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Non-Redox Reactions of the Dirhenium(II) A-Frame-Like Monocarbonyl Complexes $Re_2(\mu\text{-}X)X_3(\mu\text{-dppm})_2(CO)$ (X = Cl or Br) with Alkynes. Structural Characterization of $[Re_2Cl_3(CO)(dppm)_2(\eta^2\text{-MeCCEt})]PF_6$

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The monocarbonyl complex $Re_2(\mu\text{-Cl})Cl_3(\mu\text{-dppm})_2(CO)$ reacts with alkynes in the presence of $TlPF_6$ at room temperature to afford the yellow-brown salts of composition $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}R^1CCR^2)]PF_6$, where R^1CCR^2 = HCCH, MeCCMe, MeCCEt, HCC-*n*-Pr, EtCCEt, HCCPh, HCC-*p*-tol, or MeCCPh. The bromide complex $[Re_2Br_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-HCCH})]PF_6$ has been prepared by a similar procedure. The identity of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-MeCCEt})]PF_6$ (**2c**) has been established by X-ray crystallography. This complex crystallizes in the space group $P2_1/n$ (No. 14) with a = 11.885 (2) Å, b = 19.702 (3) Å, c = 23.830 (3) Å, β = 99.05 (1)°, V = 5510(3) Å^3, and Z = 4. The structure, which was refined to R = 0.029 (R_w = 0.037) for 5069 data with $I < 3.0\sigma(I)$, shows the presence of a η^2-2-pentyne ligand which lies perpendicular to the Re–Re vector; the Re–Re distance of 2.3407 (4) Å is in accord with the preservation of a Re–Re multiple bond. The structure of the cation can be represented as $[(OC)Cl_2Re(\mu\text{-dppm})_2ReCl(\eta^2\text{-MeCCEt})]^+$ and is the first example of the binding of an alkyne to a compound that contains an electron-rich metal–metal triple bond based upon the $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration.

Introduction

A very extensive array of beautiful and significant reaction chemistry has been developed over the last ten years by Chisholm[1] and Schrock[2] and their co-workers from studies of the reactions of alkynes with $X_3M{\equiv}MX_3$ compounds which contain the electron-poor $\sigma^2\pi^4$ triple bond.[3] The most extensive chemistry has been developed in the cases where M is tungsten and X an alkoxide ligand and has included simple adduct formation, alkyne metathesis via alkylidyne formation, the coupling of alkynes, the coupling of alkynes with nitriles, and other important reactions.[4] Surprisingly, the development of related chemistry for other multiply bonded dimetal complexes in which the metal centers are more electron-rich is very limited. The first instances of the alkyne addition to a metal–metal quadruple bond have only recently been reported,[5] but no such chemistry has yet been reported for compounds that contain the electron-rich triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ configuration).[6] In the present report we describe the first examples of complex formation between alkynes and the triply bonded complexes $Re_2X_4(\mu\text{-dppm})_2(CO)$ (X = Cl or Br) from which compounds of the type $[Re_2X_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}R^1CCR^2)]PF_6$ can be isolated. Surprisingly, these reactions proceed with retention of a Re–Re multiple bond.

Experimental Section

Starting Materials. The compounds $Re_2X_4(\mu\text{-dppm})_2(CO)$ (X = Cl or Br) were prepared according to the literature procedures.[7,8] Carbon monoxide and acetylene, both unlabeled and ^{13}C labeled (99.1%), were obtained from Matheson Gas Products. All other alkynes were obtained from the Aldrich Chemical Co. Solvents were obtained from commercial sources and were used as received. Syntheses were performed under an atmosphere of dry nitrogen, and solvents were deoxygenated prior to use.

A. Synthesis of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}R^1CCR^2)]PF_6$. (i) $R^1 = R^2$ = H (2a). A solution of $Re_2Cl_4(\mu\text{-dppm})_2(CO)$ (**1a**) (0.100 g, 0.076 mmol) and $TlPF_6$ (0.030 g, 0.085 mmol) in CH_2Cl_2 (10 mL) was treated with a slow stream of gaseous acetylene for 3 min. The resulting mixture was then stirred at room temperature for 5 h and the pale orange precipitate (mainly TlCl) filtered off. The orange-brown filtrate was reduced to ca. 4 mL and then treated with an excess of diethyl ether (50 mL) to induce the precipitation of the title complex. After a period of ca. 30 min the tan precipitate was filtered off and washed with diethyl ether (2 × 10 mL). Additional product was obtained by extracting the initial pale orange precipitate with 15 mL acetone, reducing the volume of the filtrate to ca. 2 mL, and then adding diethyl

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[1] Representative example of the studies of Chisholm and co-workers are contained in a series of important review articles: (a) Chisholm, M. H. *J. Organomet. Chem.* **1990,** *400,* 235. (b) Chisholm, M. H. *New J. Chem.* **1987,** *11,* 459. (c) Buhro, W. H.; Chisholm, M. H. *Adv. Organomet. Chem.* **1987,** *27,* 311. (d) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Chem. Soc. Rev.* **1985,** *14,* 69.

