2$ = Ph). For compounds **3b–e**, exclusive formation of the *E* isomer occurred. Treatment of 2 with *n*-BuLi followed by either $CF_3SO_3CH_3$ or $CH_2{=}CHCH_2Br$ afforded complexes **4a** and **4b** (70–90%), $(CO)_5W[C(NMe_2)CH(R)SiMe_3]$ (**4a**, R = CH_3; **4b**, R = $CH_2CH{=}CH_2$), respectively. Complexes **4a** or **4b** could not be obtained by reacting the corresponding complexes **5a** or **5b**, $(CO)_5W[C(NMe_2)CH_2R]$ (**5a**, R = CH_3; **5b**, R = $CH_2CH{=}CH_2$), with *n*-BuLi followed by Me_3SiCl. Furthermore, the lithium anions $(CO)_5W[C(NMe_2)C(R)SiMe_3]Li$ (R = CH_3, $CH_2CH{=}CH_2$) from **4a** or **4b** did not react with aldehydes or ketones to afford the desired α-substituted (alkenylaminocarbene)tungsten complexes. One example of such a complex, $(CO)_5W[C(NMe_2)C(CH_3){=}CH_2]$ (**7**), could, however, be prepared in 75–80% yield by treating $(CO)_5W[C(OCH_3)C(CH_3){=}CH_2]$ (**6**) with $HNMe_2$ in ether. $(CO)_5W[C(NMe_2)CHSiMe_3]Li$ was made to react with PhCOCl to yield the enol silyl ether derivative $(CO)_5W[C(NMe_2)CH{=}C(OSiMe_3)Ph]$ (**8**) (26%) along with a trace of an air-sensitive complex $(CO)_5W[C(NMe_2)CH_2C(O)Ph]$ (**9**). (*E*)-$(CO)_5W[C(NMe_2)CH{=}CH(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$ (**3e**) was further characterized by single-crystal X-ray diffraction methods. Complex **3e** crystallizes in the monoclinic space group $P2_1/c$ with (at 20 °C) a = 12.022 (4) Å, b = 12.857 (8) Å, c = 13.826 (8) Å, β = 102.19 (4)°, and D_{calcd} = 1.88 g cm^{-3} for Z = 4. Least-squares refinement based on 2604 independent observed [$F_o \geq 5\sigma(F_o)$] reflections led to a final conventional R value of 0.044.

Introduction

Although Fischer-type carbene complexes have been studied extensively over the past 15 years,[1] research on these interesting species continues unabated. Of the many systems currently under investigation, aminocarbene complexes and alkenylcarbene complexes are receiving their proportional share of study. Organic synthetic applications of (aminocarbene)chromium complexes include reactions with alkynes, imines, or nucleophiles to afford indene derivatives,[2] β-lactams,[3] or α-amino acid derivatives,[3b] respectively. (Aminocarbene)iron complexes also react with alkynes to produce 5-aminofurans.[4] Moreover, Dötz and co-workers have recently described the synthesis and X-ray crystal structure of a novel Diels–Alder adduct obtained from an α,β-unsaturated (aminocarbene)tungsten complex.[5] On the other hand, alkenylcarbene complexes undergo many interesting transformations including Diels–Alder reactions,[6] cyclohexadienone annulations,[7] conversions to pyrroles,[8] δ-carbolines,[9] or 3-imidazoline complexes,[10] transmetalations,[11] formation of dimetallic

(1) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983.

(2) (a) Dötz, K. H.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 851. (b) Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915. (c) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. O. *J. Organomet. Chem.* **1987**, *334*, 9.

(3) (a) Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101. (b) Hegedus, L. S.; de Weck, G.; D'Andrea, S. *Ibid.* **1988**, *110*, 2122. (c) Hegedus, L. S.; D'Andrea, S. *J. Org. Chem.* **1988**, *53*, 3113.

(4) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550.

(5) Dötz, K. H.; Noack, R.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1988**, 302.

(6) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726.

(7) (a) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132. (b) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293.

(8) Aumann, R.; Heinen, H. *Chem. Ber.* **1986**, *119*, 3801.

(9) Aumann, R.; Heinen, H.; Krüger, C.; Tsay, Y. H. *Chem. Ber.* **1986**, *119*, 3141.

(10) Aumann, R.; Heinen, H.; Krüger, C. *Chem. Ber.* **1987**, *120*, 1287.

(11) Aumann, R.; Heinen, H.; Krüger, C.; Goddard, R. *Chem. Ber.* **1986**, *119*, 401.

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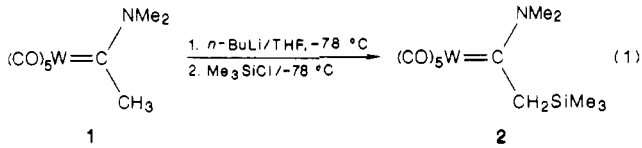
complexes containing either the μ-η^1,η^3-allylidene ligand[12] or μ-bis(carbene) ligand,[13] and polymerizations to novel organometallic polymers.[14]

(Alkenylaminocarbene)chromium, -tungsten, and -manganese complexes have been prepared by several methods by using a variety of organometallic precursors and reagents. The most obvious method, which takes advantage of the facile aminolysis of alkoxycarbene complexes,[15] involves treating (alkenylalkoxycarbene)chromium or -tungsten complexes with amines. Interestingly, the first reported (alkenylaminocarbene)metal complex $(CO)_5Cr[C(NHC_6H_{11})C(OCH_3)=CH_2]$ was not prepared by this method;[16] moreover, to our knowledge only one alkenylaminocarbene complex has been synthesized in this manner.[5] Dötz and co-workers have developed a general route to (alkenylaminocarbene)chromium, -tungsten, and -manganese complexes, which bear an alkoxy group on the β-carbon, by reacting (alkenylalkoxycarbene)metal complexes with ynamines and yndiamines.[2a,17] (Alkynylalkoxycarbene)chromium and -tungsten complexes undergo both aminolysis and conjugate addition reactions with two amine molecules to afford (alkenylaminocarbene)metal complexes bearing an amino group on the β-carbon.[18] Furthermore, the preparation of two (alkenylaminocarbene)chromium complexes[19] and one (alkenylaminocarbene)tungsten complex,[20] using three different specialized methods, have recently been described.

Results and Discussion

As part of our continuing efforts to synthesize and polymerize carbene vinyl monomers,[14,21] we sought to prepare the parent (alkenylaminocarbene)tungsten complex **3a**. Thus, treatment of $(CO)_5W[C(OCH_3)CH=CH_2]$[21] with $HNMe_2$, following standard aminolysis conditions (Et_2O, −110 to −50 °C),[15] always led to polymer formation (80–90%)[22] and a trace of **3a**. Apparently $HNMe_2$ initiates the polymerization of this monomer $(CO)_5W[C(OCH_3)CH=CH_2]$ by conjugate addition to the terminal vinylic carbon. We also attempted to prepare **3a** by two slightly different methods, which were originally developed to synthesize (alkenylalkoxycarbene)chromium complexes from (alkylalkoxycarbene)chromium complexes.[23] Unfortunately both methods,[23] when applied to (alkylaminocarbene)tungsten complexes, failed. We reasoned, however, that the failure of Aumann's method,[23b] which involved a one-pot reaction of 1, aldehyde, Et_3N, and Me_3SiCl, was due to Et_3N being too weak a base to abstract an α-proton on **1**. By substituting *n*-BuLi as a stronger base for Et_3N and conducting the reaction in several steps (eq 1 and 2), we were able to prepare not only **3a** (57%) but also several other (alkenylaminocarbene)tungsten complexes (**3**) (eq 2). The synthesis of alkenes from α-silyl carbanions, like $(CO)_5W[C(NMe_2)CHSiMe_3]Li$, and aldehydes or ketones (eq 2) is, of course, the well-known Peterson reaction.[24]

The requisite [(α-(trimethylsilyl)alkyl)aminocarbene]-tungsten complex (**2**) for the Peterson reactions (eq 2) was prepared in 90% as an air-stable yellow oil by treating **1** with *n*-BuLi followed by Me_3SiCl (eq 1). Because the



(1)

