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Article

Complexation of the Triply-Bonded Dirhenium(II) Complex $Re_2Cl_4(\mu\text{-dppm})_2$ (dppm = $Ph_2PCH_2PPh_2$) by Up to Three Acetylene Molecules

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The triply bonded dirhenium(II) synthons $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) react with acetylene at room temperature in CH_2Cl_2 and acetone to afford the bis(acetylene) complexes $Re_2X_4(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})$ (X = Cl (**3**), Br(**4**)). Compound **3** has been derivatized by reaction with RNC ligands in the presence of $TlPF_6$ to give unsymmetrical complexes of the type $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})(CNR)]PF_6$ (R = Xyl (**5**), Mes (**6**), *t*-Bu (**7**)), in which the RCN ligand has displaced the chloride ligand cis to the η^2-HCCH ligand. The reaction of **3** with an additional 1 equiv of acetylene in the presence of $TlPF_6$ gives the symmetrical all-cis isomer of $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})_2]PF_6$ (**8**). The two terminal η^2-HCCH ligands in **8** are very labile and can be displaced by CO and XylNC to give the complexes $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(L)_2]Y$ (L = CO when Y = PF_6 (**9**); L = CO when Y = $(PF_6)_{0.5}/(H_2PO_4)_{0.5}$ (**10**); L = XylNC when Y = PF_6 (**11**)). These substitution reactions proceed with retention of the all-cis stereochemistry. Single-crystal X-ray structure determinations have been carried out on complexes **3**, **5**, **8**, **10**, and **11**. In no instance have we found that the acetylene ligands undergo reductive coupling reactions.

Introduction

Several examples of the binding of alkynes to compounds that contain Mo–Mo and W–W quadruple bonds ($\sigma^2\pi^4\delta^2$ configuration) and electron-poor triple bonds ($\sigma^2\pi^4$ configuration) have been reported in which the alkynes assume η^2- and $\mu{:}\eta^2,\eta^2$-coordination modes.[1−7] In addition, in some circumstances the triply bonded dimetal complexes have been found to participate in important C–C bond coupling and metathesis reactions.[1−3,6−10] In contrast to this fairly extensive body of data, reactions of alkynes with the synthons that contain the electron-rich triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ configuration) have not previously reported although we have described the reactions of acetylene and other alkynes with carbonyl, isocyanide, and mixed carbonyl–isocyanide complexes derived from the triply bonded synthons $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$).[11−15] To

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establish how the reactivity of $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl (**1**), Br (**2**)) with alkynes compares with that shown by compounds that contain the quadruply-bonded $[M_2]^{4+}$ and triply-bonded $[M_2]^{6+}$ cores (M = Mo, W),[1−10] we have examined the reactions of **1** and **2** with acetylene. In so doing, we have sought to determine to what extent the well-documented redox activity of the electron-rich triple bond in $[Re{\equiv}Re]^{4+}$ compounds[1] might influence the course of these reactions.

Experimental Section

A. Starting Materials and General Procedures. The complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl (**1**), Br (**2**)) were prepared by the usual literature method.[16] Samples of *tert*-butyl isocyanide (*t*-BuNC) and 2,6-dimethylphenyl isocyanide (XylNC) were purchased from Fluka Chemical Corp., while samples of 2,4,6-trimethylphenyl isocyanide (MesNC) were available from an earlier study.[17] The thallium(I) reagent $TlPF_6$ was obtained from Strem Chemicals and samples of $NaBPh_4$ were from Aldrich Chemical Co., while the oxidant $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ was prepared by the standard procedure.[18] Carbon monoxide was purchased from Matheson Gas Products or Airco, and acetylene, both unlabeled and ^{13}C labeled (99.1%), was obtained from Matheson Gas Products. Solvents were obtained from commercial sources and were generally dried and distilled under a dinitrogen atmosphere before use. All reactions were carried out under an atmosphere of dinitrogen.

Caution! *Special precautions should be taken in handling thallium(I) compounds, which are toxic*.

B. Synthesis of Acetylene Complexes of Dirhenium(II). (i) $Re_2Cl_4(\mu\text{-dppm})_2(\mu\text{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})$ (3). A quantity of **1** (100 mg, 0.078 mmol) was suspended in acetone (8 mL), and a stream of acetylene was passed through the mixture for 2 min. The mixture was stirred for 20 h at room temperature, and the yellow precipitate filtered off, washed with diethyl ether (15 mL), and dried under a vacuum; yield 82 mg (79%). Anal. Calcd for $C_{54}H_{48}Cl_4P_4Re_2$: C, 48.56; H, 3.59. Found: C, 48.23; H, 3.66.

