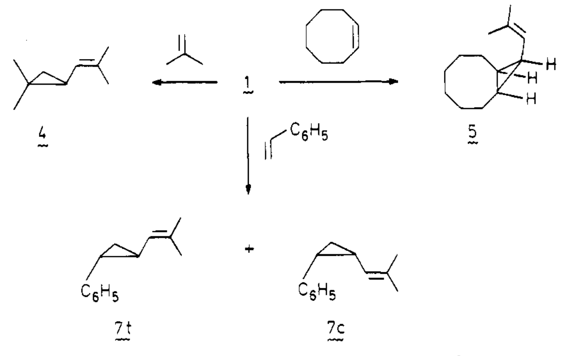
with ether at −23 °C and dried under vacuum at −23 °C. **1** is unstable at room temperature but was fully characterized spectroscopically by low-temperature NMR.[18]

In the ^{1}H NMR of **1** in CD_2Cl_2 at −50 °C, the proton on the carbene carbon and the vinyl proton appear as two doublets at δ 15.96 and 8.21, respectively. In the ^{13}C NMR of **1** at −50 °C, the carbene carbon appears at δ 315.5 and the vinyl carbons appear at δ 177.9 and 155.3. Solutions of **1** in CD_2Cl_2 are stable for hours at −50 °C but decompose on warming to room temperature. We have not succeeded in isolating the decomposition products.

The isolated vinylcarbene complex **1** reacts with alkenes to give moderate yields of (vinylcyclopropane)iron complexes from which the vinylcyclopropane product can be released by treatment with NaI in acetone.[19] Isobutylene (1.35 mmol) was condensed into a CH_2Cl_2 solution of vinylcarbene iron complex **1** (0.45 mmol)[20] at −78 °C. The reaction mixture was stirred for 45 min at −23 °C and then for 1 h at room temperature. The volatile fraction of the solution was transferred under high vacuum, and NaI in acetone (0.47 mmol in 1 mL) was added to the remaining solid to free the complexed 2,2-dimethyl-1-(2-methyl-1-propenyl)cyclopropane (**4**). The volatile fraction of the acetone solution was transferred under vacuum and combined with the previous volatile fraction. The yield of **4** was 56% as determined by gas chromatography, and pure **4** was isolated by preparative gas chromatography.[21]



Reaction of **1** (2.37 mmol in 10 mL of CH_2Cl_2) with cyclooctene (7.1 mmol) followed by workup with NaI in acetone and isolation by silica gel chromatography and Kugelrohr distillation gave *cis*-9-(2-methyl-1-propenyl)-bicyclo[6.1.0]nonane (**5**) in 37% yield. A single isomer was seen by gas chromatography on several columns, and *cis*-**5** appeared pure by both ^{1}H and ^{13}C NMR.[23] The cis stereochemistry of **5** was conclusively established by ozonolysis to give *cis*-bicyclo[6.1.0]nonane-9-carboxylic acid (**6**)[24] whose stereochemistry was established by Eu shift studies on the related ethyl esters.[25,26] The selective formation of *cis*-cyclopropanes from electrophilic metal carbene complexes is a common phenonmenon.[2,5–7]

In the reaction of **1** (2.37 mmol in 10 mL of CH_2Cl_2) with styrene (6.9 mmol), we were surprised to find that a 2:1 mixture of *trans*- and *cis*-1-phenyl-2-(2-methyl-1-propenyl)cyclopropane, **7t** and **7c**, was formed in 45% yield. Pure samples of **7t** and **7c** were obtained by preparative gas chromatography, and the stereochemistry of each isomer was conclusively established by measurement of ^{1}H NMR coupling constants of the cyclopropyl hydrogens.[27] The unexpected selectivity for formation of *trans*-cyclopropane is particularly surprising since Helquist has found cis selectivity in the reaction of styrene with the closely related complex $(C_5H_5)[P(OCH_3)_3](CO)Fe{=}CHCH{=}CH(CH_3)_2{}^+$.[14]

Although the moderate yields of vinylcyclopropanes obtained here have been encouraging, we have not yet been successful in the synthesis of chrysanthemic acid derivatives. The reaction of **1** with $(CH_3)_2C{=}CHCH_2OSi(CH_3)_2C(CH_3)_3$ did not lead to detectable (<1%) yields of vinylcyclopropane products.