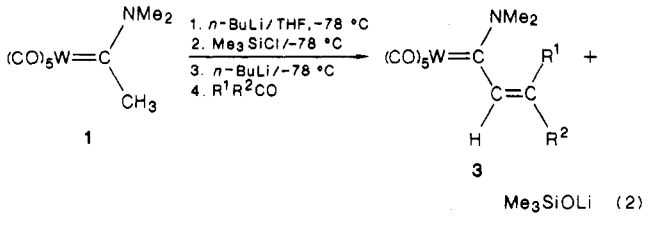
1 **2**

$(CO)_5W$=C fragment is electronically similar to the carbonyl fragment (O=C) (i.e. the protons on the carbon α to the carbene carbon in $(CO)_5M[C(OCH_3)CH_3]$ (M = Cr, W) complexes are very acidic; the pK_a is approximately 8),[25] complex **2** can be considered to be the carbene analogue of an α-trimethylsilyl amide. Complex **2** is more stable to the mild protodesilyation conditions of silica gel chromatography than the only other reported (α-(trimethylsilyl)alkyl)carbene complex $(CO)_5Cr[C(OC_2H_5)CH_2SiMe_3]$.[26,27] Furthermore, when the same conditions described in eq 1 are applied to $(CO)_5M[C(OCH_3)CH_3]$ (M = Cr, W) the expected (α-(trimethylsilyl)alkyl)alkoxycarbene complexes $(CO)_5M[C(OCH_3)CH_2SiMe_3]$ were not obtained. The products from this reaction, which are both sensitive to temperature and silica gel chromatography, have not, as yet, been characterized. It should also be noted, however, that $(CO)_5Cr[C(OC_2H_5)CH_2SiMe_3]$ was prepared by treating $Cr(CO)_6$ with Me_3SiCH_2Li, followed by exchange of Li^+ for NMe_4^+ in the resulting metal acylate anion, and finally alkylation with $(C_2H_5)_3O^+BF_4^-$.[26]

With complex **2** readily available from eq 1, we were able to use it in the Peterson reaction with a variety of organic carbonyl compounds. Thus, treatment of **2** with *n*-BuLi followed by certain aldehydes or ketones produced the (alkenylaminocarbene)tungsten complexes **3** in moderate yields (eq 2). In fact, the reported yields of complexes **3** (eq 2) are actually those obtained in a one-pot reaction starting from complex **1** (see Experimental Section for details).

Upon purification, which included chromatography on silica gel followed by crystallization, complexes **3** were isolated as yellow to yellow-orange air-stable crystalline materials, except **3c**, which was obtained as a yellow-orange oil. The structures of complexes **3** were easily determined by using ^1H NMR, ^{13}C NMR, and MS spectroscopic techniques; moreover, the spectral values are similar to other (aminocarbene)tungsten complexes. Typically, because of rotational barriers associated with the C(carbene)–N partial double bond,[29] two different alkyl resonances are observed in the ^1H and ^{13}C NMR spectra of [(dialkylamino)carbene]chromium and -tungsten com-

(12) Macomber, D. W.; Liang, M. Rogers, R. D. *Organometallics* **1988**, 7, 416 and references therein.
(13) Macomber, D. W.; Hung, M. H.; Verma, A. G.; Rogers, R. D. *Organometallics* **1988**, 7, 2072.
(14) Macomber, D. W.; Hung, M. H.; Liang, M.; Verma, A. G.; Madhukar, P. *Macromolecules* **1988**, *21*, 1187.
(15) Reference 1, pp 153–156, pp 252–256.
(16) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954.
(17) (a) Dötz, K. H.; Kreiter, C. G. *J. Organomet. Chem.* **1975**, *99*, 309. (b) Dötz, K. H.; Kreiter, C. G. *Chem. Ber.* **1976**, *109*, 2026. (c) Dötz, K. H.; Pruskil, I. *J. Organomet. Chem.* **1977**, *132*, 115. (d) Dötz, K. H. *Chem. Ber.* **1977**, *110*, 78. (e) Dötz, K. H.; Fügen-Köster, B.; Neugebauer, D. *J. Organomet. Chem.* **1979**, *182*, 489. (f) Dötz, K. H.; Strum, W.; Alt, H. G. *Organometallics* **1987**, *6*, 1424.
(18) (a) Fischer, E. O; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47. (b) Fischer, E. O.; Kalder, H. J. *J. Organomet. Chem.* **1977**, *131*, 57.
(19) (a) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680. (b) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, 7, 702.
(20) Aumann, R.; Kuckert, E. *Chem. Ber.* **1987**, *120*, 1939.
(21) Macomber, D. W.; Liang, M.; Madhukar, P.; Verma, A. G. *J. Organomet. Chem.* **1989**, *361*, 187.
(22) ^1H NMR ($CDCl_3$) analysis showed this soluble polymer to contain mainly methoxycarbene fragments along with a few (dimethylamino)-carbene fragments.
(23) (a) Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503. (b) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.
(24) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; pp 58–78.
(25) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230.
(26) Connor, J. A.; Jones, E. M. *J. Organomet. Chem.* **1973**, *60*, 77.
(27) [(α-(Trimethylsilyl)alkyl)alkoxycarbene]tungsten complexes have also been proposed as reactive intermediates in the preparation of [μ-bis(carbene)]ditungsten complexes[13] and (alkylalkoxycarbene)tungsten complexes.[28]
(28) Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1986**, 514.
(29) Reference 1, pp 114–149.



3	R^1	R^2	% yield of 3
a	H	H	57
b	H	Ph	61
c	H	2-furyl	45
d	H	*trans*-CH=CHPh	53
e	H	(η-C_5H_4)Fe(η-C_5H_5)	51
f	Ph	Ph	54

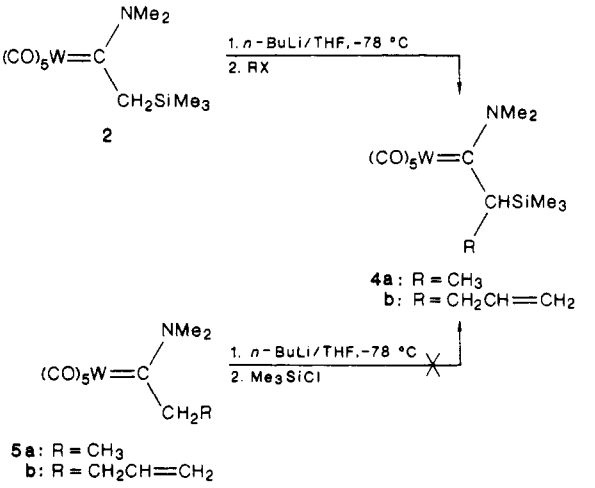
plexes.[17,18,19b,30] For example, the methyl resonances of the $N(CH_3)_2$ group in **3b** are observed at δ 3.82 and 3.40 in the ^1H NMR spectrum ($CDCl_3$) and δ 53.52 and 44.11 in the ^{13}C NMR spectrum ($CDCl_3$). Furthermore, on the basis of Fischer's stereochemical assignments,[31] the low-field CH_3 resonance (δ 3.82) in **3b** is assigned to the CH_3 group cis to the $W(CO)_5$ fragment whereas the high-field CH_3 resonance (δ 3.40) is assigned to the CH_3 group trans to the $W(CO)_5$ fragment. Similar assignments can be made for all the other compounds (**2**, **3a**,**c**–**f**, **4a**,**b**, **5a**,**b**, **7**, and **8**) described in this paper. For complexes **3b**–**e** only the isomer with the *E* configuration about the carbon–carbon double bond was isolated. These stereochemical assignment for complexes **3b**–**e** were easily determined by observing the vicinal vinylic coupling constants, which, for a trans disubstituted carbon–carbon double bond, typically fall in the 12–18 Hz range.[32] The ^{13}C NMR chemical shift values for the W=*C* (ca. δ 250-253), W—*C*O, trans (ca. δ 203), and W—*C*O, cis (ca. δ 198) carbons in compounds **3a**–**f** are similar to each other as well as to other (aminocarbene)tungsten complexes.[5,20,30,33] Interestingly, for comparison purposes with **3a**–**f**, we could not find any ^{13}C NMR data available for simple (alkenylaminocarbene)-tungsten complexes; however, Hegedus and co-workers have recently reported the ^{13}C NMR spectrum of the chromium analogue of **3b**.[19b] Thus, complex **3b** exhibits ^{13}C NMR resonances ($CDCl_3$) at δ 253.00 (W=*C*), 203.43 (W—*C*O, trans), and 198.50 (W—*C*O, cis), whereas (*E*)-$(CO)_5Cr[C(NMe_2)CH{=}CHPh]$ exhibits ^{13}C NMR resonances ($CDCl_3$) at δ 270.93 (Cr=*C*), 223.52 (Cr—*C*O, trans), and 217.49 (Cr—*C*O, cis). In general, the M=*C* and M—*C*O ^{13}C NMR resonances are seen at higher field for tungsten carbene complexes (alkoxy and amino) than for the analogous chromium carbene complexes.[34] The mass spectra of complexes **3a**–**f** all exhibit parent molecular ions (M^+) along with ions for the successive loss of one (M^+ – CO), two (M^+ – 2CO), three (M^+ – 3CO), four (M^+ – 4CO), and five (M^+ – 5CO) carbon monoxide ligands; this is consistent with that observed for other (aminocarbene)-tungsten and -chromium complexes.[8,17d,19a,33,34]