The identical product was obtained by exposing a solution of **1** (500 mg, 0.39 mmol) in dichloromethane (50 mL) to a slow stream of acetylene for 90 min. The mixture was allowed to stand for 18 h and then filtered. The filtrate was concentrated to ca. 15 mL and carefully layered with hexanes (50 mL) to give a crop of orange-yellow crystals of composition $\mathbf{3}\cdot 3CH_2Cl_2$ (as established by X-ray crystallography) after 7 days. Upon pumping of this product under vacuum, the solvent molecules were lost to afford **3**; yield 440 mg (85%). Anal. Found: C, 48.35; H, 3.75. When this same synthetic procedure was used, but the reaction filtrate was layered with diethyl ether rather than hexanes, crystals of a compound that appeared to be of composition $Re_2Cl_4(OReO_3)(\mu\text{-dppm})_2(\mu,\eta^2\text{-HCCH})\cdot 3CH_2Cl_2$ were isolated after 7 days. The identity of this compound was established by X-ray crystallography which demonstrated that it was structurally very similar to the previously characterized complex $Re_2Cl_5(\mu\text{-dppm})_2(\mu,\eta^2\text{-HCCH})$,[19] with a Re−Re distance of 2.68 A. However, because the perrhenate ligand appeared to be disordered with hydroxide (the $OReO_3$:OH multiplicity was 0.43:0.57 by refinement); further details are not reported at this time. Suffice it to say that this product appears to be the consequence of the oxidation of **3** by small amounts of adventitious O_2 and/or H_2O during the slow crystal growing process.

(ii) $Re_2Br_4(\mu\text{-dppm})_2(\mu\text{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})$ (4). The complex was prepared from the reaction between **2** and HCCH in acetone with use of the procedure similar to that described for **3**; yield 69%. Anal. Calcd for $C_{57}H_{54}Br_4OP_4Re_2$ (i.e. $\mathbf{4}\cdot(CH_3)_2CO$): C, 43.56; H, 3.43. Found: C, 43.73; H, 3.36.

(iii) $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})(CNXyl)]PF_6$ (5). A mixture of **3** (100 mg. 0.075 mmol), XylNC (40 mg, 0.305 mmol), and $TlPF_6$ (27 mg, 0.077 mmol) in dichloromethane (20 mL) was stirred for 2 days at room temperature and then centrifuged to remove the TlCl, and the filtrate was layered with hexanes. The resulting dark red crystals of composition $\mathbf{5}\cdot CH_2Cl_2$ were filtered off and dried under vacuum which led to loss of the CH_2Cl_2 solvent molecule; yield 70 mg (59%). Anal. Calcd for $C_{63}H_{57}Cl_3F_6NP_5Re_2$: C, 47.97; H, 3.62; N, 0.88. Found: C, 48.50; H, 3.73; N, 0.95.

The same product **5** was obtained when acetone was used as the reaction solvent; yield 79%.

(iv) $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})(CNMes)]PF_6$ (6). A procedure similar to that described for complex **5** with acetone as the reaction solvent was used to prepare **6**; yield 87%. Anal. Calcd for $C_{64}H_{59}Cl_3F_6NP_5Re_2$: C, 48.35; H, 3.75. Found: C, 47.51; H, 3.65.

(v) $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})(CN\text{-}t\text{-Bu})]PF_6$ (7). A procedure similar to that described for the synthesis of **5** and **6** was used to prepare **7**; yield 80%. The identity of this compound was based upon its spectroscopic and cyclic voltammetric properties.

(vi) $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})_2]PF_6$ (8). A slow stream of acetylene was passed through a mixture of **1** (250 mg, 0.19 mmol) and $TlPF_6$ (68 mg, 0.19 mmol) in 50 mL of dichloromethane for 90 min at room temperature. The flow of acetylene was stopped, the reaction vessel was closed off, and the contents were stirred for 24 h. The reaction mixture was centrifuged to remove insoluble materials and the filtrate evaporated to give **8** as a red solid; yield 220 mg (77%). It was recrystallized from dichloromethane/hexanes to give crystals of composition $\mathbf{8}\cdot H_2O$. Anal. Calcd for $C_{56}H_{52}Cl_3F_6OP_5Re_2$: C, 45.14; H, 3.35. Found: C, 44.22; H, 3.56.

A similar reaction of the bis(acetylene) complex **3** with acetylene and $TlPF_6$ afforded **8** in high yield. Workup is similar to that described above.

(vii) $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{:}\eta^2,\eta^2\text{-HCCH})(CO)_2]PF_6$ (9). A stream of CO was passed through a solution of **8** (100 mg, 0.068 mmol) in 25 mL of dichloromethane for 1 h and the mixture then stirred under a static CO atmosphere for 3 days. The solvent was evaporated to afford a red-brown solid that washed with dichloromethane/hexanes and dried under a vacuum; yield 81 mg (81%). Anal. Calcd for $C_{54}H_{46}Cl_3F_6O_2P_5Re_2$: C, 43.94; H, 3.12. Found: C, 43.83; H, 3.27.

An alternative synthesis of **9** involved the reaction of CO with a mixture of the bis(acetylene) complex **3** (100 mg, 0.075 mmol) and $TlPF_6$ (27 mg, 0.077 mmol) in 25 mL of dichloromethane for 3 days. The volume was reduced to about 15 mL and the mixture centrifuged to separate the insoluble TlCl. The filtrate was evaporated and the residue washed with a dichloromethane/hexane mixture and then dried under a vacuum; yield 95 mg (86%).