[2] (a) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982,** *104,* 4291. (b) Schrock, R. R.; Listermann, M. L. *Organometallics* **1985,** *4,* 74. (c) Strutz, H.; Schrock, R. R. *Organometallics* **1983,** *3,* 1600. (d) Freudenberger, J. H.; Pedersen, S. F.; Schrock, R. R. *Bull. Soc. Chim. Fr.* **1985,** 349. (e) Latham, I. A.; Sita, L. R.; Schrock, R. R. *Organometallics* **1986,** *5,* 1508.

[3] (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982. (b) Cotton, F. A.; Walton, R. A. *Struct. Bonding (Berlin)* **1985,** *62,* 1.

[4] An overview of this chemistry will shortly be published in the second edition of ref 3a.

[5] Kerby, M. C.; Eichhorn, B. W.; Doviken, L.; Vollhardt, K. P. C. *Inorg. Chem.* **1991,** *30,* 156.

[6] The addition of alkynes to the $Mo{\equiv}Mo$ bonds of $(\eta^5\text{-}C_5R_5)_2Mo_2(CO)_4$ is of course well documented, but the metal–metal bonding in these systems is quite distinct from that based upon the $\sigma^2\pi^4\delta^a\delta^{*b}$ configurations (a = 1 or 2 when b = 0, b = 1 or 2 when a = 2) as present in L_3MML_3, L_4MML_4, and L_5MML_5 compounds. For a review of this chemistry, see: (a) Curtis, M. D. *Polyhedron* **1987,** *6,* 759 and (b) ref. 3(a), pp 250–252.

[7] Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M., Walton, R. A. *J. Am. Chem. Soc.* **1985,** *107,* 3524.

[8] Cotton, F. A.; Dunbar, K. R.; Price, A. C.; Schwotzer, W.; Walton, R. A. *J. Am. Chem. Soc.* **1986,** *108,* 4843.

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ether (30 mL) to precipitate a further quantity of this compound: combined yield 0.092 g (84%). Anal. Calcd for $C_{54}H_{48}Cl_5F_6OP_5Re_2$ (i.e. $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(HCCH)]PF_6{\cdot}CH_2Cl_2$): C, 42.35; H, 3.17. Found: C, 42.81; H, 3.06. The presence of a small amount of lattice CH_2Cl_2 was confirmed by ^1H NMR spectroscopy. IR spectrum: ν(CO) 1944 (s), ν(P–F) 838 (s) cm^{-1}.

The ^{13}C-labeled complex $[Re_2Cl_3(\mu\text{-dppm})_2(^{13}CO)(\eta^2\text{-HC}{\equiv}CH)]PF_6$ can be prepared from $Re_2Cl_4(\mu\text{-dppm})_2(^{13}CO)$ by the use of a procedure identical to that described above. IR spectrum: $\nu(^{13}CO)$ 1919 (s), ν(P–F) 834 (s) cm^{-1}.

(ii) $R^1 = R^2 = Me$ (2b). A mixture of **1a** (0.050 g, 0.038 mmol) and $TlPF_6$ (0.018 g, 0.052 mmol) in CH_2Cl_2 (5 mL) was reacted with 0.05 mL of 2-butyne. The reaction mixture was worked up after a reaction time of 6 h as described in section A(i), except that additional product was not obtained by extraction of the initial insoluble precipitate (mainly TlCl) but was obtained instead by reducing the final reaction filtrate to ca. 1 mL and adding a further volume of diethyl ether (30 mL): combined yield 0.038 g (67%). IR spectrum: ν(CO) 1936 (s), ν(P–F) 841 (s) cm^{-1}.

(iii) R^1 = Me, R^2 = Et (2c). A mixture of **1a** (0.050 g, 0.038 mmol), $TlPF_6$ (0.018 g, 0.052 mmol), and 0.05 mL of 2-pentyne was reacted in 5 mL of CH_2Cl_2 and worked up as described in section A(ii): yield 0.041 g (72%). Anal. Calcd for $C_{57}H_{54}Cl_5F_6OP_5Re_2$ (i.e. $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(MeCCEt)]PF_6{\cdot}CH_2Cl_2$): C, 43.50; H, 3.47. Found: C, 43.56; H, 3.39. The presence of a small amount of lattice CH_2Cl_2 was confirmed by ^1H NMR spectroscopy. IR spectrum: ν(CO) 1937 (s), ν(P–F) 830 (s) cm^{-1}.