As mentioned above, only the *E* isomers of complexes **3b**–**e** were isolated. Although the exclusive formation of only the *E* isomers is striking, it is not without precedent for the Peterson reaction.[36] For example, treatment of $Me_3SiCH_2CO_2C_2H_5$ with $(c\text{-}C_6H_{11})_2NLi$ followed by benzaldehyde gave ethyl cinnamate (84%, *E*/*Z* = 3:1),[37] whereas treatment of $Me_3SiCH_2CO_2CH_3$ with LDA/$MgBr_2$ followed by benzaldehyde and then hydrolysis and BF_3·Et_2O produced methyl cinnamate (87%, *E*/*Z* = >99:1).[36c]

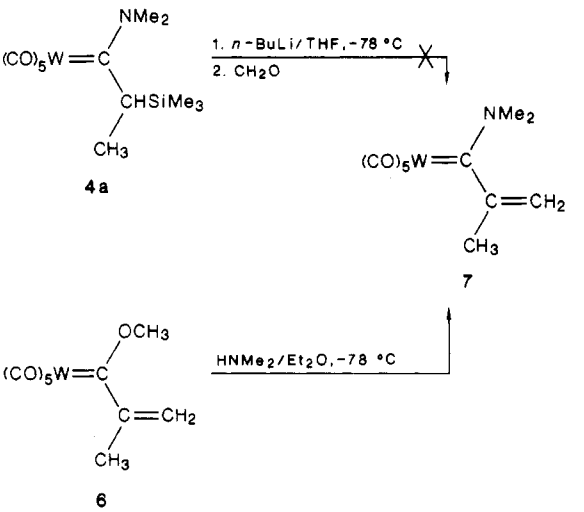
In contrast to successful Peterson reactions involving anions of α-silyl esters with enolizable aldehydes or ketones,[36c,37] $(CO)_5W[C(NMe_2)CHSiMe_3]Li$, when reacted with enolizable aldehydes or ketones, failed to give alkene products. For example, treatment of **2** with *n*-BuLi followed by acetone resulted only in recovered **1** (72%). The failure of $(CO)_5W[C(NMe_2)CHSiMe_3]Li$ to add to the carbonyl group of enolizable ketones is not due to steric restrictions; this anion cleanly reacted with benzophenone to afford **3f** (54%). We suspect $(CO)_5W[C(NMe_2)CHSiMe_3]Li$ reacts with acetone by enolization; however, this assumption has not been rigorously proven as it has for other α-carbene anions.[38]

We next attempted to extend the Peterson reaction outlined in eq 2 to synthesize (alkenylaminocarbene)-tungsten complexes with substituents at the α-position (e.g.

Scheme I



Scheme II



(30) (a) Casey, C. P.; Shusterman, A. J.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2417. (b) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *Ibid.* **1984**, *106*, 3754. (c) Casey, C. P.; Shusterman, A. J. *Organometallics* **1985**, *4*, 736. (d) Parlier, A.; Rudler, H.; Daran, J. C.; Alvarez, C.; Delgado Reyes, F. *J. Organomet. Chem.* **1987**, *327*, 339.

(31) (a) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1969**, *16*, 275. (b) Fischer, E. O.; Leupold, M. *Chem. Ber.* **1972**, *105*, 599. (c) Brunner, H.; Doppelberger, J.; Fischer, E. O.; Lappus, M. *J. Organomet. Chem.* **1976**, *112*, 65.

(32) Rahman, A. *Nuclear Magnetic Resonance*; Springer-Verlag: New York, 1986; pp 80–81.

(33) Aumann, R.; Kuckert, E.; Heinen, H. *Chem. Ber.* **1987**, *120*, 1293.

(34) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: New York, 1981.

(35) Weiss, K.; Fischer, E. O. *Chem. Ber.* **1973**, *106*, 1277.

(36) (a) Hudrlik, P. F.; Peterson, D. *Tetrahedron Lett.* **1974**, 1133. (b) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464. (c) Larchevêque, M.; Debal, A. *J. Chem. Soc., Chem. Commun.* **1981**, 877.

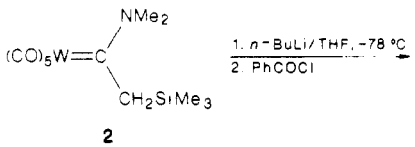
(37) Shimoji, K.; Taguchi, H.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 1620.

(38) Xu, Y.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263.

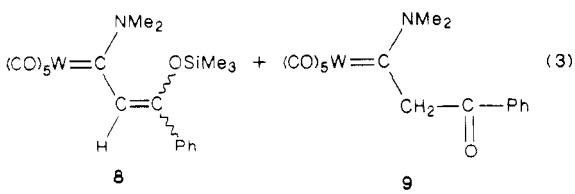
complex **7**). This required preparing the appropriately substituted [(α-(trimethylsilyl)alkyl)aminocarbene]tungsten complexes **4** (Scheme I). Treating **5a** or **5b**[39] with *n*-BuLi followed by Me_3SiCl, under identical conditions used to prepare **2** from **1** (eq 1), led only to recovered **5a** or **5b** and not, as desired, to complexes **4a** and **4b**. We were, however, successful in preparing **4a** and **4b** by treating **2** with *n*-BuLi followed by either $CF_3SO_3CH_3$ or CH_2=$CHCH_2Br$, respectively (Scheme I). Complexes **4a** and **4b**, prepared in this manner, were obtained in good yields (70–90%) as yellow oils containing small amounts of unreacted **2**. The mixtures of **4a**/**2** and **4b**/**2** could not be separated into their pure components, and, therefore, analytical samples of **4a** and **4b** could not be obtained. It is interesting that $(CO)_5W[C(NMe_2)CHSiMe_3]Li$ reacts with RX ($CF_3SO_3CH_3$ or CH_2=$CHCH_2Br$), whereas α-anions from **5a** or **5b**, $(CO)_5W[C(NMe_2)CH(R)]Li$ (R = CH_3, CH_2CH=CH_2), do not react with Me_3SiCl (Scheme I). The different reactivities observed for $(CO)_5W[C(NMe_2)CHR]Li$ (R = CH_3, CH_2CH=CH_2, $SiMe_3$) (Scheme I) are not, as yet, understood; however, there may be analogies to the reactivities of α-silyl esters to draw upon.[41]

Having compounds **4** in hand allowed us to evaluate their suitability with various aldehydes and ketones in the Peterson reaction. Unfortunately, treatment of **4a** with *n*-BuLi followed by paraformaldehyde resulted only in recovered **4a** (40–50%) and not, as expected, complex **7** (Scheme II). Complex **7** could, however, be prepared in 75–80% yield through the aminolysis of **6**[12] using $HNMe_2$. Unlike the above-mentioned parent (alkenylalkoxycarbene)tungsten complex $(CO)_5W[C(OCH_3)CH$=$CH_2]$, complex **6** *did not* undergo homopolymerization upon treatment with $HNMe_2$. For that matter, **6** could not be polymerized by using any other anionic initiator.[42] Although α-substituted α-silyl esters undergo the Peterson reaction with a variety of aldehydes and ketones,[43] the analogous α-substituted α-silyl (aminocarbene)tungsten complexes **4** failed to react with aldehyes or ketones to afford the desired α-substituted (alkenylaminocarbene)tungsten complexes **7**. This failure may be due to steric factors.

Shown in eq 3 is an example of a reaction of $(CO)_5W[C(NMe_2)CHSiMe_3]Li$ with an acid chlorides. Thus,



2



8 **9** (3)

treatment of **2** with *n*-BuLi followed by benzoyl chloride afforded the enol silyl ether derivative **8** (26%) as a single isomer with unspecified stereochemistry about the carbon–carbon double bond. Also obtained in this reaction was a small amount of a compound tentatively assigned as **9**. Complex **8** was obtained as an air-stable, slightly moisture-sensitive yellow crystalline material, whereas **9**, which was characterized only by its ^1H NMR spectrum, was obtained as a yellow oil that decomposed and turned blue-green upon exposure to air. We believe the formation of **8** occurs by attack of $(CO)_5W[C(NMe_2)CHSiMe_3]Li$ at the carbonyl group of benzoyl chloride, followed by transfer of the trimethylsilyl group from carbon to oxygen,[36c] and finally elimination of chloride, and not by the β-ketosilane (i.e. $(CO)_5W[C(NMe)_2CH(SiMe_3)C(O)Ph]$) to enol silyl ether (i.e. **8**) rearrangement.[44] It should also be noted that the enol acetate derivative (*E*)-$(CO)_5W[C(OCH_3)CH$=$C(CH_3)O_2CCH_3]$, which is similar in structure to **8** has

Table I. Bond Distance (Å) and Angles (deg) for Complex 3e[a]

