Acknowledgment. This work was supported by a grant from the National Institutes of Health, for which we are grateful. We thank Dr. G. Wallraff of IBM Almaden Research Center for his help with the molecular mechanics calculations.

Synthesis of Simple CrL_4(alkyne) Complexes by Displacement of a Labile Cyclooctadiene Ligand

Donald J. Wink* and B. Timothy Creagan

Department of Chemistry, New York University
New York, New York 10003

Received June 27, 1990

We have shown that, in contrast to the simple tetracarbonyl system $M(CO)_4$(diene)[1,2] (M = Cr, Mo, W), 1,5-cyclooctadiene (1,5-COD) is displaced from $M(CO)_3(P(OMe)_3)(\eta^4\text{-1,5-COD})$ by conjugated dienes.[3] As reported here, alkynes, which are similar to 1,3-dienes in their frontier orbital characteristics,[4] also displace the COD in $Cr(CO)_3(P(OMe)_3)(\eta^4\text{-1,5-COD})$ to afford unprecedented $CrL_4(PhC{\equiv}CR)$ complexes.

Diphenylacetylene and phenylacetylene react in a few hours with *mer*-$Cr(CO)_3(P(OMe)_3)(\eta^4\text{-1,5-COD})$ to give products of COD substitution and phosphite and carbonyl ligand redistribution (eq 1).[7,8] The $PhC{\equiv}CPh$ complex **1a**[9] forms in good yield as black crystals *directly from the reaction mixture* in pentane while the $PhC{\equiv}CH$ complex **1b** is crystallized separately in lower yield. A superior route to **1b** is alkyne exchange with **1a** (eq 2).[10]

$$mer\text{-}Cr(CO)_3P(OMe)_3(\eta^4\text{-1,5-COD}) + RC{\equiv}CPh \xrightarrow{C_5H_{12}} Cr(CO)_2(P(OMe)_3)_2(\eta^2\text{-}RC{\equiv}CPh) + COD +$$

1a, R = Ph; **1b**, R = H

$$Cr(CO)_4(1,5\text{-COD}) \quad (1)$$

$$Cr(CO)_2(P(OMe)_3)_2(\eta^2\text{-}PhC{\equiv}CPh) + HC{\equiv}CPh \xrightarrow{C_5H_{12}} Cr(CO)_2(P(OMe)_3)_2(\eta^2\text{-}HC{\equiv}CPh) + PhC{\equiv}CPh \quad (2)$$

Integration of the ^1H NMR spectra supports a 2:1 phosphite:alkyne stoichiometry, and a pair of bands in the IR spectra for ν(CO) indicates a *cis*-dicarbonyl structure. The signals for the alkyne carbons for **1a** appear at δ 180.2 and for **1b** at δ 174.3 ($\equiv$CPh) and δ 163.7 ($\equiv$CH). These are downfield from the region generally cited for the carbons of a four-electron alkyne,[11] but of course the metal in this case is quite electron rich. Resonances for the alkyne and carbonyl carbons for both complexes and for the alkyne hydrogen in **1b** appear as *triplets* due to coupling to two phosphorus ligands. This is consistent with either structure **2**, with magnetically equivalent phosphorus atoms, or **3**, in which the phosphorus atoms would be rendered equivalent only by rotation of the alkyne. Variable-temperature NMR experiments with **1b** establish that the ground-state structure is **3**; the triplet with J_{PH} = 20 Hz for the acetylenic proton "loses" the central resonance and becomes a doublet with J_{PH} = 40 Hz upon cooling.[12] A barrier to formal rotation of the alkyne of 13.3 (3) kcal mol^{-1} is calculated from the decoalescence of the ^{13}C NMR resonance for the phosphite methyl carbons at ca. −5 °C (Δ = 51 Hz).[13]