The analogous $[BF_4]^-$ salt of **2c** was prepared by the use of a procedure similar to that described above except that the reaction filtrate, after removal of the TlCl precipitate, was treated with 0.3 mL of 85% $HBF_4{\cdot}Et_2O$ and stirred at room temperature for 20 min. The resulting solution was reduced to half-volume, and diethyl ether (50 mL) was added to induce precipitation of the complex. The yellow-brown powder was filtered off and washed with diethyl ether (3 × 10 mL): yield 0.032 g (59%). IR spectrum: ν(CO) 1936 (s), ν(B–F) 1056 (s, br) cm^{-1}. The identity of this compound was also based upon the similarity of its ^1H and $^{31}P\{^1H\}$ NMR spectra and cyclic voltammogram to those of the $[PF_6]^-$ salt **2c**.[9]

The following complexes were prepared using the same quantities of **1a**, $TlPF_6$ and alkyne as described in sections A(ii) and A(iii) and with the use of very similar procedures.

(iv) R^1 = H, R^2 = *n*-Pr (2d): 1-pentyne; yield 0.042 g (74%). Anal. Calcd for $C_{57}H_{54}Cl_5F_6OP_5Re_2$ (i.e. $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(HCC\text{-}n\text{-}Pr)]PF_6{\cdot}CH_2Cl_2$): C, 43.50; H, 3.47. Found: C, 43.54; H, 3.16. The presence of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy. IR spectrum: ν(CO) 1944 (s), ν(P–F) 830 (s) cm^{-1}.

(v) $R^1 = R^2$ = Et (2e): 3-hexyne; yield 0.040 g (69%). IR spectrum: ν(CO) 1941 (s), ν(P–F) 830 (s) cm^{-1}.

(vi) R^1 = H, R^2 = Ph (2f): phenylacetylene; yield 0.045 g (77%). Anal. Calcd for $C_{60}H_{52}Cl_5F_6OP_5Re_2$ (i.e. $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(HCCPh)]PF_6{\cdot}CH_2Cl_2$): C, 44.82; H, 3.27. Found: C, 44.53; H, 3.13. The presence of lattice CH_2Cl_2 was confirmed by ^1H NMR spectroscopy. IR spectrum: ν(CO) 1950 (s), ν(P–F) 834 (s) cm^{-1}.

(vii) R^1 = H, R^2 = *p*-tol (2g): *p*-tolylacetylene; yield 0.039 g (66%). Anal. Calcd for $C_{61}H_{54}Cl_5F_6OP_5Re_2$ (i.e. $[Re_2Cl_3(\mu\text{-dppm})_2)(CO)(HCC\text{-}p\text{-}tol)]PF_6{\cdot}CH_2Cl_2$): C, 45.18; H, 3.36. Found: C, 45.41; H, 3.36. The presence of lattice CH_2Cl_2 was confirmed by ^1H NMR spectroscopy. IR spectrum: ν(CO) 1943 (s), ν(P–F) 834 (s) cm^{-1}.

(viii) R^1 = Me, R^2 = Ph (2h): methylphenylacetylene; yield 0.036 g (61%). IR spectrum: ν(CO) 1936 (s), ν(P–F) 835 (s) cm^{-1}.

B. Synthesis of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-HCCH})]PF_6$ (3a). This complex was prepared by the reaction of $Re_2Br_4(dppm)_2(CO)$ (**1b**) (0.100 g, 0.067 mmol), $TlPF_6$ (0.030 g, 0.085 mmol), and acetylene in CH_2Cl_2 as described in section A(i) for the analogous chloride complex **2a**: yield 0.088 g (79%). Anal. Calcd for $C_{56}H_{52}Br_3F_6O_2P_5Re_2$ (i.e. $[Re_2Br_3(\mu\text{-dppm})_2(CO)(HCCH)]PF_6{\cdot}(CH_3)_2CO$: C, 41.06; H, 3.21. Found: C, 41.63; H, 3.08. The presence of lattice acetone was confirmed by IR spectroscopy (ν(CO) 1698 cm^{-1}) and ^1H NMR spectroscopy. IR spectrum: ν(CO) 1937 (s), ν(P–F) 838 (s) cm^{-1}.

Table I. Crystallographic Data for $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-MeCCEt})]PF_6$ (2c)

chem formula	$Re_2Cl_3P_5F_6OC_{56}H_{52}$	T, °C	20
fw	1488.66	λ, Å (Mo Kα)	0.710 73
space group	$P2_1/n$ (No. 14)	ρ_{calcd}, g cm^{-3}	1.794
a, Å	11.885 (2)	μ(Mo Kα), cm^{-1}	47.98
b, Å	19.702 (3)	transm coeff	1.00–0.73
c, Å	23.830 (3)	R^a	0.029
β, deg	99.05 (1)	$R_w{}^b$	0.037
V, Å^3	5510 (3)	goodness of fit	1.153
Z	4		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|^2)/\sum w|F_o|^2\}^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Preparation of Single Crystals of 2c. Crystals of this complex were grown by layering a dichloromethane solution of **2c** with isopropyl ether.