Bond Distances			
W–C(1)	2.05 (1)	W–C(2)	1.97 (1)
W–C(3)	2.00 (1)	W–C(4)	2.03 (1)
W–C(5)	1.92 (2)	W–C(6)	2.25 (1)
Fe–C(9)	2.04 (1)	Fe–C(10)	2.03 (1)
Fe–C(11)	2.01 (2)	Fe–C(12)	1.98 (2)
Fe–C(13)	1.99 (2)	Fe–C(14)	2.02 (2)
Fe–C(15)	2.01 (2)	Fe–C(16)	2.02 (2)
Fe–C(17)	2.00 (3)	Fe–C(18)	2.00 (1)
O(1)–C(1)	1.11 (2)	O(2)–C(2)	1.18 (2)
O(3)–C(3)	1.15 (2)	O(4)–C(4)	1.15 (2)
O(5)–C(5)	1.20 (2)	N–C(6)	1.32 (1)
N–C(19)	1.49 (1)	N–C(20)	1.47 (2)
C(6)–C(7)	1.43 (2)	C(7)–C(8)	1.17 (3)
C(7)–C(8)′	1.04 (3)	C(8)–C(9)	1.48 (2)
C(8)′–C(9)	1.63 (3)	C(9)–C(10)	1.39 (2)
C(9)–C(13)	1.40 (2)	C(10)–C(11)	1.41 (3)
C(11)–C(12)	1.36 (3)	C(12)–C(13)	1.36 (3)
C(14)–C(15)	1.35 (2)	C(15)–C(16)	1.37 (4)
C(14)–C(18)	1.32 (3)	C(16)–C(17)	1.38 (3)
Cent 1–Fe	1.63	C(17)–C(18)	1.37 (3)
		Cent 2–Fe	1.64
Bond Angles			
C(1)–W–C(2)	91.3 (5)	C(1)–W–C(3)	88.9 (5)
C(2)–W–C(3)	92.1 (5)	C(1)–W–C(4)	172.5 (5)
C(2)–W–C(4)	88.6 (5)	C(3)–W–C(4)	83.6 (5)
C(1)–W–C(5)	88.5 (6)	C(2)–W–C(5)	175.5 (5)
C(3)–W–C(5)	92.4 (6)	C(4)–W–C(5)	92.2 (6)
C(1)–W–C(6)	90.4 (5)	C(2)–W–C(6)	86.6 (4)
C(3)–W–C(6)	178.5 (5)	C(4)–W–C(6)	97.1 (4)
C(5)–W–C(6)	88.9 (5)	C(6)–N–C(19)	123.7 (9)
C(6)–N–C(20)	123.2 (9)	C(19)–N–C(20)	113.1 (9)
W–C(1)–O(1)	173 (1)	W–C(2)–O(2)	178 (1)
W–C(3)–O(3)	179 (1)	W–C(4)–O(4)	177 (1)
W–C(5)–O(5)	174 (1)	W–C(6)–N	129.0 (7)
W–C(6)–C(7)	115.4 (9)	N–C(6)–C(7)	116 (1)
C(6)–C(7)–C(8)	149 (2)	C(6)–C(7)–C(8)′	146 (2)
C(7)–C(8)–C(9)	131 (2)	C(7)–C(8)′–C(9)	128 (2)
C(8)–C(9)–C(10)	108 (1)	C(8)′–C(9)–C(10)	149 (1)
C(8)–C(9)–C(13)	146 (2)	C(8)′–C(9)–C(13)	105 (1)
C(10)–C(9)–C(13)	106 (1)	C(9)–C(10)–C(11)	108 (2)
C(10)–C(11)–C(12)	108 (2)	C(11)–C(12)–C(13)	109 (2)
C(9)–C(13)–C(12)	109 (1)	C(15)–C(16)–C(17)	109 (2)
C(15)–C(14)–C(18)	110 (2)	C(16)–C(17)–C(18)	105 (2)
C(14)–C(15)–C(16)	107 (2)	C(14)–C(18)–C(17)	110 (2)
Cent 1–Fe–Cent 2	178.4		

[a] C(8) and C(8)′ refer to the two orientations of this atom. Cent 1 and Cent 2 refer to the centroids of the planes defined by atoms C(9)–C(13) and C(14)–C(18), respectively.

(39) Complex **5a** was prepared in quantitative yield from $(CO)_5W[C(OCH_3)CH_2CH_3]$[40] and $HNMe_2$, whereas **5b** was prepared from **1** (90%) using *n*-BuLi followed by CH_2=$CHCH_2Br$. Details are given in the Experimental Section.

(40) Macomber, D. W. *Organometallics* **1984**, *3*, 1589.

(41) (a) Larson, G. L.; Fuentes, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2418. (b) Helmchen, G.; Schmierer, R. *Tetrahedron Lett.* **1983**, *24*, 1235. (c) Larson, G. L.; Hernandez, D.; Montes de Lopez-Cepero, I.; Torres, L. E. *J. Org. Chem.* **1985**, *50*, 5260.

(42) Macomber, D. W.; Hung, M. H. *J. Organomet. Chem.*, in press.

(43) Larson, G. L.; Fernandez de Kaiter, C.; Seda, R.; Torres, L. E.; Ramirez, J. R. *J. Org. Chem.* **1984**, *49*, 3385.

(44) Kwart, H.; Barnette, W. E. *J. Am. Chem. Soc.* **1977**, *99*, 614.

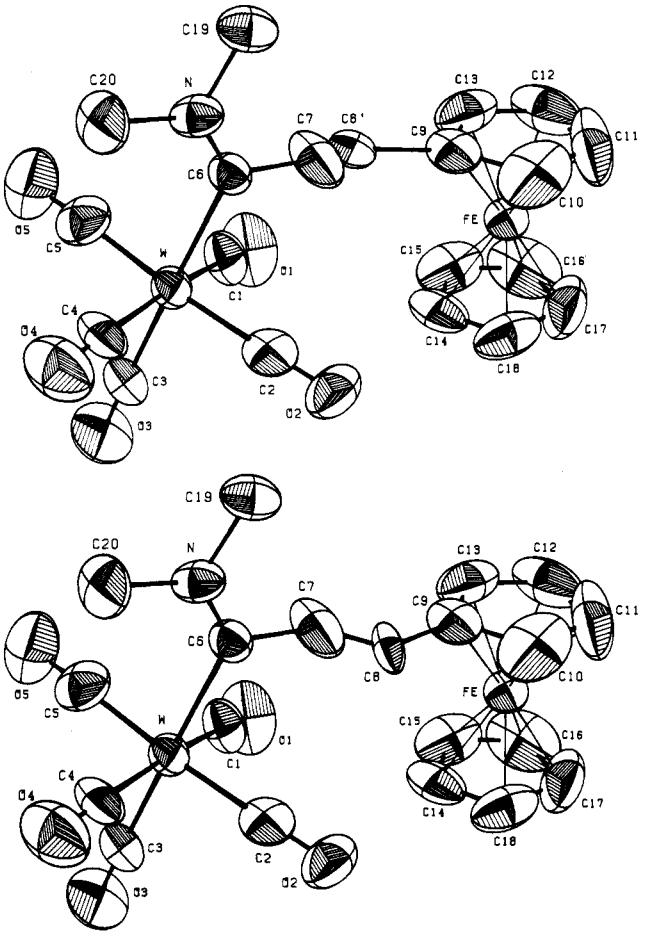


Figure 1. Molecular structure and atom-labeling scheme for the two orientations of (*E*)-$(CO)_5W[C(NMe_2)CH{=}CH(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$ (**3e**). The atoms are represented by their 50% probability thermal ellipsoids.

previously been isolated by the reaction of $(CO)_5W[C(OCH_3)CH_2]Li$ with 2 equiv of acetyl chloride.[45]

The molecular structure and atom-labeling scheme for the two orientations of complex **3e** are presented in Figure 1, whereas bond distances and angles are presented in Table I. The overall structure of **3e** contains an octahedrally disposed (aminocarbene)tungsten pentacarbonyl fragment connected through a carbon–carbon double bond to a ferrocenyl group. The W–C(carbene) (W–C(6)) distance of 2.25 (1) Å is typical of (aminocarbene)tungsten complexes;[5,30a,b,d] moreover, because the amino group is a better π-donor than the alkoxy group,[46] the C(carbene)–N distances in (aminocarbene)tungsten complexes are generally equal to or shorter than the C(carbene)–O distances in (alkoxycarbene)tungsten complexes.[47] The C(6)–N bond distance of 1.32 (1) Å is shorter than the $C(sp^2)$–N theoretical bond distance of 1.45 Å[48] and indicates considerable π-bonding between C(6) and N. As expected, W, C(6), C(7), and N are coplanar to within 0.01 Å, which is a prerequisite for π-bonding. The bond angles about the carbene carbon W–C(6)–N (129.0 (7)°), W–C(6)–C(7) (115.4 (9)°), and N–C(6)–C(7) (116 (1)°) are similar to other (aminocarbene)tungsten complexes.[5,30a,b,d] Although a disorder at C(8) exists in this structure, the stereochemistry of the carbon–carbon double bond, in which the carbene fragment and the ferrocenyl group are on opposite sides, clearly has the *E* configuration. The bond distances (Fe–C, 2.01 Å (av); C–C in ring, 1.37 Å (av)) and angles (C–C in ring, 108° (av)) associated with the ferrocenyl group are unexceptional and are similar to those reported in other structures.[49]