Acknowledgment. We would like to express our appreciation to Professor Paul Helquist for keeping us informed of his related studies. Helpful discussions with Hideyuki Tukada and research support from the National Science Foundation are gratefully acknowledged.

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[18] The ether wash contained no nonvolatile material and ^{1}H NMR indicated >95% purity for **1**. **1**: ^{1}H NMR (CD_2Cl_2, 270 MHz) δ 15.96 (d, *J* = 14.7 Hz, 1 H), 8.21 (d, *J* = 14.7 Hz, 1 H), 5.66 (s, 5 H), 2.22 (s, 6 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 15.04 MHz) δ 315.5, 207.1, 177.9, 153.3, 91.9, 29.9, 23.4.

[19] Rosan, A.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1973**, *95*, 3062.

[20] **1** was prepared by the addition of HBF_4 (0.45 mmol) in diethyl ether to a diethyl ether solution of **3** (0.45 mmol).

[21] 2,2-Dimethyl-1-(2-methyl-1-propenyl)cyclopropane was isolated by preparative gas chromatography (SE-30) and identified by spectral and chromatographic comparison with an authentic sample.[22] **4**: ^{1}H NMR (C_6D_6, 270 MHz) δ 4.96 (dm, *J* = 8.1 Hz, 1 H), 1.69 (br s, 3 H), 1.67 (d, *J* = 1.5 Hz, 3 H), 1.29 (ddd, *J* = 8.6, 8.1, 4.6 Hz, 1 H), 1.04 (s, 3 H), 1.02 (s, 3 H), 0.63 (dd, *J* = 8.6, 4.6 Hz, 1 H), 0.22 (t, *J* = 4.6 Hz, 1 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 15.04 MHz) δ 132.4, 125.3, 27.6, 26.0, 24.6, 22.9, 21.4, 18.6, 18.2.

[22] Nelson, E. R.; Maienthal, M.; Lane, L. A.; Benderly, A. A. *J. Am. Chem. Soc.* **1957**, *79*, 3467.

[23] *cis*-**5**: ^{1}H NMR (C_6D_6, 270 MHz) δ 5.14 (dm, *J* = 7.8 Hz, 1 H), 1.75 (s, 3 H), 1.70 (s, 3 H), 1.28–1.70 (m, 11 H), 1.10 (m, 2 H), 0.74 (m, 2 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 15.04 MHz) δ 133.8, 120.6, 30.4, 27.4, 26.2, 23.3, 21.1, 18.9, 17.9; exact mass (70 eV) 178.1722; calcd for $C_{13}H_{22}$ 178.1722.

[24] *cis*-**6**: ^{1}H NMR (C_6D_6, 270 MHz) δ 12.26 (br s, 1 H), 1.93 (m, 2 H), 1.10–1.65 (m, 11 H), 0.80 (m, 2 H). The ^{1}H NMR spectra of *cis*-**6** from ozonolysis of *cis*-**5** was identical with the ^{1}H NMR spectra of *cis*-**6** prepared by the saponification of the pure ethyl ester of *cis*-**6**. *trans*-**6** was prepared by saponification of the pure ethyl ester of *trans*-**6**. *trans*-**6**: ^{1}H NMR (C_6D_6, 270 MHz) δ 13.2 (br s, 1 H), 1.72 (m, 2 H), 1.0–1.5 (m, 11 H), 0.66 (m, 2 H).

[25] Ethyl *cis*- and *trans*-bicyclo[6.1.0]nonane-9-carboxylate[26] were separated by preparative gas chromatography (QF-1). Ethyl ester of *trans*-**6**: ^{1}H NMR (C_6D_6, 270 MHz) δ 4.01 (q, *J* = 7.1 Hz, 2 H), 1.81 (m, 2 H), 1.0–1.5 (m, 11 H), 0.99 (t, *J* = 7.1 Hz, 3 H), 0.74 (m, 2 H). The resonance due to the proton attached to carbon 9 of the ethyl ester of *trans*-**6** was shifted to δ 2.92 by 15 mol % Eu(fod)$_3$ shift reagent (0.004 M in C_6D_6) and appeared as a triplet with *J* = 4.6 Hz, unambiguously establishing the trans stereochemistry. Ethyl ester of *cis*-**6**: ^{1}H NMR (C_6D_6, 270 MHz) δ 4.00 (q, *J* = 7.1 Hz, 2 H), 2.14 (m, 2 H), 1.1–1.7 (m, 11 H), 0.99 (t, *J* = 7.1 Hz, 3 H), 0.85 (m, 2 H).