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Table 1. Crystallographic Data for the Dirhenium(II) Complexes $Re_2Cl_4(\mu\text{-dppm})_2(\mu,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})\cdot 3CH_2Cl_2$ (**3**$\cdot 3CH_2Cl_2$), $[Re_2Cl_3(\mu\text{-dppm})_2(\mu,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})(CNXyl)]PF_6\cdot CH_2Cl_2$ (**5**$\cdot CH_2Cl_2$), $[Re_2Cl_3(\mu\text{-dppm})_2(\mu,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})_2]PF_6\cdot H_2O$ (**8**$\cdot H_2O$), $[Re_2Cl_3(\mu\text{-dppm})_2(\mu,\eta^2\text{-HCCH})(CO)_2](PF_6)_{0.5}(H_2PO_4)_{0.5}\cdot 1.5H_2O$ (**10**$\cdot 1.5H_2O$), and $[Re_2Cl_3(\mu\text{-dppm})_2(\mu,\eta^2\text{-HCCH})(CNXyl)_2]PF_6$ (**11**)

	3	**5**	**8**	**10**	**11**
empirical formula	$C_{57}H_{54}Cl_{10}P_4Re_2$	$C_{64}H_{59}Cl_5F_6NP_5Re_2$	$C_{56}H_{52}Cl_3F_6OP_5Re_2$	$C_{54}H_{50}Cl_3F_3O_{5.50}P_5Re_2$	$C_{70}H_{64}Cl_3F_6N_2P_5Re_2$
fw	1589.89	1660.72	1488.66	1477.62	1680.92
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_1/m$ (No. 11)	$C2/c$ (No. 15)	*Pnma* (No. 62)
a, Å	15.1686(2)	34.8244(4)	12.9178(3)	29.8864(3)	22.3350(3)
b, Å	14.7343(2)	17.9886(2)	14.7997(4)	15.59070(10)	23.2975(5)
c, Å	26.6033(3)	24.6451(3)	14.9895(5)	26.0873(3)	12.5653(7)
β, deg	91.8566(7)	114.1010(10)	93.0710(10)	94.6298(4)	90
V, Å^3	5942.7(2)	14092.9(6)	2861.6(2)	12115.7(3)	6538.3(5)
Z	4	8	2	8	4
ρ_{calcd}, g/cm^3	1.777	1.565	1.728	1.620	1.708
μ, mm^{-1}	4.723	3.834	4.620	4.362	4.054
$R(F_o)^a$	0.041	0.040	0.047	0.036	0.057
$R_w(F_o^2)^b$	0.089	0.087	0.126	0.097	0.142
GOF	1.026	0.932	1.039	0.975	1.070

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

Attempts were made to obtain single crystals of **9** by dissolving a sample of this complex in dichloromethane and layering this solution with hexanes. The X-ray-quality single crystals were shown to be of composition $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(CO)_2](PF_6)_{0.5}(H_2PO_4)_{0.5}\cdot 1.5H_2O$ (**10**$\cdot 1.5H_2O$), indicating that partial hydrolysis of some of the $[PF_6]^-$ anion had occurred during the slow crystal growing process. We have previously encountered instances of the hydrolysis of $[PF_6]^-$ to $[H_2PO_4]^-$ (due to the presence of adventitious water) in other dirhenium systems during attempts to grow single crystals.[20]

(viii) $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(CNXyl)_2]PF_6$ (11). A dichloromethane solution (25 mL), comprising a mixture of **8** (60 mg, 0.041 mmol) and XylNC (35 mg, 0.27 mmol), was stirred at room temperature for 3 days. The volume of the reaction mixture was then reduced to ca. 10 mL and filtered, and the filtrate was carefully layered with diethyl ether. Crystals of **11** were filtered off and dried; yield 22 mg (32%). Anal. Calcd for $C_{70}H_{64}Cl_3F_6N_2P_5Re_2$: C, 49.97; H, 3.80; H, 1.66. Found: C, 49.31; H, 3.78; N, 1.96.

C. X-ray Crystallography. Single crystals of complexes of composition **3**$\cdot 3CH_2Cl_2$, **5**$\cdot CH_2Cl_2$, **8**$\cdot H_2O$, **10**$\cdot 1.5H_2O$, and **11** were obtained as described in the individual synthetic procedures in section B. In all instances, data collections were carried out at 150(±1) K with graphite-monochromated Mo Kα radiation (λ = 0.710 73 A) on a Nonius KappaCCD diffractometer. Lorentz and polarization corrections were applied to the data sets. The key crystallographic data are given in Table 1.