We have successfully prepared, using the Peterson reaction, a series of (alkenylaminocarbene)tungsten complexes (**3**) in moderate yields from a common precursor, $(CO)_5W[C(NMe_2)CH_2SiMe_3]$ (**2**), and aldehyes or ketones. The scope and limitations of this reaction have been delineated; moreover, it appears the chromium analogues of complexes **3** can be prepared in a similar manner. For example, $(CO)_5Cr[C(NMe_2)CH_2SiMe_3]$ has been synthesized from $(CO)_5Cr[C(NMe_2)CH_3]$ in 38% yield and converted, with paraformaldehyde, to $(CO)_5Cr[C(NMe_2)CH{=}CH_2]$ (31%).[50]

Experimental Section

General Data. All reactions were carried out under an inert nitrogen atmosphere. Hexane, methylene chloride, and trimethylsilyl chloride were distilled from CaH_2 under nitrogen. Diethyl ether and tetrahydrofuran were distilled from sodium–benzophenone ketyl under nitrogen. Flash chromatography[51] was conducted on E. Merck silica gel 60 (40–63 μm). $(CO)_5W[C(NMe_2)CH_3]$ (**1**) was prepared from $(CO)_5W[C(OCH_3)CH_3]$[40] and dimethylamine according to literature procedures.[30] $(CO)_5W[C(OCH_3)CH_2CH_3]$[40] and $(CO)_5W[C(OCH_3)C(CH_3){=}CH_2]$ (**6**)[12] were also prepared according to literature procedures. Dimethylamine was obtained as a 1.0 M solution in diethyl ether from Alfa Products. All other chemicals and reagents were obtained from Aldrich Chemical Co. and used without further purification.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WM-400 instrument operating at 400.1 and 100.6 MHz, respectively. ^1H NMR data are reported as follows: chemical shift in parts per million referenced to TMS or residual solvent proton resonance (multiplicity, coupling constants(s) in hertz, and number of protons). ^{13}C NMR data are reported as follows: chemical shift in parts per million referenced to residual solvent carbon resonance. Low-resolution mass spectra were acquired on a Finnigan 4000 instrument, and spectral data are listed as *m/e* (intensity of base peak) for only the tungsten-184 isotope. Elemental analyses were performed by Microlytics, South Deerfield, MA.

X-ray Data Collection, Structure Determination, and Refinement for (*E*)-$(CO)_5W[C(NMe_2)CH{=}CH(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$ (3e). A transparent orange single crystal of the title compound was mounted on a pin and transferred to the gon-

(45) Casey, C. P.; Boggs, R. A.; Anderson, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8947.

(46) Reference 1, pp 74–111.

(47) (a) Daran, J.; Jeannin, Y. *Acta Crystallogr.* **1980**, *B36*, 1392. (b) fischer, E. O.; Gammel, F. J.; Besenhard, J. O.; Frank, A.; Neugebauer, D. *J. Organomet. Chem.* **1980**, *191*, 261. (c) Toledano, C. A.; Levisalles, J.; Rudler, M.; Rudler, H.; Daran, J. C.; Jeannin, Y. *J. Organomet. Chem.* **1982**, *228*, C7. (d) Toledano, C. A.; Rudler, H.; Daran, J. C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 574. (e) Toledano, C. A.; Parlier, A.; Rudler, H.; Daran, J. C.; Jeannin, Y. *Ibid*, **1984**, 576. (f) Parlier, A.; Rudler, M.; Rudler, H.; Daran, J. C. *J. Organomet. Chem.* **1987**, *323*, 353. (e) Toledano, C. A.; Parlier, A.; Rudler, H.; Rudler, M.; Daran, J. C.; Knobler, C.; Jeannin, Y. *Ibid.* **1987**, *328*, 357.

(48) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960, p 282.

(49) Deeming, A. J. In *Comprehensive Organometallic* Chemistry; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 4, pp 475–491.

(50) $(CO)_5Cr[C(NMe_2)CH_2SiMe_3]$: ^1H NMR ($CDCl_3$) δ 3.81 (s, 3 H), 3.24 (s, 3 H), 3.13 (s, 2 H), 0.19 (s, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 274.40, 223.16, 218.17, 53.06, 48.48, 42.97 0.57; MS (15.8 eV), *m/e* 335 (M^+, 2%) 307 (15), 279 (2), 223 (1). Anal. Calcd for $C_{12}H_{17}CrNO_5Si$: C, 43.18; H, 5.09; N, 4.16. Found: C, 42.98; H, 4.98; N, 4.38. $(CO)_5Cr[C(NMe_2)CH{=}CH_2]$: ^1H NMR ($CDCl_3$) δ 6.71 (dd, *J* = 18.4, 12.3 Hz, 1 H), 4.91 (d, *J* = 12.3 Hz, 1 H), 4.89 (d, *J* = 17.4 Hz, 1 H), 3.86 (s, 3 H), 3.40 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 271.66, 223.43, 217.62, 146.12, 105.51, 50.99, 45.28; MS (22.0 eV) *m/e* 275 (M^+, 9%), 247 (39), 163 (1), 135 (1). Anal. Calcd for $C_{10}H_9CrNO_5$: C, 43.65; H, 3.30; N, 5.09. Found: C, 43.54; H, 3.43; N, 5.07.

(51) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(52) Sheldrick, G. M.; SHELX, a system of computer programs for X-ray structure determination as locally modified (1976).

(53) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1972; Vol. IV, pp 72, 99, 149.

Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement (E)-$(CO)_5W[C(NMe_2)CH{=}CH(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$ (3e)

color/shape	orange/parallelepiped
mol wt	591.06
space group	$P2_1/c$
temp, °C	20
cell const[a]	
a, Å	12.022 (4)
b, Å	12.857 (8)
c, Å	13.826 (8)
β, deg	102.19 (4)
cell vol, Å^3	2088.9
molecules/unit cell	4
D(calcd), g cm^{-3}	1.88
μ(calcd), cm^{-1}	59.6
diffractometer/scan	Enraf-Nonius CAD-4/θ–2θ
range of relative transm factors	79/100
radiatn, graphite monochromator	Mo Kα (λ = 0.71073 Å)
max cryst dimens, mm	0.18 × 0.20 × 0.23
scan width	0.80 + 0.35 tan θ
std reflctns	10, 0, 0; 008; 080
decay of stds	±1%
reflctns measd	4009
2θ range, deg	$2 \le 2\theta \le 50$
range of h, k, l	+14, +15, ±16
reflctns obsd [$F_o \ge 5\sigma(F_o)$][b]	2604
computer programs[c]	SHELX[52]
structure soln	heavy-atom techniques
no. of parameters varied	262
weights	$[\sigma(F_o)^2 + 0.000\,03F_o^2]^{-1}$
GOF	0.67
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.044
R_w	0.044
largest feature final diff map	1.3 e Å^{-3} near W

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 20°$. [b] Corrections: Lorentz–polarization and absorption (empirical, psi scan). [c] Neutral scattering factors and anomalous dispersion corrections from ref 53.

iometer. The space group was determined to be the centric $P2_1/c$ from the systematic absences. A summary of data collection parameters is given in Table II. Least-squares refinement with isotropic thermal parameters led to R = 0.083. The cyclopentadienyl hydrogens were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. High thermal motion was initially observed for C(8) of the C_2H_2 fragment. Further investigation revealed two orientations of 50% occupancy each for this carbon position. Each was refined in alternate cycles. Due to the disorder the remaining hydrogen atoms were not included in the final refinement. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of R = 0.044 and R_w = 0.044. The final values of the positional parameters are given in Table III.

$(CO)_5W[C(NMe_2)CH_2SiMe_3]$ (2). Complex 1 (0.50 g, 1.3 mmol) was dissolved in 20 mL of THF and cooled to −78 °C. To this solution was added 2.5 M n-BuLi in hexane (0.61 mL, 1.5 mmol) and stirred at −78 °C for 30 min. Trimethylsilyl chloride (0.24 mL, 1.9 mmol) was then added, stirred for 30 min at −78 °C, and allowed to warm to 25 °C with removal of the solvent under vacuum. The resulting yellow residue was dissolved in a minimum of methylene chloride and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/hexane and removal of the solvent under vacuum gave **2** (0.53 g, 90%): yellow oil; ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 3 H), 3.26 (s, 2 H, 3.24 (s, 3 H), 0.22 (s, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 256.26, 203.10, 199.55, 55.68, 49.87, 41.59, 0.69; MS (11.9 eV) m/e 467 (M^+, 7%), 439 (12), 411 (8), 383 (2), 355 (1), 326 (0.4). Anal. Calcd for $C_{12}H_{17}NO_5SiW$: C, 30.85; H, 3.67; N, 2.99. Found: C 30.81; H, 3.65; N, 3.00.