[26] Dauben, W. G.; Michno, D. M. *J. Am. Chem. Soc.* 1981, *103*, 2284.

[27] GC separation was achieved with a 20% OV-225 column at 180 °C. *cis*-**7**: ^{1}H NMR ($(CD_3)_2CO$, 270 MHz) δ 7.2 (m, 5 H), 4.52 (dm, *J* = 8.7 Hz, 1 H), 2.28 (ddd, *J* = 6.2, 8.6, 8.6 Hz, 1 H), 1.89 (m, 1 H), 1.67 (d, *J* = 1.1 Hz, 3 H), 1.50 (d, *J* = 0.9 Hz, 3 H), 1.21 (ddd, *J* = 4.7, 8.6, 8.6 Hz, 1 H), 0.89 (ddd, *J* = 4.8, 6.0, 6.0 Hz, 1 H); exact mass (70 eV) 172.1252, calcd for $C_{13}H_{16}$ 172.1252. *trans*-**7**: ^{1}H NMR ($(CD_3)_2CO$, 270 MHz) δ 7.2 (m, 5 H), 4.77 (dm, *J* = 8.7 Hz, 1 H), 1.81 (m, 1 H), 1.73 (m, 1 H), 1.68 (d, *J* = 1.2 Hz, 3 H), 1.67 (s, 3 H), 1.16 (ddd, *J* = 8.7, 5.5, 4.6 Hz, 1 H), 0.94 (ddd, *J* = 8.5, 5.6, 4.5 Hz, 1 H); exact mass (70 eV) 172.1252, calcd for $C_{13}H_{16}$ 172.1252.

Reactions of $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (M = Mo or W) with BR_3H^- and LiR Nucleophiles. Proton-Induced Cleavage of M–(μ-PPh$_2$) Bonds in Binuclear Anionic Complexes

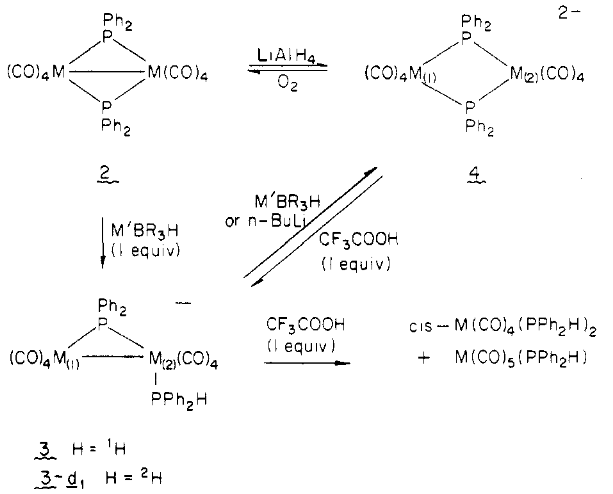
Shin-Guang Shyu and Andrew Wojcicki*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received January 13, 1984

Summary: Reactions of $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (**2**, M = Mo or W) with 1 equiv of $M'BR_3H$ (M' = Li or K; R = Et or *sec*-Bu) in THF proceed to $[(CO)_4\overline{M(\mu\text{-}PPh_2)M}(CO)_4\text{-}$

Scheme I



(PPh$_2$H)]$^-$ (3) and with 2 equiv of M'BR$_3$H or LiAlH$_4$, to [M$_2$(CO)$_8$(μ-PPh$_2$)$_2$]$^{2-}$ (4). Treatment of 4 with 1 equiv of CF$_3$COOH in THF affords 3, whereas treatment of 3 with 1 equiv of CF$_3$COOH yields *cis*-M(CO)$_4$(PPh$_2$H)$_2$ and M(CO)$_5$(PPh$_2$H) as major and minor products, respectively. Reactions of 2 with LiR (R = Me, *n*-Bu, and Ph) proceed regiospecifically to the equatorial isomers of [M$_2$(CO)$_7$(COR)(μ-PPh$_2$)$_2$]$^-$, which are alkylated by Me$_3$O$^+$BF$_4$$^-$ to yield M$_2$(CO)$_7$[C(OMe)R](μ-PPh$_2$)$_2$ (R = Me).