The structure of **3** was solved with the use of the structure solution program PATTY in DIRDIF92,[21] while for the other structure solutions DIRDIF99[22] was used. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with C−H = 0.95 A and $U(H) = 1.3U_{eq}(C)$. They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK[23] was applied. The final refinements were performed by the use of the program SHELXL-97.[24] All non-hydrogen atoms were refined with anisotropic thermal parameters unless indicated otherwise. Crystallographic drawings were done using the program ORTEP.[25]

In all structures except that of **11**, the crystals were found to contain identifiable solvent molecules (see Table 1), the non-hydrogen atoms of which refined satisfactorily with anisotropic thermal parameters. The dirhenium cation in the structure of **8**$\cdot H_2O$ possesses a crystallographic plane of symmetry that bisects the Re−Re bond and contains the methylene C atoms of the dppm ligands, the C atoms (C(11) and C(12)) of the bridging acetylene ligand, and the bridging chloride ligand Cl(11). The $[PF_6]^-$ anion in this complex is also located about a mirror plane, which contains the P atom and fluorine atoms F(2)−F(5); the lattice H_2O molecule is not hydrogen-bonded to this anion. While the dirhenium cation present in the crystal of **10**$\cdot 1.5H_2O$ has no crystallographically imposed symmetry, the $[PF_6]^-$ anion is located on an inversion center and the $[H_2PO_4]^-$ anion has a 2-fold rotational symmetry axis. The closest approach between the O atom of a water molecule and either of these anions is 3.769 A (O(1W)···O(912)). The dirhenium cation in the crystal of **11** has a crystallographically imposed plane of symmetry (like **8**$\cdot H_2O$), and the $[PF_6]^-$ is also located on a plane of symmetry which contains the P atom and fluorine atoms F(1), F(2), F(4), and F(6). Some of the carbon atoms of the phenyl rings of one of the dppm ligands of the $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(CNXyl)_2]^+$ cation are disordered such that there are two half-positions for two adjacent carbon atoms in each ring; this gives half-atoms C(25A), C(25B), C(26A), and C(26B) for one ring and C(25C), C(25D), C(26C), and C(26D) for the other. The disorder was modeled satisfactorily with isotropic thermal parameters for atoms C(25A)−C(25D) and C(26A)−C(26D).

D. Physical Measurements. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 2000 FT-IR spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained with the use of a Varian INOVA 300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuterated solvent. The $^{31}P\{^1H\}$ spectra were recorded at 121.6 MHz, with 85% H_3PO_4 as an external standard. Natural-abundance $^{13}C\{^1H\}$ NMR spectra of **3** and **5** were obtained on a GE QE-300 spectrometer operated at 75.61 MHz. The $^{13}C\{^1H\}$ NMR spectrum

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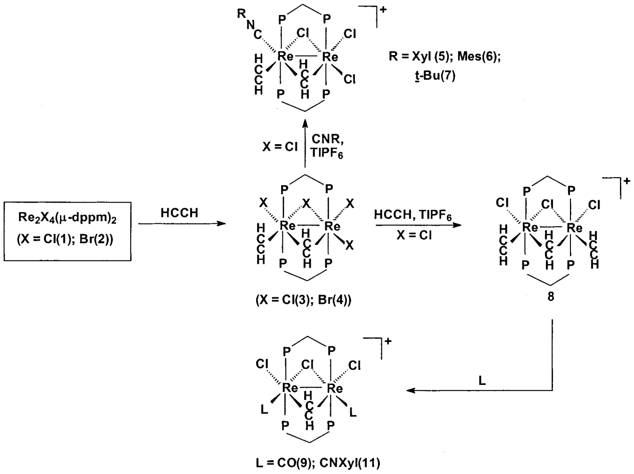
Scheme 1. Products from the reactions of $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl (**1**); Br (**2**)) with Acetylene



of a sample of $Re_2Cl_4(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-}H^{13}C^{13}CH)(\eta^2\text{-}H^{13}C^{13}CH)$ was recorded at MIT on an XL-300 instrument. Electrochemical measurements were carried out with use of a BAS Inc. model CV-27 instrument in conjunction with a BAS model RXY recorder and were recorded 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 25 °C and were uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple.

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

Results and Discussion

The reactions of $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl (**1**), Br (**2**)) with acetylene, which are summarized in Scheme 1, afford the first examples of alkyne complexes that are obtained directly from the reactions of dimetal compounds with electron-rich triple bonds[1] that contain only halide and phosphine ancillary ligands and are unencumbered by π-acceptor ligands such as CO and RNC.[12,15] The important spectroscopic and cyclic voltammetric properties of the new compounds isolated in the present report are summarized in Table 2.

The product that is formed by the reaction of **1** with acetylene at room temperature is the diamagnetic, yellow-orange bis(acetylene) adduct $Re_2Cl_4(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-}HCCH)(\eta^2\text{-}HCCH)$ (**3**). It is formed as the sole reaction product with the use of either acetone or dichloromethane as the reaction solvent, and the reaction course does not appear to be dependent upon reaction time. This complex, which contains both terminally bound and bridging acetylene ligands, was characterized by X-ray crystallography. An ORTEP[25] representation of the structure is shown in Figure 1; the important bond distances and angles are given in the caption for this figure. The structure is that of an edge-shared bioctahedron and resembles the previously reported structure of the bis(carbonyl)dirhenium complex $Re_2(\mu\text{-Cl})(\mu\text{-CO})Cl_3(\mu\text{-dppm})_2(CO)$.[26] However, there is a significant difference between the Re−Re bond distances for these two structures; the distance in **3** is 2.8094(3) Å, while in the carbonyl complex, which contains a Re═Re bond, it is 2.584(1) Å.[26] The long Re−Re bond distance in **3** accords with the presence of a single bond formed between two 17-e metal centers; this formal electron count follows from the terminal acetylene ligand behaving as a 2-e donor and the bridging $\mu{:}\eta^2,\eta^2$ acetylene as a 4-e donor. In accord with this conclusion we note that the C−C distance for the terminal HCCH ligand (C(1)−C(2) = 1.195(9) Å) is much shorter than for the formally 4-e donor bridging ligand (C(11)−C(12) = 1.340(8) Å).