$(CO)_5W[C(NMe_2)CH{=}CH_2]$ (3a). Complex 1 (1.00 g, 2.5 mmol) was dissolved in 50 mL of THF and cooled to −78 °C. To this solution was added 1.2 mL (3.0 mmol) of 2.5 M n-BuLi in hexane and the mixture stirred at this temperature for 30 min. Trimethylsilyl chloride (0.48 mL, 3.8 mmol) was then added, stirred for 30 min at −78 °C, and allowed to warm to 25 °C with removal of the solvent under vacuum. The resulting yellow oil was dissolved in 50 mL of THF and cooled to −78 °C, and 1.2 mL (3.0 mmol) of 2.5 M n-BuLi in hexane was added with stirring for an additional 1 h. To this solution was then added a THF suspension (20 mL) of paraformaldehyde (0.15 g, 5.0 mmol) with stirring at −78 °C for 30 min. The reaction mixture was allowed to warm to 25 °C and the solvent removed under vacuum. The resulting yellow-brown residue was taken up in a minimum of methylene chloride and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/hexane produced a yellow band which was collected, and the solvent was removed under vacuum. Recrystallization of the resulting residue from pentane at 0 °C afforded **3a** (0.58 g, 57%): yellow needles; mp 58–59 °C; ^{1}H NMR ($CDCl_3$) δ 6.90 (dd, J = 18.3, 12.5 Hz, 1 H), 4.88 (d, J = 12.6 Hz, 1 H), 4.63 (d, J = 18.6 Hz, 1 H), 3.79 (s, 3 H), 3.37 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 253.90, 203.58, 198.59, 147.16, 107.77, 53.50, 43.80; MS (11.2 eV) m/e 407 (M^+, 16%), 379 (100), 351 (35), 323 (12), 295 (1). Anal. Calcd for $C_{10}H_9NO_5W$: C, 29.51; H, 2.23; N, 3.44. Found: C, 29.45; H, 2.22; N, 3.48.

Table III. Final Fractional Coordinates for Complex 3e

atom	x/a	y/b	z/c	B(eqv)[a]
W	0.20371 (4)	0.31328 (4)	0.80281 (4)	3.06
Fe	0.7117 (1)	0.3290 (1)	0.8398 (1)	3.19
O(1)	0.3811 (9)	0.4917 (8)	0.8802 (9)	7.16
O(2)	0.3408 (8)	0.2455 (7)	0.6423 (6)	5.03
O(3)	0.0656 (9)	0.4819 (8)	0.6612 (8)	6.93
O(4)	0.0009 (8)	0.1672 (8)	0.6978 (7)	6.03
O(5)	0.0833 (9)	0.3762 (9)	0.9724 (9)	7.30
N	0.2717 (8)	0.1158 (7)	0.9500 (6)	3.09
C(1)	0.323 (1)	0.425 (1)	0.857 (1)	4.55
C(2)	0.288 (1)	0.2714 (9)	0.702 (1)	3.90
C(3)	0.115 (1)	0.421 (1)	0.714 (1)	4.52
C(4)	0.075 (1)	0.218 (1)	0.7375 (9)	4.07
C(5)	0.129 (1)	0.347 (1)	0.908 (1)	4.90
C(6)	0.3071 (8)	0.1928 (9)	0.9014 (7)	2.82
C(7)	0.428 (1)	0.199 (1)	0.910 (1)	6.41
C(8)	0.507 (2)	0.189 (2)	0.874 (2)	2.97
C(8)′[b]	0.501 (2)	0.245 (2)	0.931 (2)	3.35
C(9)	0.626 (1)	0.224 (1)	0.908 (1)	4.00
C(10)	0.693 (2)	0.173 (1)	0.853 (1)	6.81
C(11)	0.807 (2)	0.204 (2)	0.888 (2)	8.97
C(12)	0.809 (1)	0.273 (2)	0.962 (1)	7.20
C(13)	0.701 (1)	0.287 (1)	0.976 (1)	5.58
C(14)	0.599 (1)	0.421 (1)	0.751 (1)	5.22
C(15)	0.670 (2)	0.480 (1)	0.818 (1)	6.94
C(16)	0.777 (2)	0.464 (2)	0.802 (2)	7.75
C(17)	0.772 (2)	0.390 (2)	0.728 (2)	8.92
C(18)	0.658 (2)	0.368 (1)	0.697 (1)	6.18
C(19)	0.350 (1)	0.0410 (8)	1.0137 (8)	3.47
C(20)	0.151 (1)	0.095 (1)	0.947 (1)	4.92

[a] B(eqv) = $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\cos(\gamma)\beta_{12} + ac\cos(\beta)\beta_{13} + bc\cos(\alpha)\beta_{23}]$. [b] Atoms C(8) and C(8)′ are disordered with 50% occupancy each.

(E)-$(CO)_5W[C(NMe_2)CH{=}CHPh]$ (3b). A THF solution (20 mL) of complex **1** (0.50 g, 1.3 mmol), which was cooled to −78 °C, was treated with 0.61 mL (1.5 mmol) of 2.5 M n-BuLi in hexane. The solution was allowed to stir at −78 °C for 30 min, treated with trimethylsilyl chloride (0.24 mL, 1.9 mmol) and allowed to stir for an additional 30 min. The solution was warmed to 25 °C and the solvent removed under vacuum. The resulting yellow oil was dissolved in 20 mL of THF and cooled to −78 °C, and 0.61 mL (1.5 mmol) of 2.5 M n-BuLi in hexane was added with stirring for an additional 1 h. To this solution was added benzaldehyde (0.26 mL, 2.6 mmol) with stirring at −78 °C for 1 h. The reaction mixture was warmed to 25 °C and the solvent removed under vacuum. The resulting residue was taken up in a minimum of methylene chloride and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/hexane produced two yellow bands, the first being complex **2** and second being **3b**. Removal of the solvent from the second band under vacuum and recrystallization from pentane at 0 °C gave **3b** (0.37 g, 61%): yellow-orange needles; mp 76–77 °C; ^{1}H NMR ($CDCl_3$) δ 7.42–7.23 (m, 5 H), 7.03 (d, J = 16.6 Hz, 1 H), 6.01 (d, J = 16.6 Hz, 1 H), 3.82 (s, 3 H), 3.40 (s, 3 H); $^{13}C\{^1H\}$ NMR

($CDCl_3$) δ 253.00, 203.43, 198.50, 138.75, 135.89, 128.82, 128.18, 126.74, 126.61, 124.15, 53.52, 44.11; MS (20 eV) *m/e* 483 (M^+, 2%) 455 (61), 427 (35), 399 (31), 371 (5), 343 (2). Anal. Calcd for $C_{16}H_{13}NO_5W$: C, 39.77; H, 2.71; N, 2.90. Found: C, 39.83; H, 2.72; N, 2.94.

(*E*)-$(CO)_5W[C(NMe_2)CH{=}CH(2\text{-furyl})]$ (3c). The procedure described for the preparation of **3b** was followed except 2-furaldehyde (0.21 mL, 2.5 mmol) was used in place of benzaldehyde. Removal of solvent from the second yellow band gave **3c** (0.27 g, 45%): yellow-orange oil; ^1H NMR ($CDCl_3$) δ 7.39 (s, 1 H), 6.99 (d, *J* = 16.6 Hz, 1 H), 6.41 (s, 1 H), 6.35 (s, 1 H), 5.96 (d, *J* = 16.4 Hz, 1 H), 3.82 (s, 3 H), 3.40 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 251.30, 203.44, 198.51, 151.33, 142.88, 136.71, 114.43, 111.76, 110.45, 53.69, 44.20; MS (11.2 eV) *m/e* 473 (M^+, 4%), 445 (35), 417 (100), 389 (7), 361 (47), 332 (6). Anal. Calcd for $C_{14}H_{11}NO_6W$: C, 35.54; H, 2.34; N, 2.96. Found: C 35.77; H, 2.72; N, 2.94.