It was recently reported[1-3] that the bridging phosphido complexes Fe$_2$(CO)$_6$(μ-PPh$_2$)$_2$ (1) and Fe$_2$(NO)$_4$(μ-PPh$_2$)$_2$ are chemically reduced either with cleavage of the Fe–Fe bond to give [Fe$_2$(CO)$_6$(μ-PPh$_2$)$_2$]$^{2-}$ and [Fe$_2$(NO)$_4$(μ-PPh$_2$)$_2$]$^{2-}$ or with scission of one of the Fe–P bonds and the formation of Fe–PPh$_2$H to afford [(CO)$_3$Fe(μ-CO)(μ-PPh$_2$)Fe(CO)$_2$(PPh$_2$H)]$^-$ and [(NO)$_2$Fe(μ-NO)(μ-PPh$_2$)Fe(NO)(PPh$_2$H)]$^-$. We have now extended these studies to M$_2$(CO)$_8$(μ-PPh$_2$)$_2$ (2, M = Mo or W) and find a behavior that essentially parallels that of the foregoing Fe complexes, albeit with some important differences. Because phosphido-bridged binuclear transition-metal complexes are the subject of much current research interest,[4] we present our findings in this communication.

The reactions that comprise the main focus of our work are set out in Scheme I. Unless specified otherwise, they were run in THF under nitrogen. ^{31}P NMR data for new binuclear complexes are given in Table I.

Table I. ^{31}P NMR Data for New Binuclear Molybdenum and Tungsten Complexes Derived from M$_2$(CO)$_8$(μ-PPh$_2$)$_2$ (M = Mo or W)[a]

complex	^{31}P NMR, δ (J, Hz)
Li$^+$**3**-Mo	106.9, 21.2 ($^1J_{PH}$ = 327.2, J_{PP} = 19.5)
Li$^+$**3**-*d*$_1$-Mo	($^1J_{PD}$ = 51.3)
Li$^+$**3**-W	87.1 (J_{PW} = 137.6, 244.1), −4.3 (J_{PW} = 228.7, $^1J_{PH}$ = 357.6, J_{PP} = 17.2)
(K$^+$)$_2$**4**-Mo	−47.9
(Li$^+$)$_2$**4**-W	−98.0 (J_{PW} = 154.7)
Li$^+$**5a**-Mo	219.9, 174.5 (J_{PP} = 10.3)
Li$^+$**5b**-Mo	219.0, 173.7 (J_{PP} = 10.3)
Li$^+$**5c**-Mo	220.5, 177.0 (J_{PP} = 10.3)
Li$^+$**5a**-W	167.4 (J_{PW} = 161.8, 175.2), 136.8 (J_{PW} = 123.9, 242.3, J_{PP} = 17.2)
Li$^+$**5b**-W	166.7 (J_{PW} = 161.6, 177.1), 137.1 (J_{PW} = 123.8, 244.1, J_{PP} = 17.2)
6-Mo	227.2, 187.1 (J_{PP} = 9.5)
6-W	173.5 (J_{PW} = 128.9, 173.6), 140.8 (J_{PW} = 230.4, 123.8, J_{PP} = 13.8)

[a] In THF solution. Recorded on a Bruker HX-90 spectrometer at 25 °C. (MeO)$_3$PO was used as a secondary standard, and the chemical shifts are relative to 85% H$_3$PO$_4$.