X-ray Crystallography. The structure of **2c** was determined at +20 °C by the application of standard procedures. The basic crystallographic parameters for these complexes are listed in Table I. The cell constants are based on 25 reflections with 20 $< \theta <$ 23°. Three standard reflections were measured after 5000 s of beam time during data collection; there were no systematic variations in intensity. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. This crystal was found to belong to the monoclinic space group $P2_1/n$. Lorentz and polarization corrections were applied to the data set. An empirical absorption correction[10] was applied, but no correction for extinction was made.

The structure was solved by the use of the Patterson heavy-atom method which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were identified in succeeding difference Fourier syntheses. The hydrogen atoms of the dppm ligands and 2-pentyne were included at fixed positions which were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. We assumed that the value of B(H), i.e., the isotropic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, their positions were not refined. The structures were refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. All non-hydrogen atoms of the dirhenium complexes were refined anisotropically; corrections for anomalous scattering were applied to these atoms.[11] Note that the methyl carbon C(5) of the 2-pentyne ligand possesses large thermal parameters. This reflects the thermal motion that is commonly associated with the terminal carbon atoms of alkyl chains; the anomalously short C–C distance (C(4)–C(5)) is an artifact of this phenomenon. The structural integrity of the alkyl groups in this complex is confirmed by ^1H NMR spectrocopy (see Table S7; supplementary material).

Positional parameters and their errors for all atoms, except the phenyl group atoms, are listed in Table II. Important intramolecular bond distances and angles are given in Table III. Full details of the crystal data, data collection parameters, and all structural parameters are available as supplementary material.

Physical Measurements. A Perkin-Elmer 1800 FTIR spectrometer was used to record the IR spectra of the compounds as mineral oil (Nujol) mulls. Electrochemical measurements were

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[9] This exact same procedure utilizing $HBF_4{\cdot}Et_2O$ can be used to prepare $[BF_4]^-$ salts of the other cations of the type $[Re_2X_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}R^1CCR^2)]^+$.

[10] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 1983, *A39*, 158.

[11] (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. *Ibid.*, Table 2.2B.

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Phenyl-Group Atoms of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-MeCCEt})]PF_6$ (2c)[a]

atom	*x*	*y*	*z*	*B*
Re(1)	0.29226 (2)	0.30178 (2)	0.02486 (1)	2.427 (6)
Re(2)	0.20507 (2)	0.19984 (2)	0.04449 (1)	2.407 (6)
Cl(11)	0.3642 (2)	0.4158 (1)	0.0005 (1)	4.69 (5)
Cl(12)	0.4862 (2)	0.2751 (1)	0.06544 (9)	3.95 (5)
Cl(21)	0.0079 (2)	0.1838 (1)	0.01628 (9)	3.87 (5)
P(11)	0.3536 (2)	0.2746 (1)	−0.06736 (9)	2.82 (4)
P(12)	0.2882 (2)	0.3631 (1)	0.11507 (9)	2.71 (4)
P(21)	0.1990 (2)	0.1537 (1)	−0.05354 (9)	2.92 (5)
P(22)	0.1246 (2)	0.2464 (1)	0.12706 (8)	2.69 (4)
O(11)	0.0521 (5)	0.3435 (3)	−0.0298 (2)	4.0 (1)
C(1)	0.4315 (8)	0.0952 (5)	0.0382 (4)	5.1 (2)
C(2)	0.3426 (7)	0.1381 (4)	0.0593 (4)	3.7 (2)
C(3)	0.3198 (7)	0.1599 (4)	0.1073 (4)	3.7 (2)
C(4)	0.3709 (8)	0.1552 (6)	0.1684 (4)	6.0 (3)
C(5)	0.473 (3)	0.147 (3)	0.182 (1)	37 (2)
C(10)	0.1409 (7)	0.3276 (4)	−0.0091 (3)	2.9 (2)
C(1B)	0.3172 (7)	0.1855 (4)	−0.0861 (4)	3.4 (2)
C(2B)	0.2211 (7)	0.3098 (4)	0.1639 (3)	3.0 (2)
P(1000)	0.5120 (2)	0.0849 (1)	0.7995 (1)	4.09 (5)
F(1001)	0.441 (1)	0.0242 (6)	0.7952 (7)	21.4 (5)
F(1002)	0.415 (1)	0.1293 (6)	0.7986 (4)	16.0 (4)
F(1003)	0.490 (1)	0.0853 (8)	0.7360 (5)	21.2 (5)
F(1004)	0.602 (1)	0.0396 (7)	0.8029 (4)	17.4 (4)
F(1005)	0.532 (1)	0.0825 (6)	0.8603 (5)	16.9 (4)
F(1006)	0.595 (1)	0.1348 (7)	0.7931 (7)	27.7 (6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