The bromo analogue of **3** was prepared from the reaction between **2** and HCCH in acetone; the identity of **4** was based primarily upon elemental microanalyses and the very close similarity of its cyclic voltammetric properties of those of **3** (Table 2). Both **3** and **4** show a reversible one-electron oxidation with $E_{1/2} \approx +0.3$ V that should be accessible with $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ as oxidant. The reaction of **3** with a stoichiometric amount of this oxidant in dichloromethane afforded a green-brown paramagnetic crystalline material in quite high yield. However, a CV measurement showed that the product was not [**3**]PF_6 since it shows processes with $E_{1/2}$ values of +0.78 and −0.10 V. While a crystal structure determination confirmed the retention of $\mu{:}\eta^2\eta^2$-bridged dirhenium unit with a fairly short Re−Re bond (2.61 Å), a disorder problem prevented us from ascertaining the fate of the original η^2-HCCH ligand, which had clearly undergone an irreversible transformation.[27]

The derivatization of **3** was accomplished by its reactions with the organic isocyanide ligands RNC (R = Xyl, Mes, or *t*-Bu) in the presence of $TlPF_6$ and with dichloromethane or acetone as the reaction solvent. The close similarity of the products of composition $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-}HCCH)(\eta^2\text{-}HCCH)(CNR)]PF_6$ (R = Xyl (**5**), Mes (**6**), *t*-Bu (**7**)) was established from a comparison of their NMR spectra and CV properties (Table 2). Each complex shows an AA′BB′ pattern in its $^{31}P\{^1H\}$ NMR spectrum, signifying an unsymmetrical structure, and a binomial septet centered at δ −144 due to the $[PF_6]^-$ anion. The CV properties of **5**−**7** are quite simple, with a reversible one-electron oxidation at $E_{1/2} \approx +0.65$ V vs Ag/AgCl and an irreversible reduction at $E_{p,c} \approx -0.95$ V. The presence of the RNC ligands is shown by v(NC) modes in the IR spectra of these complexes (recorded as Nujol mulls) at 2188 (s) cm^{-1} (**5**), 2195 (s) and 2158 (sh, br) cm^{-1} (**6**), and 2159 (m) cm^{-1} (**7**); the ν(P−F) mode for $[PF_6]^-$ is in the range 841−847 (vs) cm^{-1}. The ^1H NMR spectra of **5**−**7** show resonances (not listed in Table 2) for the aliphatic CH_3 group protons of the RNC ligands; these are at $\delta = +1.65$ (s, 6H) for **5**, $\delta = +1.61$ (s, 6H) and +2.23 (s, 3H) for **6**, and $\delta = +0.95$ (s, 9H) for **7**. Other aspects of the NMR spectra of **5**−**7** (and of complex **3**) will be discussed later. The ease of replacing the $[PF_6]^-$ anion in these complexes by other anions was demonstrated by the conversion of **7** to its $[BPh_4]^-$ salt through the reaction of an acetone solution of **7** with $NaBPh_4$. The $^{31}P\{^1H\}$ and ^1H

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Table 2. Selected Spectroscopic and Electrochemical Data for Dirhenium(II) Complexes Containing Acetylene

	chem shift, δ[a]		CV half-wave potentials, V[b]		
compd no.	$^{31}P\{^1H\}$ NMR[c,d]	^1H NMR[e]	$E_{p,a}$	$E_{1/2}(ox)$	$E_{p,c}$
3	−3.2 (m), −9.1 (m)	+6.31 (t, 2H, 2-HCCH), +3.55 (m, 2H, μ-HCCH), +3.32 (m, 2H, dppm), +2.70 (m, 2H, dppm)[f]	+1.38	+0.27 (60)	−1.77
4	−10.8 (m), −17.5 (m)	*g*	+1.36	+0.31 (65)	−1.62
5	−3.5 (m), −16.4 (m)[h]	+6.68 (t, 2H, 2-HCCH), +6.18 (m, 2H, μ-HCCH), +3.75 (m, 2H, dppm), +2.45 (m, 2H, dppm)[h]		+0.68 (60)	−0.92
6	−3.2 (m), −20.2 (m)[h]	+6.71 (t, 2H, 2-HCCH), +6.14 (m, 2H, μ-HCCH), +3.72 (m, 2H, dppm), +2.41 (m, 2H, dppm)[h]		+0.67 (60)	−0.98
7	+3.4 (m), −11.1 (m)[h]	+5.53 (t, 2H, 2-HCCH), +4.67 (m, 2H, μ-HCCH), +3.05 (m, 4H, dppm)[h]		+0.64 (60)	−0.93
8	-15.7 (s)[i]	+5.88 (t, 4H, 2-HCCH), +4.34 (m, 2H, μ-HCCH), +4.74 (m, 2H, dppm), +4.10 (m, 2H, dppm)[i]	+1.42, +1.20		−1.20
9	+4.0 (s)	+4.80 (m, 2H, μ-HCCH), +3.48 (m, 2H, dppm), +3.27 (m, 2H, dppm)		+1.40 (100)	−0.25 (90)[j]
11	+4.2 (s)	+4.03 (m, 2H, μ-HCCH), +3.37 (m, 2H, dppm), +3.00 (m, 2H, dppm)	+1.46 (100)	+0.66 (90)	−1.08[k]