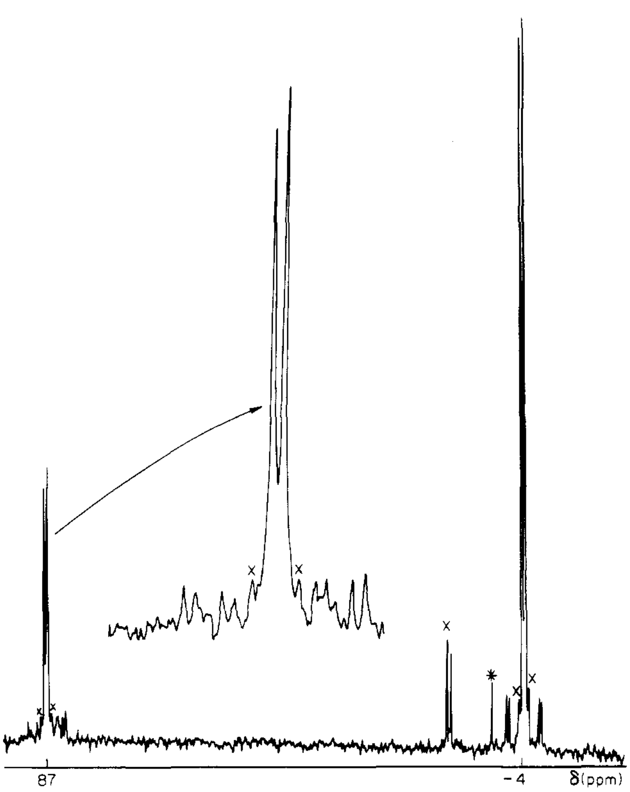


Figure 1. ^{31}P{^{1}H} NMR spectrum of Li$^+$3-W in THF. Signals due to impurities and sidebands are marked ×, and the signal of (MeO)$_3$PO is marked with an asterisk.

Complexes 2 (2-Mo and 2-W)[5] are reduced in two steps, first to 3 and then to 4 by use of M'BR$_3$H (M' = Li or K; R = Et or *sec*-Bu). The first step occurs very fast, as for 1, and the second step more rapidly than for 1, where it generally requires heating.[2] Thus, addition of 1 equiv of LiBEt$_3$H to a suspension of orange 2-Mo or orange-red 2-W at −78 °C affords after warming to 25 °C a red solution of the corresponding Li$^+$3. The anions 4 are best prepared by treatment of 2 with 2 equiv of KB(*sec*-Bu)$_3$H at 25 °C; under these conditions the complexes (K$^+$)$_2$4 precipitate

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(1) Collman, J. P.; Rothrock, R. K.; Finke, R. G; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146.

(2) Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826.

(3) Yu, Y.-F.; Chau, C.-N.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Balducci, G. *J. Am. Chem. Soc.*, in press.

(4) (a) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163. (b) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113. (c) Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349. (d) Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Morrison, E. D.; Duttera, M. R.; DeBrosse, C. W.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 846. (e) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, C. W. *J. Am. Chem. Soc.* **1983**, *105*, 1069. (f) Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *Ibid.* **1981**, *103*, 1394. (g) Finke, R. G.; Gaughan, G.; Pierpont, C.; Noordik, J. H. *Organometallics* **1983**, *2*, 1481. (h) Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E. *Ibid.* **1983**, *2*, 1437. (i) McKennis, J. S.; Kyba, E. P. *Ibid.* **1983**, *2*, 1249. (j) Huttner, G.; Schneider, J.; Müller, H. D.; Mohr, G.; von Seyerl, J.; Wohlfahrt, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 76. (k) Beurich, H.; Madach, T.; Richter, F.; Vahrenkamp, H. *Ibid.* **1979**, *18*, 690. (l) Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319. (m) Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47.

(5) Treichel, P. M.; Dean, W. K.; Douglas, W. M. *J. Organomet. Chem.* **1972**, *42*, 145. We employed thermal rather than photochemical conditions to isolate 2 in ≥50% yields.

as yellow solids. The use of 1 equiv of $KB(sec\text{-}Bu)_3H$ or 2 equiv of $LiBEt_3H$ affords mixtures of **3** and **4**. Treatment of **2** with ca. 2 equiv of $LiAlH_4$ for 30 min gives **4** only.

The anions **3**, which are very air sensitive, have been characterized spectroscopically in solution.[6] Attempts at isolation of **3**-Mo by addition of PNP^+Cl^- to Li^+**3**-Mo afforded PNP^+**3**-Mo as an orange powder of poor analytical purity. Both **3**-Mo and **3**-W show IR ν_{CO} absorptions of terminal CO groups and ^{31}P NMR signals characteristic of a bridging PPh_2 group with a supporting M–M bond[4a] and of a terminal PPh_2H ligand. The appearance of ^{183}W satellites[7] in the $^{31}P\{^1H\}$ NMR spectrum of Li^+**3**-W further supports the $\overline{M(\mu\text{-}PPh_2)M}(PPh_2H)$ structural feature of **3**. These satellites are observed as a doublet on each side of the resonance of PPh_2H at δ −4.3 (approximate relative intensities 1:11:1) and as two doublets on each side of the resonance of μ-PPh_2 at δ 87.1 (approximate relative intensities 1:1:11:1:1). The spectrum is shown in Figure 1. Reaction of **2**-Mo with $LiBEt_3D$ affords **3**-d_1-Mo to demonstrate that the source of the PH hydrogen in **3** is the reducing agent.