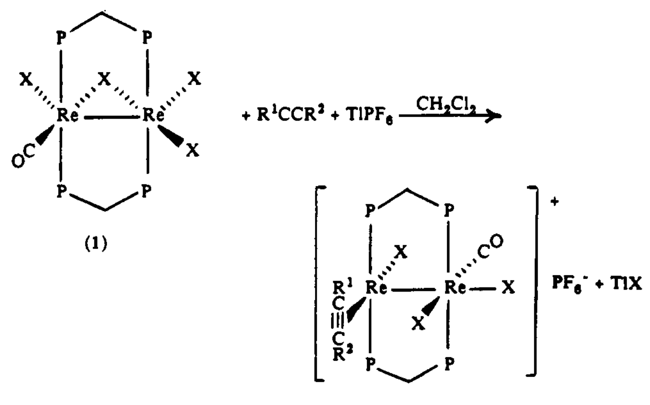
Table III. Important Bond Distances (Å) and Bond Angles (deg) for $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-MeCCEt})]PF_6$ (2c)[a]

	Distances		
Re(1)–Re(2)	2.3407 (4)	Re(2)–P(22)	2.494 (2)
Re(1)–Cl(11)	2.504 (2)	Re(2)–C(2)	2.023 (9)
Re(1)–Cl(12)	2.413 (2)	Re(2)–C(3)	2.020 (8)
Re(1)–P(11)	2.480 (2)	O(11)–C(10)	1.136 (9)
Re(1)–P(12)	2.473 (2)	C(1)–C(2)	1.50 (1)
Re(1)–C(10)	1.921 (9)	C(2)–C(3)	1.29 (1)
Re(2)–Cl(21)	2.355 (2)	C(3)–C(4)	1.49 (1)
Re(2)–P(21)	2.497 (2)	C(4)–C(5)	1.21 (3)
	Angles		
Re(2)–Re(1)–Cl(11)	173.76 (6)	Re(1)–Re(2)–C(3)	102.4 (3)
Re(2)–Re(1)–Cl(12)	99.08 (6)	Cl(21)–Re(2)–P(21)	78.63 (7)
Re(2)–Re(1)–P(11)	101.11 (5)	Cl(21)–Re(2)–P(22)	77.71 (7)
Re(2)–Re(1)–P(12)	100.12 (5)	Cl(21)–Re(2)–C(2)	135.2 (3)
Re(2)–Re(1)–C(10)	84.1 (3)	Cl(21)–Re(2)–C(3)	133.2 (3)
Cl(11)–Re(1)–Cl(12)	87.09 (9)	P(21)–Re(2)–P(22)	156.03 (7)
Cl(11)–Re(1)–P(11)	80.19 (8)	P(21)–Re(2)–C(2)	81.3 (3)
Cl(11)–Re(1)–P(12)	79.50 (8)	P(21)–Re(2)–C(3)	117.9 (3)
Cl(11)–Re(1)–C(10)	89.8 (3)	P(22)–Re(2)–C(2)	118.9 (3)
Cl(12)–Re(1)–P(11)	85.00 (7)	P(22)–Re(2)–C(3)	81.7 (3)
Cl(12)–Re(1)–P(12)	84.62 (7)	C(2)–Re(2)–C(3)	37.2 (3)
Cl(12)–Re(1)–C(10)	176.8 (3)	Re(2)–C(2)–C(1)	150.7 (8)
P(11)–Re(1)–P(12)	157.59 (7)	Re(2)–C(2)–C(3)	71.3 (5)
P(11)–Re(1)–C(10)	94.0 (2)	C(1)–C(2)–C(3)	137.9 (9)
P(12)–Re(1)–C(10)	95.3 (2)	Re(2)–C(3)–C(2)	71.5 (5)
Re(1)–Re(2)–Cl(21)	120.68 (6)	Re(2)–C(3)–C(4)	150.8 (7)
Re(1)–Re(2)–P(21)	94.24 (5)	C(2)–C(3)–C(4)	137.4 (9)
Re(1)–Re(2)–P(22)	94.52 (5)	C(3)–C(4)–C(5)	120 (2)
Re(1)–Re(2)–C(2)	100.3 (3)	Re(1)–C(10)–O(11)	178.9 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions $E_{1/2}$ = +0.47 V vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments wee performed with a BAS Inc. Model CV-27 instrument in conjunction with a BAS Model RXY recorder. NMR spectra were recorded on CD_2Cl_2, $CDCl_3$, or $(CD_3)_2CO$ solutions of the complexes. The $^{31}P\{^1H\}$ spectra were obtained with use of a Varian XL-200A spectrometer operated at 80.98 MHz or a GE QE-300 spectrometer equipped with a multinuclear Quad probe operated at 121.5 MHz with 85% H_3PO_4 as an external standard. ^1H NMR and $^{13}C\{^1H\}$ spectra were obtained on a GE QE-300 spectrometer operated at 300 MHz and 75.61 MHz, respectively. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent.

