812 *Organometallics* **1984,** *3,* 812–814

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^+.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation through Grant CHE-7911882.

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

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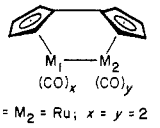
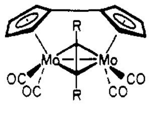
Received November 28, 1983

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. $(\eta^5:\eta^5\text{-}C_{10}H_8)(CO)_5MoRu$ (**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 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]



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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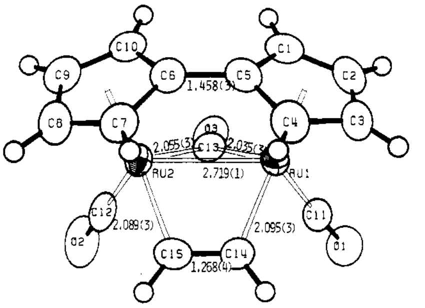

Figure 1. ORTEP drawing showing the geometry, labeling, and important bond lengths (Å) for all non-hydrogen atoms in 6. Ellipsoids are scaled to represent the 50% probability surface.

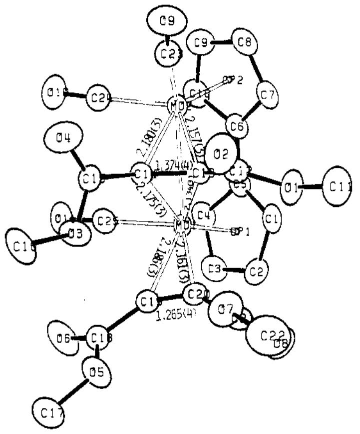

Figure 2. ORTEP drawing of 8.

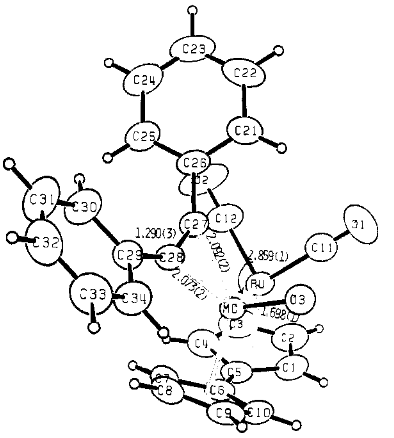

Figure 3. ORTEP drawing of 11.

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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(1) Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1983,** *105,* 1676; *Organometallics* **1984,** *3,* 82.

(2) Bowden, F. L.; Lever, A. B. P. *Organomet. Chem. Rev.* **1968,** *3,* 227. Yur'eva, L. P. *Russ. Chem. Rev. (Engl. Transl.)* **1974,** *43,* 48. Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983,** *83,* 135. Sappa, E.; Tiripicchio, A.,; Braunstein, P. *Ibid.* **1983,** *83,* 203.

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(4) Hoffman, D.M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982,** *104,* 3858.

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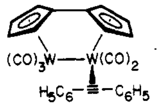
shown by an X-ray structural investigation (Figure 1). Similar complexes are obtained[5] with diphenylethyne (63%, mp 220 °C dec) and dimethyl ethynedicarboxylate (76%, mp 200 °C dec). Attempts to induce further alkyne uptake in these systems have been unsuccessful. Thus, their structure and chemical behavior are in sharp contrast to their relatives derived from $[Ru(CO)_2(\eta\text{-}C_5H_5)]_2$.[6]

Similar divergence is exhibited by the group 6B analogues 2–4. Whereas 2 furnishes only decomposition products on irradiation in the presence of diphenylethyne, 3 results in both mono(alkyne) (8.8%, mp 162 °C dec) as well as bis(alkyne) (23%, mp 179 °C dec) substitution products.[5] Similar complexes 7 and 8 are obtained from dimethyl ethynedicarboxylate.[5] The narrow multiplets for the fulvalene protons are particularly indicative of the symmetry of the compounds generated. Thus, 7 exhibits four signals whereas in 8 all protons are distinct. An X-ray analysis of 8 (Figure 2) reveals that the two alkynes are uncoupled (vide infra)[12] even though close, one functioning as a two-electron and the other as a four-electron [as in $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2R_2)$][7] ligand. The molecule has a Mo–Mo bond length of 2.906 (1) Å, considerably shorter (by 0.33 Å) than $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$,[8] somewhat shorter even than those in alkyne complexes of the latter (by 0.05–0.08 Å).[9] It is interesting to compare these distances with the unusually long W–W bond (3.347 Å) in hexacarbonyl(η^5:η^5-fulvalene)ditungsten[10] and the corresponding distance in $(\eta^5\text{-}C_5H_5)_2W_2(CO)_4(C_2H_2)$ (2.987 Å).[11]