(*E,E*)-$(CO)_5W[C(NMe_2)CH{=}CHCH{=}CHPh]$ (3d). The procedure described for the preparation of **3b** was followed except *trans*-cinnamaldehyde (0.32 mL, 2.5 mmol) was used in place of benzaldehyde. Removal of solvent from the second yellow band and recrystallization of the resulting residue from pentane at 0 °C gave **3d** (0.35 g, 53%): yellow-orange needles; mp 91–92 °C; ^1H NMR ($CDCl_3$) δ 7.44–7.22 (m, 5 H), 6.82 (dd, *J* = 15.5, 10.4 Hz, 1 H), 6.66 (d, *J* = 15.8 Hz, 1 H), 6.63 (d, *J* = 15.6 Hz, 1 H), 5.94 (dd, *J* = 15.9, 10.5 Hz, 1 H), 3.82 (s, 3 H), 3.40 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 251.68, 203.49, 198.38, 141.65, 136.72, 135.11, 128.70, 128.09, 127.44, 126.62, 126.44, 53.64, 44.24; MS (19.5 eV) *m/e* 510 (M^+, 1%) 481 (27), 425 (18), 379 (3), 369 (4). Anal. Calcd for $C_{18}H_{15}NO_5W$: C, 42.46; H, 2.97; N, 2.75. Found: C, 42.56; H, 2.98; N, 2.77.

(*E*)-$(CO)_5W[(NMe_2)CH{=}CH(\eta\text{-}C_5H_4)\text{-}Fe(\eta\text{-}C_5H_5)]$ (3e). The procedure described for the preparation of **3b** was followed except ferrocenecarboxaldehyde (0.54 g, 2.5 mmol) was used in place of benzaldehyde. Removal of solvent from the second band (yellow-orange) and recrystallization from 10% methylene chloride/hexane at 0 °C gave **3e** (0.38 g, 51%): orange-brown cubes; mp 153 °C dec; ^1H NMR ($CDCl_3$) δ 6.66 (d, *J* = 16.1 Hz, 1 H), 6.08 (d, *J* = 16.0 Hz, 1 H), 4.38 (br s, 2 H, 4.32 (br s, 2 H), 4.19 (s, 5 H), 3.79 (s, 3 H), 3.35 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 251.26, 203.41, 198.82, 136.69, 127.62, 82.07, 69.49, 69.20, 67.03, 53.95, 43.80; MS (24.2 eV) *m/e* 591 (M^+, 13%), 563 (24), 507 (6), 479 (31), 451 (98). Anal. Calcd for $C_{20}H_{17}FeNO_5W$: C, 40.65; H, 2.90; N, 2.37. Found: C, 40.71; H, 2.80; N, 2.34.

$(CO)_5W[C(NMe_2)CH{=}CPh_2]$ (3f). The procedure described for the preparation of **3b** was followed except benzophenone (0.46 g, 2.5 mmol) was used in place of benzaldehyde. Removal of the solvent from the second yellow band and recrystallization from pentane at 0 °C gave **3f** (0.38 g, 54%): yellow-orange needles; mp 116–117 °C; ^1H NMR ($CDCl_3$) δ 7.38–7.15 (m, 10 H), 6.82 (s, 1 H), 3.64 (s, 3 H), 3.05 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 250.20, 203.00, 198.32, 141.83, 139.00, 137.78, 131.69, 129.46, 128.65, 128.45, 128.33, 127.95, 52.74, 44.64; MS (15.1 eV) *m/e* 559 (M^+, 0.3%), 503 (1), 475 (8), 447 (2), 419 (2). Anal. Calcd for $C_{22}H_{17}NO_5W$: C, 47.25; H, 3.06; N, 2.50. Found: C, 47.18; H, 3.10; N, 2.53.

$(CO)_5W[C(NMe_2)CH(CH_3)SiMe_3]$ (4a). A THF solution (20 mL) of **1** (0.50 g, 1.3 mmol), which was cooled to −78 °C, was treated with 0.61 mL (1.5 mmol) of 2.5 M *n*-BuLi in hexane. The solution was allowed to stir at −78 °C for 30 min, treated with trimethylsilyl chloride (0.24 mL, 1.9 mmol), and allowed to stir for an additional 30 min. The solution was warmed to 25 °C and the solvent removed under vacuum. The resulting yellow oil was dissolved in 20 mL of THF and cooled to −78 °C, and 0.61 mL (1.5 mmol) of 2.5 M *n*-BuLi in hexane was added with stirring for 1 h. To this solution was added methyl trifluoromethanesulfonate (0.29 mL, 2.6 mmol) with stirring at −78 °C for 30 min. The reaction mixture was warmed to 25 °C and the solvent removed under vacuum. The resulting residue was taken up in a minimum of methylene chloride and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/hexane produced a yellow band which upon removal of the solvent under vacuum gave 0.34 g of a 4:1 mixture of **4a** and **2** as a yellow oil. Complexes **4a** and **2** could not be separated from each other by preparative thin-layer chromatography nor low-temperature recrystallization. ^1H NMR of **4a** ($CDCl_3$): δ 4.10 (q, 1 H), 3.80 (s, 3 H), 3.26 (s, 3 H), 1.20 (d, 3 H), 0.20 (s, 9 H).

$(CO)_5W[C(NMe_2)CH(CH_2CH{=}CH_2)SiMe_3]$ (4b). The procedure described for the preparation of **4a** was followed except allyl bromide (0.22 mL, 2.5 mmol) was used in place of methyl trifluoromethanesulfonate. Eluting the column with 20% methylene chloride/hexane produced a yellow band which upon removal of the solvent under vacuum gave 0.43 g of a 9:1 mixture of **4b** and **2** as a yellow oil. Complexes **4b** and **2** could not be separated from each other by preparative thin-layer chromatography nor low-temperature crystallization. ^1H NMR of **4b** ($CDCl_3$): δ 5.85 (m, 1 H), 5.09 (dd, *J* = 16.7, 10.0 Hz, 2 H), 4.14 (dd, *J* = 9.4, 5.3 Hz, 1 H), 3.80 (s, 3 H), 3.28 (s, 3 H), 0.20 (s, 9 H).

$(CO)_5W[C(NMe_2)CH_2CH_3]$ (5a). A diethyl ether solution (100 mL) of $(CO)_5W[C(OCH_3)CH_2CH_3]$ (7.00 g, 17.6 mmol), which was cooled to −50 °C, was treated with 27.2 mL (35.4 mmol) of 1.3 M dimethylamine in diethyl ether. The solution was stirred at this temperature for 6 h and then warmed to 25 °C with removal of the solvent under vacuum. The resulting residue was taken up in a minimum of methylene chloride and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/hexane produced a yellow band which was collected, and the solvent was removed under vacuum. Recrystallization of the resulting residue from pentane at 0 °C gave **5a** (7.20 g, 100%): yellow needles; mp 58–59 °C; ^1H NMR ($CDCl_3$) δ 3.78 (s, 3 H), 3.31 (s, 3 H), 3.18 (q, *J* = 7.6 Hz, 2 H), 1.08 (t, *J* = 7.6 Hz, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 259.83, 203.28, 198.90, 55.81, 46.36, 40.38, 9.18; MS (14.2 eV) *m/e* 409 (M^+, 6%), 381 (8), 353 (9), 325 (4), 297 (1). Anal. Calcd for $C_{10}H_{11}NO_5W$: C, 29.37; H, 2.71; N, 3.42. Found: C, 29.35; H, 2.63; N, 3.44.

$(CO)_5W[C(NMe_2)CH_2CH_2CH{=}CH_2]$ (5b). A THF solution (20 mL) of complex **1** (0.50 g, 1.3 mmol), which was cooled to −78 °C, was treated with 0.61 mL (1.5 mmol) of 2.5 M *n*-BuLi in hexane. The solution was allowed to stir at −78 °C for 30 min, treated with 0.22 mL (2.5 mmol) of allyl bromide, and then allowed to stir for an additional 30 min. The reaction mixture was warmed to 25 °C and the solvent removed under vacuum. The resulting residue was taken up in a minimum of methylene chloride and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/hexane produced a yellow band which was collected, and the solvent was removed under vacuum. Recrystallization of the resulting residue from pentane at 0 °C gave **5b** (0.50 g, 90%): yellow needles; mp 54 °C; ^1H NMR ($CDCl_3$) δ 5.86 (m, 1 H), 5.08 (dd, *J* = 16.7, 10.3 Hz, 2 H), 3.79 (s, 3 H), 3.32 (s, 3 H), 3.22 (t, 2 H), 2.20 (q, 2 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 259.44, 203.01, 198.90, 135.80, 116.04, 55.98, 52.95, 40.85, 29.08; MS (19.4 eV) *m/e* 435 (M^+, 38%) 407 (27), 379 (37), 351 (100), 323 (74), 295 (90). Anal. Calcd for $C_{12}H_{13}NO_5W$: C, 33.13; H, 3.01; N, 3.22. Found: C, 32.98; H, 3.09; N, 3.19.