Scheme I



(2, X = Cl; 3, X = Br)

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results

The A-frame-like monocarbonyl complexes $Re_2(\mu\text{-}X)X_3(\mu\text{-dppm})_2(CO)$ (**1a**, X = Cl; **1b**, X = Br) react with a variety of alkynes in the presence of $TlPF_6$ as shown in Scheme I. These reactions have been carried out in the case of X = Cl with the alkynes HCCH, MeCCMe, MeCCEt, HCC-*n*-Pr, EtCCEt, HCCPh, HCC-*p*-tol, and MeCCPh, thereby demonstrating the comparable stability of the adducts with terminal and internal alkynes. A stable complex with PhCCPh was not formed. In the case of X = Br only the ethyne complex was prepared. In the absence of $TlPF_6$, the monocarbonyl complexes **1** show little tendency to react with alkynes.

The corresponding $[BF_4]^-$ salts of **2** can be obtained upon the addition of $HBF_4{\cdot}Et_2O$ to the reaction filtrates following removal of the insoluble TlX. This was demonstrated by the isolation of the analogous $[BF_4]^-$ salts of **2b**, **2c**, **2d**, and **2f**; preparative details are given in the Experimental Section for $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-MeCCEt})]BF_4$. Their spectroscopic and electrochemical properties are identical to those of the $[PF_6]^-$ salts (see below), except for differences in the IR and $^{31}P\{^1H\}$ NMR spectra that arise from the different anions present.

The yellow-brown, diamagnetic complexes **2** and **3** display a single intense ν(CO) mode in their Nujol mull IR spectra between 1950 and 1936 cm^{-1}. The ν(P–F) mode of the $[PF_6]^-$ anion is found at ca. 835 cm^{-1} in all these spectra; for the $[BF_4]^-$ salts this band is replaced by one at ca. 1055 cm^{-1} assigned to ν(B–F). Solutions of **2c** and **2b** in acetone (c_M ca. 1 × 10^{-3} M) had conductivities (Λ_m = 100–115 Ω^{-1} cm^2 mol^{-1}) in accord with 1:1 electrolyte behavior.[12] The cyclic voltammetric (CV) properties of **2** and **3** are very similar (Table IV). Solutions in 0.1 M TBAH–CH_2Cl_2 show a reversible one-electron reduction very close to −0.50 V vs Ag/AgCl and an irreversible

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Table IV. Selected Electrochemical and Spectral Data for Complexes of the Type $[Re_2X_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}R^1CCR^2)]PF_6$

complex	R^1	R^2	CV half-wave potentials, V[a] $E_{1/2}$(red)[b]	$E_{p,c}$	$^{31}P\{^1H\}$ NMR, δ[c,d]
2a	H	H	−0.48 (60)	−1.26	−1.5, −3.5[e]
2b	CH_3	CH_3	−0.50 (80)	−1.45	+2.9, −1.4[f]
2c	CH_3	C_2H_5	−0.51 (100)	−1.58	+2.2, −1.1[f]
2d	H	*n*-C_3H_7	−0.50 (60)	−1.32	+0.3, −2.6
2e	C_2H_5	C_2H_5	−0.52 (80)	−1.47	+2.0, −1.8[g]
2f	H	C_6H_5	−0.45 (60)	−1.30	−3.5
2g	H	4-Me-C_6H_4	−0.45 (60)	−1.21	−3.5
2h	CH_3	C_6H_5	−0.50 (120)	−1.54	+2.9, −1.4
3	H	H	−0.45 (80)	−1.25	−5.1, −13.5[e]

[a] Measured on 0.1 M TBAH–CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode with a scan rate (v) of 200 mV/s at a Pt-bead electrode. Under our experimental conditions $E_{1/2}$ = +0.47 V vs Ag/AgCl for the ferrocenium/ferrocene couple. [b] ΔE_p ($E_{p,a} - E_{p,c}$) values are given in parentheses. [c] Spectra recorded in CD_2Cl_2 unless otherwise indicated. [d] In all instances, the $[PF_6]^-$ salts show a binomial heptet centered at ca. δ −144 due to this anion. [e] This complex has relatively poor solubility in CD_2Cl_2. [f] Spectrum is that of the $[BF_4]^-$ salt. [g] Spectrum recorded in $CDCl_3$.