The mono(alkyne) adducts of the type 7 show fluxional behavior in the ^{1}H NMR experiment. For example, 7 reveals equilibration of the methyl ester protons and coalescence (at 35 °C) of the fulvalene signals to two sets ($\Delta G^\ddagger = 15.0 \pm 0.5$ kcal mol^{-1}). These and the spectral data are consistent with (but do not prove) an alkyne ligand which is bound to the dinuclear framework in an unsymmetrically bridging manner, as the μ ligand in 8 and as shown in the picture for 7. Fluxionality would then arise by rotating the alkyne around the Mo–Mo bond from one side of the fulvalene ligand to the other. Whereas 7 can be converted to 8 with added alkyne, further alkyne incorporation could not be effected. On the other hand the corresponding $\eta^5\text{-}C_5H_5Mo$ dimers are well-known to lead to multiple alkyne coupling.[12] Indeed, the nonoccurrence of such couplings is very rare.[3,13]

The ditungsten system 4 also undergoes[5] single and double alkyne photosubstitution (di-*p*-tolylethyne, 16%, mp 140 °C dec; 18%, mp 200 °C dec; diphenylethyne, 9 and 10). In contrast to 3, however, monosubstitution gives a different product involving a terminal, unsymmetrically bound alkyne, as indicated by the nonequivalency of all fulvalene protons as well as the two sides of the alkyne.[5] No change was observable in the NMR spectrum of 9 up to 70 °C. This chemistry again differs from that of the analogous (η^5-cyclopentadienyl)tungsten carbonyl dimer.[14]



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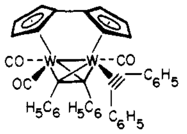

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Perhaps most remarkable is the behavior of the mixed-metal system 5 which has potential catalytic applications.[15] On irradiation with diphenylethyne the novel and very reactive oxo complex 11 is formed,[5] the structural features of which were confirmed by X-ray analysis (Figure 3).[5] The source of the oxygen in 11 appears to be traces of moisture and not air,[3] since the yields drop off drastically when flame-dried glassware is used. (η^5-Cyclopentadienyl)metal oxo complexes are relatively rare,[3,16] and alkyne complexes of the type 11 could well be active catalysts.[17] Preliminary tests show 11 to actively polymerize