$(CO)_5W[C(NMe_2)C(CH_3){=}CH_2]$ (7). A diethyl ether solution (100 mL) of complex **6** (5.00 g, 12.3 mmol), which was cooled to −50 °C, was treated with 18.8 mL (17.5 mmol) of 1.3 M diethylamine in diethyl ether. The solution was stirred at this temperature for 6 h and then warmed to 25 °C with removal of the solvent under vacuum. The resulting residue was taken up in a minimum amount of methylene chloride and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/hexane produced a yellow band which was collected, and the solvent was removed under vacuum. Recrystallization of the resulting residue from pentane at 0 °C gave **7** (4.14 g, 80%): yellow needles; mp 56–58 °C; ^1H NMR ($CDCl_3$) δ 4.66 (br s, 1 H), 4.41 (br s, 1 H), 3.78 (s, 3 H), 3.33 (s, 3 H), 1.86 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 258.62, 203.21, 199.32, 154.92, 104.95, 53.31, 47.71, 19.55; MS (20 eV) *m/e* 421 (M^+, 25%), 393 (64), 365 (57), 350 (8), 337 (56), 322 (5), 309 (100), 394 (6), 281 (93), 266 (8), 230 (19). Anal. Calcd for $C_{11}H_{11}NO_5W$: C, 31.38; H, 2.63; N, 3.33. Found: C, 31.37; H, 2.68; N, 3.26.

$(CO)_5W[C(NMe_2)CH{=}C(OSiMe_3)Ph]$ (8). The procedure described for the preparation of **3b** was followed except benzoyl chloride (0.30 mL, 2.6 mmol) was used in place of benzaldehyde. Eluting the column with 20% methylene chloride/hexane produced three bands; the first being **2**, the second being **8**, and the third being 63.0 mg of, as yet, not fully characterized air-sensitive organometallic compound **9**. Removal of the solvent from the second yellow band under vacuum gave **8** (0.19 g, 26%): bright yellow cubes; mp 73 °C dec; ^1H NMR ($CDCl_3$) δ 7.54–7.35 (m, 5 H), 6.61 (s, 1 H), 3.79 (s, 3 H), 3.42 (s, 3 H), 0.10 (s, 9 H); $^{13}C\{^1H\}$

NMR ($CDCl_3$) δ 244.41, 203.24, 198.82, 140.00, 137.81, 128.90, 128.44, 126.49, 122.99, 53.43, 45.76, 0.86; MS (20.0 eV) *m/e* 571 (M^+, 1%), 543 (1), 515 (8), 487 (6), 459 (2), 431 (14). Anal. Calcd for $C_{19}H_{21}NO_6SiW$: C, 39.95; H, 3.70; N, 2.45. Found: C, 39.89; H, 3.60; N, 2.45. Removal of the solvent from the third yellow band under vacuum afforded 63.0 mg of a yellow oil which turns blue-green upon exposure to air: ^1H NMR ($CDCl_3$) δ 7.54–7.35 (m, 5 H), 5.08 (s, 2 H), 3.96 (s, 3 H), 3.28 (s, 3 H).

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Registry No. 1, 52394-35-1; 2, 119567-36-1; 3a, 119567-37-2; 3b, 119567-43-0; 3c, 119567-44-1; 3d, 119567-45-2; 3e, 119567-46-3; 3f, 119567-47-4; 4a, 119567-38-3; 4b, 119567-48-5; 5a, 119567-39-4; 5b, 119567-49-6; 6, 108104-17-2; 7, 119567-40-7; 8, 119567-41-8; 9, 119567-42-9; $(CO)_2W[C(OCH_3)CH_2CH_3]$, 37956-78-8; paraformaldehyde, 30525-89-4; benzaldehyde, 100-52-7; 2-furaldehyde, 98-01-1; *trans*-cinnamaldehyde, 14371-10-9; ferrocenecarboxaldehyde, 12093-10-6; benzophenone, 119-61-9.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen atom positions, least-squares plane results, and torsion angles (6 pages); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

High-Yield Synthesis of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ and Its Dimerization To Form $\{Mo(\mu\text{-}\eta^1,\eta^6\text{-}PMe_2Ph)(PMe_2Ph)_2\}_2$, a Complex Characterized by X-ray Crystallography

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The reduction of Mo_2Cl_{10} with Mg in THF in the presence of PMe_2Ph at 70 °C yields the η^6-bonded arylphosphine complex $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ in high yields. This complex does not undergo substitution reactions with CO and $P(OMe)_3$ at ca. 25 °C. A substitution reaction occurs with 1 mol of $P(OMe)_3$ at 45 °C to form the monosubstituted derivative $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_2(P(OMe)_3)$. The reaction of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ with $^1/_2[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) initially results in the bimetallic complex $Mo(\eta^6\text{-}PhP\{RhCl(COD)\}Me_2)(PMe_2Ph)_3$. The dinuclear complex $[Mo(\mu\text{-}\eta^1,\eta^6\text{-}PMe_2Ph)(PMe_2Ph)_2]_2$ is obtained in the reaction of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ and $ReH_7(PPh_3)_2$. The structural assignments are based on ^1H and $^{31}P\{^1H\}$ NMR spectra, elemental analysis, and in the case of the dimer a single-crystal X-ray structural determination. The cyclic voltammograms for $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ and some analogues are also reported. The dimer crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions a = 11.699 (2) Å, b = 12.117 (1) Å, c = 16.352 (2) Å, β = 93.1 (1)°, V = 2314.6 (7) Å^3, and D_{calcd} = 1.465 g/cm^3 for Z = 2. The structure was solved by a three-dimensional Patterson map and refined by least-squares and Fourier methods to final residuals R = 0.031 (R_w = 0.039) for 3299 observed ($F_o^2 > 3\sigma(F_o)^2$) reflections. The geometry about the molybdenum is distorted octahedral. Averaged principal bond lengths are Mo–C(ring) = 2.27 [1] and Mo–P = 2.433 [2] Å, and the Mo–Mo distance is 4.9706 (3) Å.

Introduction

The reductions of high-valent molybdenum halides, such as Mo_2Cl_{10} or $MoCl_4(THF)_2$, with either Mg or Na/Hg in the presence of tertiary phosphines under N_2 are very useful routes to the reactive bis(dinitrogen) complexes of the type $Mo(N_2)_2L_4$, where L = $PMePh_2$ (George;[1a] Morris;[1b] Makhaev[1c]), PMe_2Ph (Chatt[1d]), and PMe_3 (Carmona;[1e] Green[1f]) or L_2 = $PPh_2CH_2CH_2PPh_2$ (dppe) (Hidai;[1g] Chatt[1d]). A dinitrogen ligand is sufficiently activated in some of these complexes that it is converted into ammonia when the complex is treated with acid.[2] An electrocatalytic conversion was accomplished recently by use of the complex $W(N_2)_2(dppe)_2$.[3]

If the reductions mentioned above are carried out in the absence of N_2 and in the presence of arylphosphines ($PPhRR'$), then complexes of the type $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ and $Mo(\eta^6\text{-}PhPRR')(PPhRR')$-(dppe) (R = Me or Ph, R' = Ph) are obtained.[4] These complexes have a rich substitution chemistry including H_2 and N_2,[4c,5] and they can be used as phosphine-like ligands to rhodium(1)[6] and group 6 metal carbonyls.[7] They are

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(1) (a) George, T. A.; Noble, M. E. *Inorg. Chem.* **1978**, *17*, 1678. (b) Lazarowych, N. J.; Morris, R. H.; Ressner, J. M. *Inorg. Chem.* **1986**, *25*, 3926. (c) Borisov, A. P.; Makhaev, V. D.; Semenko, K. N. *Koord. Khim.* **1979**, *5*, 948. (d) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, 589. (e) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014. (f) Cloke, F. G. N.; Cox, K. P.; Green, M. L. H.; Bashkin, J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 393. (g) Hidai, M.; Tominari, K.; Uchida, Y. *J. Am. Chem. Soc.* **1972**, *94*, 110.

(2) Dilworth, J. R.; Richards, R. L. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: London, 1982; Vol. 8, Chapter 40, p 1073.

(3) Pickett, C. J.; Talarmin, J. *Nature (London)* **1985**, *317*, 652.

(4) (a) Azizian, H.; Luck, R. L.; Morris, R. H.; Wong, H. *J. Organomet. Chem.* **1982**, *238*, C24. (b) Luck, R. L.; Morris, R. H.; Sawyer, J. F. *Organometallics* **1984**, *3*, 247. (c) Frizzell, J. J.; Luck, R. L.; Morris, R. H.; Peng, S. H. *J. Organomet. Chem.* **1985**, *284*, 243.

(5) Luck, R. L.; Morris, R. H. *Inorg. Chem.* **1984**, *23*, 1489.

(6) Luck, R. H.; Morris, R. H. *J. Organomet. Chem.* **1983**, *255*, 221.

(7) Luck, R. H.; Morris, R. H. *J. Organomet. Chem.* **1988**, *347*, 349.

0276-7333/89/2308-1282$01.50/0