Attempted preparation of $[(CO)_4\overline{M(\mu\text{-}PPh_2)M}(CO)_4(PPh_2)]^{2-}$ by deprotonation of Li^+**3**-Mo or Li^+**3**-W with 1 equiv of n-BuLi at −78 °C immediately resulted in the formation of a yellow precipitate of the appropriate $(Li^+)_2$**4**. Thus, deprotonated **3** has a much lower stability with respet to isomerization to the symmetrical dianion (**4**-Mo or **4**-W) than does the analogous species derived from **1**, which is stable to ca. −40 °C.[8]

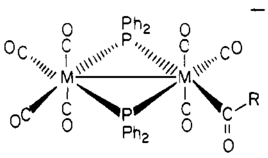
The characterization of **4**-W by IR and ^{31}P NMR spectroscopy was reported by Keiter,[9] and the corresponding data obtained in this study compare well with his published values. The anion **4**-Mo has spectroscopic properties[10] that are very similar to those of **4**-W. It was isolated (95% yield) as $(K^+)_2$**4**-Mo·~2 THF (the amount of THF was determined by ^1H NMR spectroscopy), which is a yellow, air-sensitive solid.

The reactions of **3** and **4** with acid provide a novel aspect of the chemistry of phosphido-bridged bimetallic anions. Thus, $(K^+)_2$**4**-W reacts with 1 equiv of CF_3COOH to afford within 5 min **3**-W. However, when 2 equiv of CF_3COOH are employed, the only products observable by ^{31}P NMR spectroscopy are cis-$W(CO)_4(PPh_2H)_2$ (major) and $W(CO)_5(PPh_2H)$ (minor).[11] The complex $(K^+)_2$**4**-Mo reacts under similar conditions with 2 equiv of CF_3COOH to give cis-$Mo(CO)_4(PPh_2H)_2$ (major product) and $Mo(CO)_5(PPh_2H)$ (minor product), which are also obtained by treatment of Li^+**3**-Mo with 1 equiv of CF_3COOH.

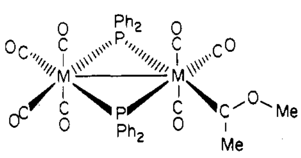
These results demonstrate that the anions **3** and **4** are interconvertible by use of base (**3** → **4**) and acid (**4** → **3**). The conversion of **4** to **3** may proceed by protonation of $M_{(1)}$ (see Scheme I) followed by reductive elimination of μ-PPh_2 and H from $M_{(1)}$ as PPh_2H bound to $M_{(2)}$ to yield **3**. The anion **3** then reacts with another equivalent of acid again by protonation of $M_{(1)}$, a similar reductive elimination of μ-PPh_2H, and cleavage of the M–M bond to afford cis-$M(CO)_4(PPh_2H)_2$ and $M(CO)_4$, from which $M(CO)_5(PPh_2H)$ may arise on ligand scrambling. Although such a mechanism involving reductive elimination of PPh_2H appears attractive and has a precedent in the chemistry of phosphido-bridged bimetallic complexes,[13] we cannot rule out direct protonation at phosphorus following M–(μ-PPh_2) bond dissociation.

The foregoing reactions differ from the corresponding reactions of the anions derived from **1**. Thus, protonation of the Fe analogue of **3** gives the isolable iron hydride $(CO)_3(H)\overline{Fe(\mu\text{-}PPh_2)Fe}(CO)_3(PPh_2H)$,[2] presumably because of a lesser tendency of the Fe system than of the Mo and W systems to undergo reductive elimination of PPh_2H. Protonation of the Fe analogue of **4** yields a binuclear iron hydride anion, formulated as $[(CO)_3(H)Fe(\mu\text{-}PPh_2)_2(\mu\text{-}CO)Fe(CO)_3]^-$.[1]

Both **2**-Mo and **2**-W react completely in 5 min with 1 equiv of LiR (R = Me, n-Bu, and Ph (Mo only)) to afford the appropriate acyl anions **5**, which can be isolated as red, somewhat air-sensitive solids Li^+**5** after removal of the solvent.[14] It is noteworthy that the reactions are *regiospecific*, proceeding by attack of LiR at the carbon atom of an *equatorial* CO. This stereochemistry of the anions **5** was elucidated from their $^{31}P\{^1H\}$ NMR spectra which show two doublets in the region characteristic of a PR_2 group bridging across an M–M bond.[4a] Moreover, for **5**-W, these doublets are surrounded on each side by two ^{183}W satellite doublets, thus indicating that the two P atoms as well as the two W atoms are inequivalent. The observed regiospecificity is best ascribed to steric factors associated with the presence of bulky μ-PPh_2 groups. On electronic grounds, the more positive carbon of an axial CO[15] would have been expected to interact with nucleophilic LiR. Interestingly, **5a**-Mo is observed by ^{31}P NMR spectroscopy after $(K^+)_2$**4**-Mo has been allowed to react with MeI in DMF for 5 h. However, this reaction is not clean, and other products have not yet been characterized.