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(5) All new compounds gave satisfactory spectral and analytical data. For example, 6: 56%, orange crystals, mp 205 °C dec; ^{1}H NMR (200 MHz for all spectra, acetone-d_6) δ 4.80 (m, 2 H), 5.15 (m, 2 H), 5.72 (m, 2 H), 6.03 (m, 2 H), 6.86 (s, 2 H); CIMS, *m/e* (relative intensity) 442 (M$^+$, highest mass peak in isotope envelope, 78%), 414 (100); IR (KBr) 1980, 1944, 1755 cm^{-1}; X-ray, crystal size 0.14 × 0.27 × 0.36 mm, orthorhombic Laue symmetry, space group *Pbca* (No. 61), $a = 8.0515$ (10) Å, $b = 15.0105$ (19) Å, $c = 21.8239$ (32) Å, $V = 2637.6$ (10) Å^3, $Z = 8$, $\mu_{calcd} = 22.50$ cm^{-1}, $d_{calcd} = 2.22$ g cm^{-3}, radiation Mo Kα ($\lambda = 0.71073$ Å), scan range $3° \le 2\theta \le 45°$, reflections collected 2016, unique 1609 with $F^2 > 3\sigma(F^2)$, $R = 0.0171$, $R_w = 0.0291$. 7: 14%, red crystals, mp 164–165 °C dec; ^{1}H NMR (acetone-d_6) δ 3.36 (bs, 3 H), 3.85 (bs, 3 H), 4.27 (m, 2 H), 4.54 (m, 2 H), 5.58 (m, 2 H), 6.00 (m, 2 H); MS, *m/e* (relative intensity) 574 (M$^+$, 27%), 344 (100); IR (KBr) 2010 (sh), 1970, 1945, 1920 (sh), 1735, 1705, 1675 cm^{-1}. 8: 67%, orange crystals, mp 161–162 °C dec; ^{1}H NMR (acetone-d_6) δ 3.50 (s, 3 H), 3.57 (s, 3 H), 3.68 (s, 3 H), 3.82 (s, 3 H), 4.72 (m, 1 H), 4.79 (m, 1 H), 5.08 (m, 1 H), 5.51 (m, 2 H), 5.57 (m, 1 H), 5.87 (m, 1 H), 6.04 (m, 1 H); MS, *m/e* (relative intensity) 688 (M$^+$, 0.06%), 57 (100); IR (KBr) 2042, 2002, 1944, 1706, 1691, 1678 cm^{-1}; X-ray, crystal size 0.05 × 0.17 × 0.40 mm; monoclinic Laue symmetry, space group $P2_1/c$, $a = 9.6984$ (6) Å, $b = 15.4379$ (21) Å, $c = 16.4863$ (17) Å, $\beta = 95.880$ (7)°, $V = 2455.4$ (8) Å^3, $Z = 4$, $d_{calcd} = 1.86$ g cm^{-3}, radiation Mo Kα ($\lambda = 0.71073$ Å), scan range $3° \le 2\theta \le 45°$; reflections collected 3494, 3210 unique, 2692 with $F^2 > 3\sigma(F^2)$, $R = 0.022$, $R_w = 0.029$. 9: yellow crystals, 26%, mp ~150 °C dec; ^{1}H NMR (CDCl$_3$) δ 3.23 (m, 1 H), 5.22 (m, 1 H), 5.31 (m, 1 H), 5.67 (m, 2 H), 5.90 (m, 1 H), 6.10 (m, 1 H), 6.96 (m, 1 H), 7.3–7.6 (m, 6 H), 7.68 (dd, $J = 7.4, 1$, 2 H), 7.89 (dd, $J = 8.0, 1$, 2 H); MS, *m/e* (relative intensity) 786 (M$^+$ – CO, 37.9%), 179 (100%); IR (KBr) 1977, 1971, 1909, 1896, 1870 cm^{-1}. 10: red-brown crystals, 22%, mp ~200 °C dec; ^{1}H NMR (CDCl$_3$) δ 4.44 (m, 1 H), 4.67 (m, 1 H), 4.94 (m, 1 H), 5.22 (m, 1 H), 5.40 (m, 1 H), 5.58 (m, 1 H), 5.64 (m, 1 H), 6.16 (m, 1 H), 6.8–7.4 (m, 20 H); MS, *m/e* (relative intensity) 936 (M$^+$, 4.9%), 786 (100%); IR (KBr) 1982, 1942, 1877 cm^{-1}. 11: 43%, orange crystals, mp 180 °C dec; ^{1}H NMR (acetone-d_6) δ 3.18 (m, 1 H), 4.61 (m, 1 H), 5.30 (m, 1 H), 5.59 (m, 1 H), 5.87 (m, 1 H), 5.96 (m, 1 H), 6.10 (m, 1 H), 7.20–7.60 (m, 8 H), 7.89 (dd, $J = 8.2, 0.6$, 2 H); MS *m/e* 574 (M$^+$, 1.4%), 178 (100); IR (KBr) 1982, 1924, 952 cm^{-1}; X-ray, crystal size 0.09 × 0.17 × 0.34 mm, monoclinic Laue symmetry, space group $P2_1/c$, $a = 10.1614$ (9) Å, $b = 16.7761$ (19) Å, $V = 2214.2$ (7) Å^3, $Z = 4$, $\mu_{calcd} = 12.46$ cm^{-1}, $d_{calcd} = 1.726$ g cm^{-3}, radiation Mo Kα ($\lambda = 0.71073$ Å), scan range $3° \le 2\theta \le 45°$, reflections collected 3143, 2539 unique with $F^2 > 3\sigma(F^2)$, $R = 0.0162$, $R_w = 0.0232$.

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(14) See: Finnimore, S. R.; Knox, S. A. R.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 411.

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alkynes. Hydrogenation in the presence of CO regenerates 5 quantitatively.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC03-76SF00098. The crystal structure analyses of 6 and 11 were performed by Dr. F. J. Hollander, U.C. Berkeley X-ray Crystallographic Facility, and that of 8 by Dr. W. Tötsch and J. Bularzik, K. Kourtakis, and J. Nitschke, at the same location. We thank Professor H. B. Abrahamson, University of Oklahoma for a preprint. M.T. is the recipient of a Royal Fellowship of Norway. K.P.C.V. was a Camille and Henry Dreyfus Teacher–Scholar (1978–1983).

Supplementary Material Available: A listing of positional and thermal parameters and tables of bond lengths and angles of 6, 8, and 11 (17 pages). Ordering information is given on any current masthead page.