[a] NMR spectra recorded on $CDCl_3$ solutions unless otherwise noted. Abbreviations: s = singlet; t = triplet; m = multiplet. [b] Data are given for dirhenium-centered processes and are based upon single scan cyclic voltammograms (scan rate (v) = 200 mV/s) measured on 0.1 M $TBAH/CH_2Cl_2$ solutions at a Pt-bead electrode and referenced to the Ag/AgCl electrode. Under our experimental conditions $E_{1/2} = +0.47$ V for the ferrocenium/ferrocene couple. $E_{1/2}$ values are for one-electron processes with $i_{p,a} = i_{p,c}$, and numbers in parentheses are the approximate values of ΔE_p ($=E_{p,a} - E_{p,c}$) for the reversible processes. [c] The spectra of compounds **3**−**7** appear as simple AA′BB′ patterns; the centers of the two multiplets (which appear as triplets) are given. [d] Compounds **5**−**9** and **11**, which contain $[PF_6]^-$, show a characteristic binomial septet at δ −144. [e] Assignments for the *H*CC*H* and dppm $-CH_aH_b-$ protons only are given. [f] Spectrum recorded in C_6D_6. [g] Spectrum not recorded. [h] Spectrum recorded in CD_2Cl_2. [i] Spectrum recorded in $(CD_3)_2CO$. [j] This process is reversible ($E_{1/2}$(red) value is given). [k] This irreversible reduction has a coupled product wave with an $E_{p,a}$ value of −0.70 V ($i_{p,c} > i_{p,a}$).

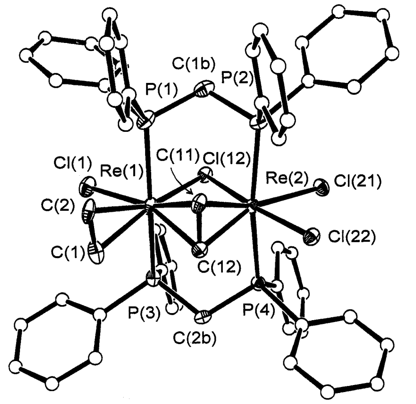

Figure 1. ORTEP[25] representation of the structure of the complex $Re_2Cl_4(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})$ as present in $\mathbf{3}{\cdot}3CH_2Cl_2$. Thermal ellipsoids are shown at the 50% probability level except for the phenyl carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Re(2) 2.8094(3), Re(1)−Cl(12) 2.4567(12), Re(2)−Cl(12) 2.4376(11), Re(1)−C(11) 2.139(5), Re(1)−C(12) 2.122(5), Re(2)−C(11) 2.088(5), Re(2)−C(12) 2.093(5), Re(1)−C(1) 2.145(6), Re(1)−C(2) 2.167(6), Re(1)−Cl(1) 2.4592(12), Re(2)−Cl(21) 2.4251(12), Re(2)−Cl(22), 2.4257(11) C(11)−C(12) 1.340(8), C(1)−C(2) 1.195(9); Re(1)−Cl(12)−Re(2) 70.06(3), Re(1)−C(11)−Re(2) 83.3(2), Re(1)−C(12)−Re(2) 83.60(19), Re(1)−C(1)−C(2) 74.9(4), Re(1)−C(2)−C(1) 72.9(4).