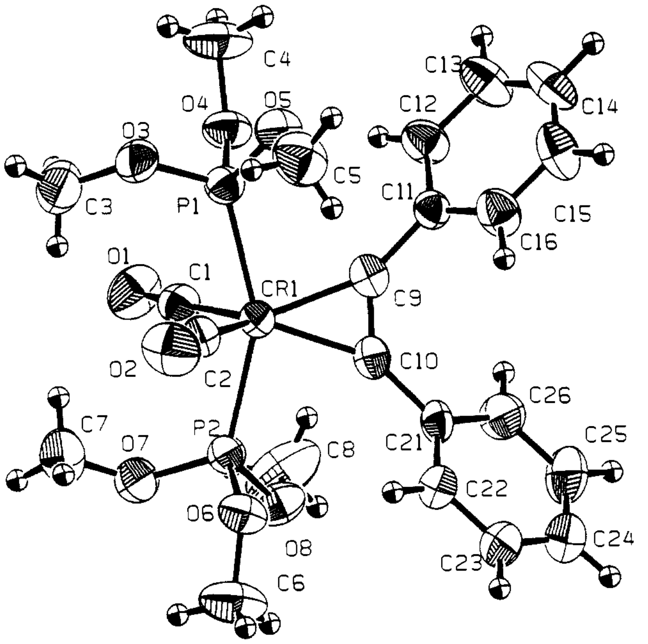
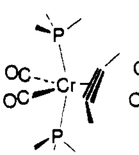
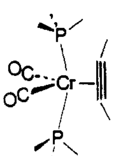


Figure 1. ORTEP diagram of $Cr(CO)_2(P(OMe)_3)_2(\eta^2\text{-}PhC{\equiv}CPh)$. Important bond lengths (Å) and angles (deg): Cr1–P1, 2.252 (2); Cr1–P2, 2.264 (2); Cr1–C1, 1.857 (7); Cr1–C2, 1.827 (7); Cr1–C9, 1.959 (6); Cr1–C10, 1.958 (5); C1–O1, 1.144 (6); C2–O2, 1.166 (7); C9–C10, 1.311 (7); P1–Cr1–P2, 153.94 (7); C1–Cr1–C2, 107.0 (3); C10–C9–C11, 135.0 (5); C9–C10–C21, 136.0 (5).



2



3

An X-ray diffraction study[14] of **1a** confirms that in the solid state the alkyne ligand lies almost perpendicular[15] with respect to the P–Cr–P plane in a distorted trigonal-bipyramidal geometry (P–Cr–P, 153.94 (7)°; OC–Cr–CO, 107.0 (3)°) (Figure 1). Distances and angles involving the alkyne are consistent with those in other chromium–diphenylacetylene complexes.[16]

The alkyne ligands in these complexes are labile to displacement by a variety of donor ligands, including carbon monoxide and trimethyl phosphite, to apparently give other CrL_6 complexes. Decomposition occurs, with liberation of free alkyne, in the presence of thf and ethyl diazoacetate. There is no reaction with conjugated or nonconjugated dienes.

Molecular orbital calculations at the extended Hückel level performed on a $Cr(CO)_4(\eta^2\text{-}HC{\equiv}CH)$ model show that the conformation with the alkyne perpendicular to the P–Cr–P plane is preferred by 15 kcal mol^{-1}. This orientation maximizes the

---

[1] Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297.

[2] Dixon, D. T.; Burkinshaw, P. M.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* **1980**, 2237.

[3] (a) Wink, D. J.; Oh, C. K. *Organometallics* **1990**, *9*, 2605. (b) Wink, D. J.; Wang, N.-F.; Creagan, B. T. *Organometallics* **1989**, *8*, 561.

[4] The isolobal character of alkynes and other four-electron donors has been discussed before.[5] This is especially true for 1,3-dienes, which also possess an excellent π-acceptor orbital.[6]

[5] Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. E., Eds.; Pergamon: 1982, Oxford; Vol. 3.

[6] Wink, D. J. *Organometallics*, in press.

[7] Michael, G.; Kreiter, C. G. *Z. Naturforsch.* **1984**, *39B*, 1738.

[8] No intermediates are detected by ^1H NMR spectroscopy when the phenylacetylene reaction is performed in CD_2Cl_2.

[9] Complex **1a** is prepared in 58% yield (29% based on Cr). ^{13}C NMR: δ 180.2 (t, J_{PC} = 15 Hz, C_{alkyne}). IR: ν(CO) = 1932, 1850 cm^{-1}. Complete details are provided in the supplementary material.

[10] Complex **1b** is prepared from **1a** in 57% yield. ^{13}C NMR: 175.5 (t, $^2J_{PC}$ = 9 Hz, $\equiv$CPh), 163.7 (t, $^2J_{PC}$ = 18 Hz, $\equiv$CH). IR: ν(CO) = 1934, 1840 cm^{-1}.

[11] Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

[12] Honeychuck, R. V.; Hersh, W. *J. Am. Chem. Soc.* **1989**, *111*, 6056.

[13] Binsch, G. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975; pp 45–82.