Reactivity of Phosphido-Bridged Heteronuclear Compounds: Insertion of CO and Diphenylacetylene into the Phosphido Bridge of $RuCo(CO)_7(\mu\text{-}PPh_2)$. X-ray Structure of $RuCo(CO)_5(\mu\text{-}CO)[\mu\text{-}\eta^2\text{-}PPh_2C(O)C(Ph)C(Ph)]$

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Summary: The reaction of the heterobinuclear phosphido-bridged compound $RuCo(CO)_6(\mu\text{-}PPh_2)$ (**1**) with diphenylacetylene leads, via acetylene and CO insertion into the phosphido bridge, to the novel complex $RuCo(CO)_6[Ph_2PCOC(Ph)C(Ph)]$ (**2**). X-ray analysis (space group $P\bar{1}$, $a = 9.820$ (1) Å, $b = 12.419$ (2) Å, $c = 14.966$ (2) Å, $\alpha = 99.58$ (1)°, $\beta = 99.55$ (1)°, $\gamma = 90.10$ (1)°, $Z = 2$; $R = 0.028$, $R_w = 0.031$ based on 4191 reflections) has revealed the presence of a $\mu\text{-}Ph_2PCOC(Ph)C(Ph)$ ligand coordinated to ruthenium via phosphorus and one carbon atom of the original alkyne and to cobalt via an η^2-interaction. **2** undergoes facile decarbonylation to $RuCo(CO)_6[Ph_2PC(Ph)C(Ph)]$ (**3**). The conversion of **1** to **2** and **3** may have wide implications for the reactivity of μ-PPh_2-bridged polynuclear compounds toward unsaturated substrates.

The phosphido (PR_2) group has recently attracted particular attention as a strongly bound yet flexible ligand capable of maintaining the integrity of a polynuclear framework during chemical transformations.[1] A substantial number of polymetallic phosphido-bridged compounds have now been synthesized,[2] and several examples of potentially significant, reversible metal–metal bond cleavage have been reported.[3] With μ-PPh_2 compounds a possible complicating factor that has not however received much attention is reactivity associated with the bridge, a problem which might be accentuated in heterobimetallic systems. To date few instances of bridge cleavage have been reported.[1,4]

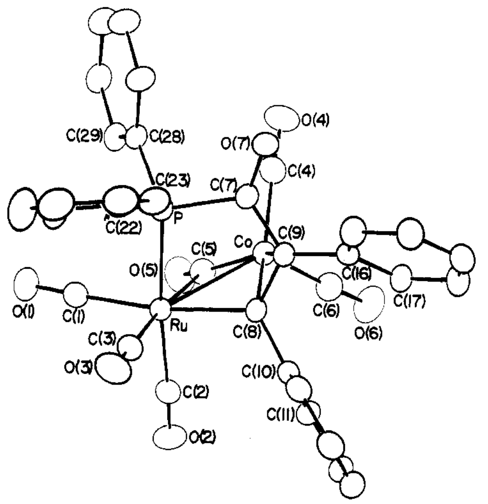
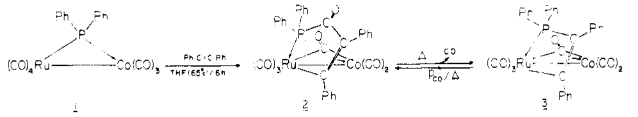


Figure 1. A perspective view of the molecular structure of $RuCo(CO)_6[Ph_2PCOC(Ph)C(Ph)]$ drawn to illustrate the interaction of the new ligand with the metal atoms.

Scheme I



While investigating the behavior of the heteronuclear phosphido-bridged dimer $RuCo(CO)_7(\mu\text{-}PPh_2)$ (1)[5] toward alkynes for comparison with homodinuclear compounds such as $Co_2(CO)_8$, we discovered that the dominant reaction pathway involves CO and acetylene insertion into the $\mu\text{-}PPh_2(RuCo)$ bridge leading to the novel derivative $RuCo(CO)_5(\mu\text{-}CO)[\mu\text{-}PPh_2COC(Ph)C(Ph)]$ (2) which subsequently decarbonylates to $RuCo(CO)_5(\mu\text{-}CO)[\mu\text{-}PPh_2C(Ph)C(Ph)]$ 3. These reactions that may have wider implications for the reactivity of μ-PPh_2 systems and for the use of heterobimetallics in organic synthesis are reported herein.

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(3) (a) Jones, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. *Organometallics*, **1983**, *2*, 470. (b) MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Ibid.* **1983**, *2*, 1194. (c) MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *J. Organomet. Chem.* **1981**, *204*, C27.

(4) (a) The only examples of insertion of an unsaturated ligand into a diphenylphosphido bridge, of which we are aware, are given in: Smith, W. F.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1976**, 896. (b) Examples of hydrogenation of a μ-PPh_2 bridge to a terminal phosphine have recently been observed: see ref 1b, 1f, and 1h. (c) Hydrogen abstraction from the more reactive μ-PPhH ligands has been used to generate face capping μ_3-PPh groups, but the nucleating properties of the phosphorus ligand are not destroyed in this conversion. See, e.g.: Iwasaki, F.; Mays, M. J.; Raithby, G. R.; Taylor, P. L.; Wheatley, P. J. *J. Organomet. Chem.* **1981**, *213*, 185.

(5) Regragui, R.; Dixneuf, P. H. *J. Organomet. Chem.* **1982**, *239*, C12.

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