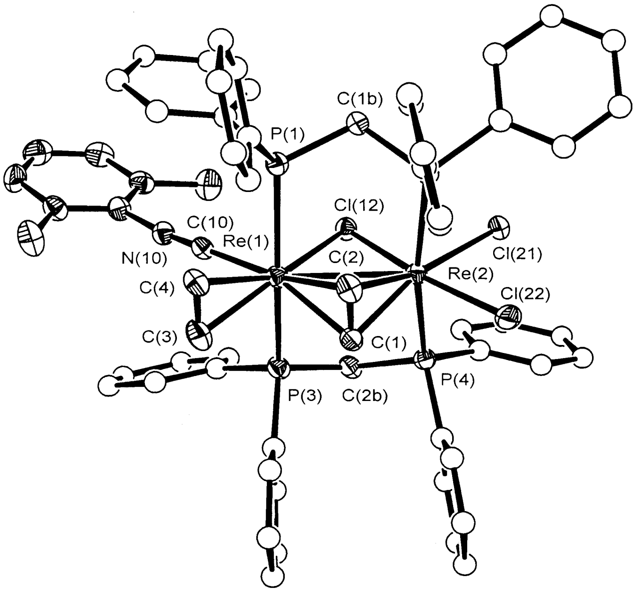

Figure 2. ORTEP[25] representation of the structure of the dirhenium cation $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})(CNXyl)]^+$ as present in $\mathbf{5}{\cdot}CH_2Cl_2$. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Re(2) 2.8437(3), Re(1)−Cl(12) 2.4206(12), Re(2)−Cl(12) 2.4348(11), Re(1)−C(1) 2.203(5), Re(1)−C(2) 2.200(5), Re(2)−C(1) 2.110(5), Re(2)−C(2) 2.119(5), Re(1)−C(3) 2.177(5), Re(1)−C(4) 2.151(6), Re(1)−C(10) 2.085(5), Re(2)−Cl(21) 2.4112(12), Re(2)−Cl(22) 2.4288(12), C(1)−C(2) 1.281(7), C(3)−C(4) 1.220(8), C(10)−N(10) 1.144(6); Re(1)−C(12)−Re(2) 71.70(3), Re(1)−C(1)−Re(2) 82.47(18), Re(1)−C(2)−Re(2) 82.33(19), Re(1)−C(3)−C(4) 72.5(4), Re(1)−C(4)−C(3) 74.8(4), Re(1)−C(10)−N(10) 179.0(5), C(10)−N(10)−C(11) 173.5(5).

NMR spectral properties (recorded in CD_2Cl_2) of $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})(CN\text{-}t\text{-Bu})]BPh_4$ are very similar to those of **7** (Table 2) with the exception that the resonance due to $[PF_6]^-$ is absent and the $-CH_2-$ resonances for the dppm ligands are now split out into a well-resolved ABX_4 pattern (multiplets centered at δ = +3.06 and +2.97). The CV of the $[BPh_4]^-$ salt shows the expected processes for the dirhenium cation of **7** at $E_{1/2} = +0.68$ V and $E_{p,c} = -0.98$ V vs Ag/AgCl and, in addition, an irreversible oxidation at $E_{p,a} = +1.02$ V that is due of the $[BPh_4]^-$ anion.

The crystal structure of the xylyl isocyanide containing derivative **5** confirmed that the basic structure of the precursor bis(acetylene) complex **3** is retained in compounds **5**−**7**. The ORTEP[25] representation of the structure of the dirhenium cation is shown in Figure 2. The XylNC ligand coordinates cis to the η^2-HCCH ligand, upon the displacement of chlorine atom Cl(1) in the structure of **3** (Figure 1). This substitution does not lead to much of a change in the Re−Re bond distance which is 2.8437(3) Å in **5** versus 2.8094(3) Å in **3**. In both structures the Re−Re bond order is formally that of a single bond, formed by uniting two 17-e fragments, if we consider that the positive charge in **5** resides at Re(1) thereby keeping both metal centers as Re(II). The difference between the C−C bond distances of the two types of acetylene ligands in **5** resembles that found in **3**, although the magnitude of this difference is smaller in **5** (the difference is 0.061 Å in **5** versus 0.145 Å in **3**); this may reflect charge differences that exist between the dimetal cores in these two structures.

In the conversion of **3** to **5**, the longest and presumably the weakest Re−Cl bond of **3** (i.e. Re(1)−l(1) in Figure 1) is the one that is substituted by XylNC. Compound **5** appears to be the thermodynamic product of this reaction. This result contrasts with the structure of the product that is isolated when **3** is reacted with a mixture of acetylene and $TlPF_6$ (Scheme 1). In this instance, the symmetrical all-cis acetylene complex $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})_2]PF_6$ (**8**) is formed. The mechanism of this reaction may proceed via an intermediate that is similar structurally to that of **5**, followed very rapidly by a partial "merry-go-round" process that converts this kinetic product to the symmetrical thermodynamically stable isomer that is isolated. This type of isomerization process is well documented in other bioctahedral dirhenium(II) complexes that are derived from the reactions of $Re_2Cl_4(\mu\text{-dppm})_2$ with π-acceptor ligands.[26,28]

The $^{31}P\{^1H\}$ NMR spectrum of **8** (Table 2) shows a singlet for the P atoms of the pair of equivalent μ-dppm ligands. Both of the terminal η^2-HCCH ligands of **8** are displaced by CO and XylNC at room temperature; these reactions proceed with retention of stereochemistry to afford the complexes $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(L)_2]PF_6$ (L = CO (**9**), CNXyl (**11**)). All three complexes were characterized by X-ray crystallography. However, during our attempts to grow single crystals of **9** a portion of the $[PF_6]^-$ counteranion hydrolyzed to $[H_2PO_4]^-$ and the crystal that was structurally characterized proved to be of composition $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(CO)_2](PF_6)_{0.5}(H_2PO_4)_{0.5}$; it is labeled as **10** to differentiate it from the salt **9**. Like compound **8**, both **9** and **11** show singlets in their $^{31}P\{^1H\}$ NMR spectra for the P atoms of the μ-dppm ligands. The IR spectra of **8**, **9**, and **11** (recorded as Nujol mulls or KBr pellets) show ν(P−F) modes for the $[PF_6]^-$ anion at ca. 840 (vs) cm^{-1}, while the spectra of **9** and **11** show ν(CO) and ν(CN) modes at 2033 and 2019 (vs) and 2133 and 2118 (vs) cm^{-1}, respectively, for the terminally bound CO and CNXyl ligands.