5a R = Me
5b R = n-Bu
5c R = Ph



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Treatment of **5a**-W with 1 equiv of $Me_3O^+BF_4^-$ in $MeNO_2$ for 10 min, removal of the solvent, and extraction of the residue into THF yielded (ca. 70%) a red, sparingly soluble solid, formulated from ^1H and $^{31}P\{^1H\}$ NMR evidence as a metal–carbene complex, **6**-W.[16] The corresponding reaction of **5a**-Mo afforded **6**-Mo[17] in poor yield.

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[6] Li^+**3**-Mo: IR (THF) $\nu_{C\equiv O}$ 2015 (w), 1980 (w), 1920 (s), 1900 (sh), 1880 (m), 1835 (w) cm^{-1}. Li^+**3**-W: IR (THF) $\nu_{C\equiv O}$ 2007 (w), 1975 (m), 1915 (s), 1900 (sh), 1880 (m), 1843 (sh) cm^{-1}. ^{31}P NMR data are in Table I.

[7] Natural abundance of ^{183}W is 14.28%.

[8] Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Chem. Soc., Chem. Commun.*, in press.

[9] Keiter, R. L.; Madigan, M. J. *Organometallics* **1982**, *1*, 409.

[10] $(K^+)_2$**4**-Mo·~2 THF: IR (Nujol) $\nu_{C\equiv O}$ 1951 (s), 1875 (s), 1825 (s), 1775 (s) cm^{-1}.

[11] These two W complexes and their Mo analogues were identified by comparison of their IR and ^1H and ^{31}P NMR spectra with the corresponding data from the literature.[5,12]

[12] (a) Keiter, R. L.; Sun, Y. Y.; Brodack, J. W.; Cary, L. W. *J. Am. Chem. Soc.* **1979**, *101*, 2638. (b) Keiter, R. L.; Kaiser, S. L.; Hansen, N. P.; Brodack, J. W.; Cary, L. W. *Inorg. Chem.* **1981**, *20*, 284. (c) Smith, J. G.; Thompson, D. T. *J. Chem. Soc. A* **1967**, 1694.

[13] Geoffroy, G. L.; Rosenberg, S.; Shulman, P. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 1519.

[14] Li^+**5a**-Mo: IR (THF) $\nu_{C\equiv O}$ 2030 (m), 1985 (m), 1920 (vs), 1875 (m), $\nu_{C=O}$ 1530 (w) cm^{-1}; ^1H NMR (acetone-d_6) δ (<6) 2.69 (d, J_{PH} = 1.2 Hz, 3 H). Li^+**5c**-Mo: IR (THF) $\nu_{C\equiv O}$ 2035 (m), 1995 (m), 1930 (vs), 1880 (m), $\nu_{C=O}$ 1505 (w) cm^{-1}. Li^+**5a**-W: IR (THF) $\nu_{C\equiv O}$ 2025 (m), 1985 (m), 1920 (vs), 1860 (m), $\nu_{C=O}$ 1525 (w) cm^{-1}; ^1H NMR (acetone-d_6) δ (<6) 2.73 (d, J_{PH} = 1.2 Hz, 3 H).

[15] This is because axial CO is less strongly π-bonded to M than equatorial CO.

[16] **6**-W: IR (THF) $\nu_{C\equiv O}$ 2045 (w), 2005 (m), 1945 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ (<6) 4.22 (s, 3 H), 3.13 (s, 3 H).

[17] **6**-Mo: IR (THF) $\nu_{C\equiv O}$ 2040 (w), 2005 (m), 1955 (s, br) cm^{-1}; ^1H NMR ($CDCl_3$) δ (<6) 4.40 (s, 3 H), 3.15 (s, 3 H).