[14] Crystals were grown from ether at −20 °C. The space group is P_{bcn} with a = 19.064 (3) Å, b = 14.070 (2) Å, c = 18.979 (2) Å, and V = 5091 (2) Å^3. Refinement of 298 least-squares parameters using 2205 reflections with $I > 2.0\sigma(I)$ gave R = 4.6% and R_w = 5.6%.

[15] There is a slight tilt (12°) from the perpendicular.

[16] (a) Koldova, N. E.; Zhvanko, O. S.; Andreanov, V. G.; Karapyetyan, A. A.; Struchkov, Y. T. *Koord. Khim.* **1980**, *6*, 1407. (b) Wink, D. J.; Fox, J. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 5012. (c) Salt, J. E.; Girolami, G. S.; Wilkinson, G.; Motevalli, M.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 685.

0002-7863/90/1512-8585$02.50/0

π-donation with a vacant metal fragment orbital in the equatorial plane and π-back-bonding with an orbital oriented in the axial direction.[17] When the system is converted to a simple square pyramid, the calculated barrier to formal rotation becomes 12 kcal mol^{-1}, reminiscent of change in the barrier for olefin rotation in d^8 Fe(CO)$_4$(olefin).[18]

We are aware of no reports concerning the synthesis of a simple four-electron monoalkyne complex of a d^6 ML$_4$ fragment.[19] This is remarkable considering the extensive group 6 alkyne chemistry that began with the synthesis of W(alkyne)$_3$(CO) complexes over 25 years ago.[21] The availability of reagents that are both electron rich and labile, such as the 1,5-COD complexes utilized here, is critical to the synthetic strategy for introducing excellent π-acceptor ligands, such as alkynes and 1,3-dienes.[3]

Acknowledgment. We are grateful to Drs. James Springer and John Dewan for helpful discussions about the crystal structure determination. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support and to the National Science Foundation for funds to purchase an X-ray diffractometer.

Supplementary Material Available: Synthetic and spectroscopic data for **1a** and **1b**, details of extended Hückel calculations, and methods and results (listings) of the crystal structure study of **1a** (11 pages); listing of observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

---

(17) (a) Wink, D. J.; Creagan, B. T. *Organometallics* **1990**, *9*, 328. (b) Kamata, M.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Yoshida, T.; Otsuka, S. *Inorg. Chem.* **1983**, *22*, 2416. (c) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466. (d) Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713.

(18) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

(19) Four-electron mono(alkyne) complexes of formally d^2 or d^4 group 6 metal centers are well-known,[20] and some d^6 bis(alkyne) containing four-electron alkynes are also known: refs 16b,c. Dötz, K. H.; Mühlmeier, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 929.

(20) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

(21) Tate, D. P.; Augl, J. M.; Ritchey, W. M.; Ross, B. L.; Grasselli, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 3261.

An Unusual, Electronically Unsaturated Dirhenium Polyhydride Complex with No Metal-Metal Bond

Karen E. Meyer, Phillip E. Fanwick, and
Richard A. Walton*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received July 20, 1990

Many mononuclear and dinuclear mixed polyhydride–phosphine (or arsine or stibine) complexes of rhenium are known, in a variety far greater than that for any other transition element. In the case of the dirhenium species, these are of the generic types [Re$_2$H$_9$(PR$_3$)$_4$]$^+$, Re$_2$H$_8$(PR$_3$)$_4$, [Re$_2$H$_7$(PR$_3$)$_5$]$^+$, Re$_2$H$_6$(PR$_3$)$_5$, [Re$_2$H$_5$(PR$_3$)$_6$]$^+$, and Re$_2$H$_4$(PR$_3$)$_6$, where PR$_3$ represents a monodentate or one-half a bidentate phosphine.[1-14] With one exception, the structural characterizations of representative examples of these compounds have revealed the presence of three or four bridging hydrido ligands and a short Re–Re distance (2.51–2.61 Å).[2,5,8-11] The latter observation has led to the conclusion that some degree of multiple metal-metal bonding is present, represented in terms of direct Re–Re bonding and/or three-center, two-electron Re–H–Re bonds.[15,16] The single exception is the complex Re$_2$(μ-H)$_2$H$_6$(μ-dppm)$_2$ (dppm = Ph$_2$PCH$_2$PPh$_2$), which contains only two bridging hydrido ligands and possesses the much longer Re–Re bond distance of 2.9335 (9) Å. We now report the isolation of a molecule, viz., [Re$_2$H$_5$(dmpm)$_3$]PF$_6$ (dmpm = Me$_2$PCH$_2$PMe$_2$), that takes this trend to its extreme, namely, no direct Re–Re interaction whatsoever and metal centers that are electronically unsaturated. This may presage the discovery of other compounds of this type with metals that normally show a propensity to form strong metal-metal interactions.[17]