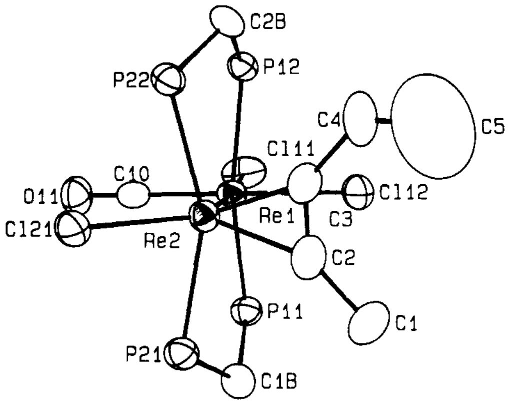

Figure 1. ORTEP representation of the structure of the $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-MeCCEt})]^+$ cation as present in complex **2c** with the phenyl-group atoms of the dppm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level.

reduction between −1.2 and −1.6 V. The similarities in the IR spectra and CV properties of these complexes imply a close structural similarity.

The structural identity of a representative member of the series, **2c**, was established by a single-crystal X-ray structure analysis. An ORTEP representation of the structure of the dirhenium cation is shown in Figure 1, while crystallographic data and important structural parameters are given in Tables I and II.

The $^{31}P\{^1H\}$ NMR spectra of this group of complexes consist generally of two well-resolved complex multiplets which are the components of either ABCD or AA′BB′ splitting patterns (see Table IV for a listing of the approximate centers of the two multiplets).[13] In the case of **2f** and **2g**, each spectrum appears as a complex, symmetric pattern spanning the range δ ca. +2 to δ ca. −10, with the most intense component centered at δ ca. −3.5. The $^{31}C\{^1H\}$ NMR spectrum of the ^{13}CO-labeled complex $[Re_2Cl_3(\mu\text{-dppm})_2(^{13}CO)(\eta^2\text{-HCCH})]PF_6$ shows an apparent triplet at δ +200.8 ($^2J_{P-C}$ = 6.7 Hz), which is in accord with the presence of a terminally bound CO ligand, while the spectrum of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}H^{13}C^{13}CH)]PF_6$ exhibits a triplet at δ +143.2 ($^2J_{P-C}$ = 10.4 Hz) for coordinated ethyne. This chemical shift is characteristic of the ethyne ligand behaving as a formal two- or three-electron donor if compared, for example, to data available[14] for mononuclear d^4 Mo(II) and W(II) monoalkyne complexes. The ^1H NMR spectra of the complexes that contain terminal η^2-RC≡CH ligands (**2a**, **2d**, **2f**, and **2g**) show multiplets at δ +10.4, +11.1, +11.4 and +10.4, respectively, which are due to the terminal acetylenic protons. For the ethyne complex **2a** this resonance is an AA′XX′ pattern, while for **2d**, **2f**, and **2g** it approximates to a doublet of doublets ($^3J_{P-H}$ = 22–26 Hz, $^3J_{P'-H}$ = 2–5 Hz). In the case of **2a**, this pattern was essentially unchanged over the temperature range +25 to −80 °C although it did broaden slightly at the low-temperature limit. The ^1H NMR spectrum of the structurally characterized complex **2c** (recorded in CD_2Cl_2 as its $[BF_4]^-$ salt) shows a series of multiplets between δ +8.1 and +7.0 due to the phenyl groups (40H) and an ABX_4 pattern with multiplets at δ +5.74 (2H) and +5.32 (2H) assigned to the bridgehead $-CH_2-$ groups of dppm, as well as alkyl group resonances at δ +3.60 (m, 1 H, $-CH_2CH_3$), +2.75 (m, 1 H, $-CH_2CH_3$), +2.83 (s, 3 H, $-CH_3$), and +1.17 (t, 3 H, $-CH_2CH_3$). The proton resonances for all the complexes are available as supplementary material (Table S7). The ^1H NMR spectrum of the bromide complex **3** was not very satisfactory because of its poor solubility properties.

Discussion

The conversions of the monocarbonyl complexes $Re_2(\mu\text{-}X)X_3(\mu\text{-dppm})_2(CO)$ (X = Cl, Br) to $[Re_2X_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}R^1CCR^2)]PF_6$ constitute the first instances where compounds that contain the electron-rich triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$) have been reported to react with alkynes. Furthermore, the resulting complexes are the first wherein a metal–metal multiple bond of such a high order has been preserved upon reaction with an alkyne or similar unsaturated organic. Other classes of dirhenium compounds are known, such as rhenium oxo complexes,[15,16] which contain η^2-coordinated alkyne ligands, but these species are quite different electronically from **2** and **3**. Invariably, the coordination of an alkyne to a metal–metal multiple bond leads to a drastic reduction in the metal–metal bond order or even to its complete elimination. This is not the case here, as established from a single-crystal X-ray structure analysis of a representative member of the series (Figure 1). The η^2-alkyne ligand is bound perpendicular to the equatorial plane of the molecule (defined as that containing the chloride and CO ligands). This contrasts, for example, with the compounds $[IrCl(CO)_3(\mu\text{-RCCR})(\mu\text{-dppm})_2]BPh_4$[17] and $Ir_2Cl_2(CO)_2(\mu\text{-RCCR})(\mu\text{-dppm})_2$,[18] in which the alkynes bridge the two Ir centers to give a planar Ir(μ-RCCR)Ir unit. It is also different from the situation in $W_2(\mu\text{-CSiMe}_3)_2(CH_2SiMe_3)_4$-