By comparison, 1 reacts with LiR to give appropriate anionic iron-acyl complexes; however, corresponding carbene derivatives have been made only when the second equivalent of the alkylating agent was provided internally.[1]

The present work points to the generality of the reduction of bimetallic, phosphido-bridged metal carbonyl and nitrosyl complexes with M'BR_3H to afford binuclear anions of the type represented by **3**. It also provides new chemistry of the bridging phosphido ligand, which surprisingly exhibits considerable lability in reactions with BR_3H^- and H^+.

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First Photosubstitution Chemistry of Fulvalene-Bridged Metal-Metal Bonded Carbonyls. Synthesis and Structural Determination of Novel Homo- and Heterobimetallic Alkyne Complexes

James S. Drage, Mats Tilset, Peter C. Vollhardt,* and Timothy W. Weidman

Department of Chemistry, University of California, Berkeley
and the Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

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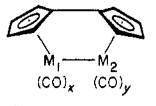
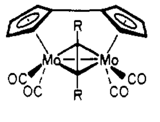
Summary: Irradiation of the carbonyl(η^5:η^5-fulvalene)dimetal complexes of molybdenum, tungsten, and ruthenium **1**, **3**, and **4** in the presence of alkynes gives not only complexes of different respective composition and structure within the series but also in comparison with the corresponding (η^5-cyclopentadienyl)metal carbonyl dimers. (η^5:η^5-$C_{10}H_8$)$(CO)_5$MoRu (**5**) furnishes a novel reactive dinuclear (alkyne)metal oxo complex.

We have recently described a facile synthesis of carbonyl(η^5:η^5-fulvalene)dimetal complexes **1**–**5**.[1] We report



1 M$_1$ = M$_2$ = Ru; $x = y = 2$
2 M$_1$ = M$_2$ = Cr; $x = y = 3$
3 M$_1$ = M$_2$ = Mo; $x = y = 3$
4 M$_1$ = M$_2$ = W; $x = y = 3$
5 M$_1$ = Ru; M$_2$ = Mo; $x = 2$; $y = 3$



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here the first substitution chemistry of these systems with alkynes which has led to the discovery of unusual modes of ligand bonding[2] and the isolation of the first structurally characterized dinuclear (alkyne)molybdenum oxo complex **11**.[3]

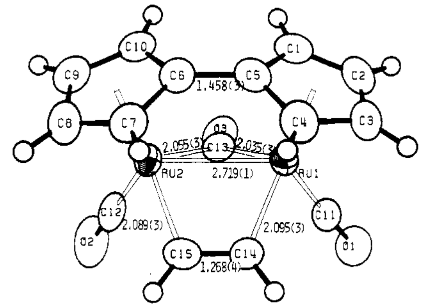

Figure 1. ORTEP drawing showing the geometry, labeling, and important bond lengths (Å) for all non-hydrogen atoms in **6**. Ellipsoids are scaled to represent the 50% probability surface.

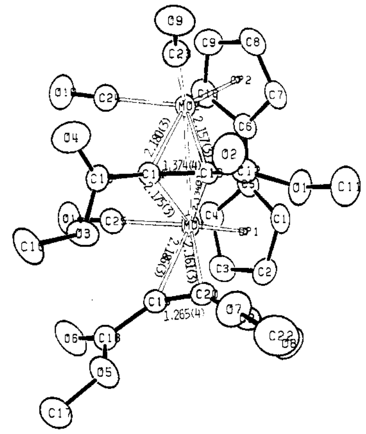

Figure 2. ORTEP drawing of **8**.

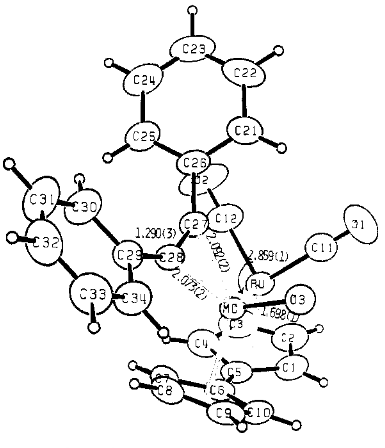

Figure 3. ORTEP drawing of **11**.

Irradiation of **1** in the presence of ethyne (purged THF, 300 nm, room temperature, 4 h) resulted in the diruthenacyclobutene **6** in which the alkyne is bound as expected[4] in the relatively rare "parallel" μ-η^2 mode[5] as

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