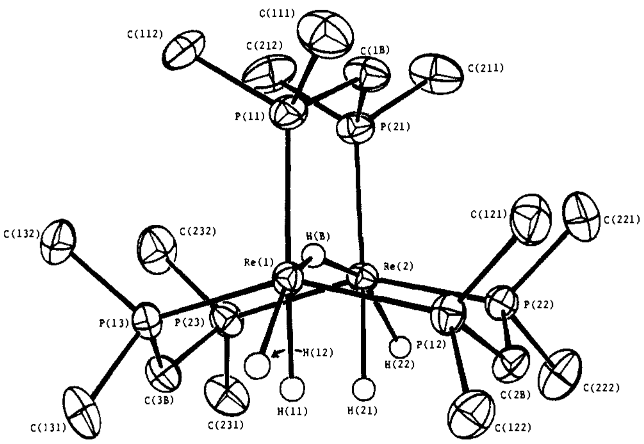


Figure 1. ORTEP view of the structure of the [Re$_2$H$_5$(dmpm)$_3$]$^+$ cation with the hydrogen atoms of the dmpm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level, except for the hydride ligands, which are circles of arbitrary radius. Some representative and important bond distances (Å) and angles (deg) and torsional angles (deg) are as follows: Re(1)–P(11) = 2.408 (2), Re(1)–P(12) = 2.365 (2), Re(1)–P(13) = 2.371 (2), Re(1)–H(B) = 1.53 (7), Re(1)–H(11) = 1.64 (8), Re(1)–H(12) = 1.7 (1), Re(2)–H(B) = 2.06 (7); Re(2)–Re(1)–P(11) = 85.48 (4), Re(2)–Re(1)–H(11) = 76 (3), Re(2)–Re(1)–H(12) = 135 (3), P(11)–Re(1)–H(12) = 139 (3), P(11)–Re(1)–P(12) = 102.73 (7), P(12)–Re(1)–P(13) = 151.07 (6); Re(1)–H(B)–Re(2) = 156 (5); P(11)–Re(1)–Re(2)–P(21) = 0.30 (7), P(12)–Re(1)–Re(2)–P(22) = 2.34 (7), P(13)–Re(1)–Re(2)–P(23) = 1.69 (7). Distances involving Re(2) are similar to those for Re(1) and, therefore, are not listed here.

The reaction of the triply bonded dirhenium(II) complex Re$_2$Cl$_4$(μ-dmpm)$_3$[18] (0.453 g, 0.49 mmol) with LiAlH$_4$ (0.32 g, 8.4 mmol) in THF (20 mL) at room temperature afforded a green solution. The mixture was stirred for 2 h, hydrolyzed with 20 mL of a H$_2$O/THF (5:15 mL) mixture, and then heated gently. After

---

(1) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963.

(2) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

(3) Allison, J. D.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 163.

(4) Moehring, G. A.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 1861.

(5) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 4522.

(6) Cotton, F. A.; Luck, R. L.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 43.

(7) Costello, M. T.; Moehring, G. A.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 1578.

(8) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695.

(9) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2319.

(10) Allison, J. D.; Cotton, F. A.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1984**, *23*, 159.

(11) Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 2239.

(12) Root, D. R.; Meyer, K. E.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 2503.

(13) Costello, M. T.; Fanwick, P. E.; Meyer, K. E.; Walton, R. A. *Inorg. Chem.*, in press.

(14) An interesting example of a complex that contains a tridentate phosphine ligand has been encountered in the case of the unsymmetrical anionic species [H$_6$Re(μ-H)$_3$Re{MeC(CH$_2$PPh$_2$)$_3$}]$^-$: Abrahams, S. C.; Ginsberg, A. P.; Koetzle, T. F.; Marsh, P.; Sprinkle, C. R. *Inorg. Chem.* **1986**, *25*, 2500.

(15) Dedieu, A.; Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141.

(16) Dahl, L. F. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 1.

(17) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(18) Anderson, L. B.; Cotton, F. A.; Falvello, L. R.; Harwood, W. S.; Lewis, D.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3637.

0002-7863/90/1512-8586\$02.50/0