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(13) A comparison of the $^{31}P\{^1H\}$ NMR spectra of **2a** and its ^{13}C-labeled derivatives $[Re_2Cl_3(\mu\text{-dppm})_2(^{13}CO)(\eta^2\text{-HCCH})]PF_6$ and $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}H^{13}C^{13}CH)]PF_6$ shows that the multiplet at δ −1.5 is due to the pair of phosphorus atoms which are bound to the Re atom that contains the coordinated ethyne ligand.

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(η^2-MeCCPh), where the η^2-alkyne resides in the same plane as the $W_2(\mu\text{-}C)_2$ unit.[19]

In the solid state, the disposition of the alkyne ligands with respect to the Re_2 axis may largely reflect a minimization of nonbonding repulsions. However, the invariance of the ^{1}H NMR spectrum of **2a** over the temperature range +25 to −80 °C, the fact that the resonance for the unique acetylenic proton of complexes **2d**, **2f**, and **2g** appears as an apparent doublet of doublets rather than a triplet, and the ABCD splitting pattern for the $^{31}P\{^1H\}$ NMR spectra **2c** and **2d**, which contain unsymmetrical alkynes, support these complexes as possessing rigid structures in solution. This is not unexpected because rotation of the alkyne is hindered both by the phenyl groups of the dppm ligands, which are folded over to that side of the molecule which contains the coordinated alkyne, and by the chloride ligand on the adjacent rhenium atom (Cl(12) in Figure 1).

In the crystal structure of **2c** the C-C bond length C(2)–C(3) (1.29(1) Å) and the angles C(1)–C(2)–C(3) and C(2)–C(3)–C(4), which are 137.9 (9) and 137.4 (9)°, respectively, are not inconsistent with the alkyne ligand being a net 4-electron donor, and neither are the short Re–C distances, Re(2)–C(2) and Re(2)–C(3), of 2.023 (9) and 2.020 (8) Å. However, the alkyne coordination apparently has relatively little effect on the nature of the Re–Re bond length which is 2.3407 (4) Å, only ca. 0.1 Å longer than that in the parent triply bonded complex $Re_2Cl_4(\mu\text{-dppm})_2$. This bond distance is similar to those in other dirhenium(II) complexes derived from $Re_2Cl_4(\mu\text{-dppm})_2$,[20] including $[Re_2Cl_3(\mu\text{-dppm})_2(NCPh)_2]PF_6$ (2.270 (1) Å),[21] $Re_2Cl_4(\mu\text{-dppm})_2(CO)$ (2.338 (1) Å),[8] and $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)_2](PF_6)_{0.5}(OMe)_{0.5}$ (2.3787 (5) Å),[22] in which the only bridging ligands are the two dppm molecules. While a net 4-electron donation is a reasonable supposition since it would give an 18-electron count to each metal atom, provided we assume the presence of a $Re\equiv Re$ bond and that the positive charge resides at Re(2), i.e., the center which has the coordinated η^2-alkyne ligand, the ^{13}C NMR spectrum of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}H^{13}C^{13}CH)]PF_6$ (triplet at δ +143.2) does not confirm this interpretation. It is of course possible, indeed even likely, that the absence of other closely related benchmark compounds limits the usefulness of this spectroscopic criterion for multiply bonded compounds of this type. It would seem reasonable to represent the Re–alkyne bonding as being composed primarily of $R^1CCR^2(\pi) \rightarrow Re(\sigma)$ and $R^1CCR^2(\pi^*) \leftarrow Re(d_\delta)$ overlaps, thereby leaving the $Re\equiv Re$ bond largely intact.

The compounds **2** and **3** show considerable air and thermal stability and are good candidates for further reactivity studies. These are currently underway and will be reported in due course.

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Supplementary Material Available: For **2c**, tables giving full details of the crystal data and data collection parameters (Table S1), atomic positional parameters (Tables S2 and S3), anisotropic thermal parameters (Table S4), bond distances (Table S5), and bond angles (Table S6) and a table giving ^{1}H NMR spectral data for complexes of type **2** and **3** (22 pages). Ordering information is given on any current masthead page.

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