The ORTEP[25] representations of the structures of the dirhenium cations present in the crystals of composition **8**$\cdot H_2O$, **10**$\cdot 1.5H_2O$, and **11**, which are shown in Figures 3−5, reveal essentially identical structures, the only difference being the presence of a pair of terminally bound HCCH, CO, and XylNC ligands, respectively. The Re−Re bond lengths, which span the range 2.7928(8)−2.8613(5) Å (see Figures 3−5) are consistent with the presence of Re−Re single bonds. These data can be contrasted with the much shorter Re−Re bond lengths in the all-cis edge-sharing bioctahedral species $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2]^+$ and $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{-CO})(\mu\text{-CNXyl})_2]^+$, which are 2.582(1) and 2.576(1) Å, respectively, and are in accord with Re═Re bonds.[29,30]

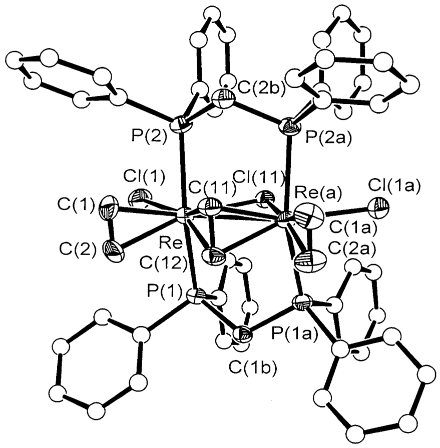

Figure 3. ORTEP[25] representation of the structure of the dirhenium cation $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(\eta^2\text{-HCCH})_2]^+$ as present in **8**$\cdot H_2O$. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) and angles (deg) are as follows: Re−Re(a) 2.8613(5); Re−Cl(11) 2.4301(18), Re−C(11) 2.102(6), Re−C(12) 2.120(7), Re−C(1) 2.164(7), Re−C(2) 2.177(7), Re−Cl(1) 2.4530(17), C(11)−C(12) 1.356(12), C(1)−C(2) 1.198(10); Re−Cl(11)−Re(a) 72.13(6), Re−C(11)−Re(a) 85.8(3), Re−C(12)−Re(a) 84.9(4), Re−C(1)−C(2) 74.6(5), Re−C(2)−C(1) 73.4(5).

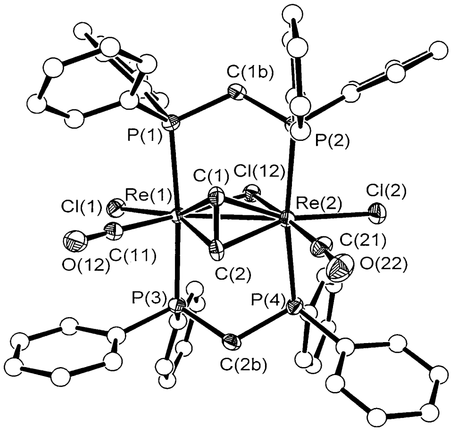

Figure 4. ORTEP[25] representation of the structure of the dirhenium cation $[Re_2Cl_2(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(CO)_2]^+$ as present in **10**$\cdot 1.5H_2O$. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Re(2) 2.7960(3), Re(1)− Cl(12) 2.4766(11), Re(2)−Cl(12) 2.4776(11), Re(1)−C(1), 2.106(4), Re(1)−C(2) 2.117(5), Re(2)−C(1) 2.123(4), Re(2)−C(2) 2.122(4), Re(1)−C(11) 1.951(5), Re(1)−Cl(1) 2.3992(12), Re(2)−C(21) 1.945(6), Re(2)−Cl(2) 2.4038(12), C(1)−C(2), 1.358(6), C(11)−O(12) 1.135(6), C(21)−O(22) 1.144(6); Re(1)−Cl(12)−Re(2) 68.72(3), Re(1)−C(1)−Re(2) 82.76(16), Re(1)−C(2)−Re(2) 82.54(17), Re(1)−C(11)−O(12) 177.4(5), Re(2)−C(21)−O(22) 174.4(5).

As mentioned already, the $^{31}P\{^1H\}$ NMR spectra are consistent with the unsymmetrical structures of **3**−**7** (AA′BB′ patterns) and symmetrical structures of **8**−**11** (singlets) (see Table 2). The $^{31}P\{^1H\}$ NMR spectrum of **3** was recorded in three solvents with similar results; multiplets centered at $\delta = -3.2$ and -9.1 in $CDCl_2$ (Table 2), $\delta = -6.8$ and -9.6 in CD_2Cl_2, and $\delta = -9.1$ and -10.8 in C_6D_6 had the appearance of "triplets" with $J_{P-P} \sim 19$ Hz. The presence of terminal and bridging acetylene ligands in **3**−**7** is clearly

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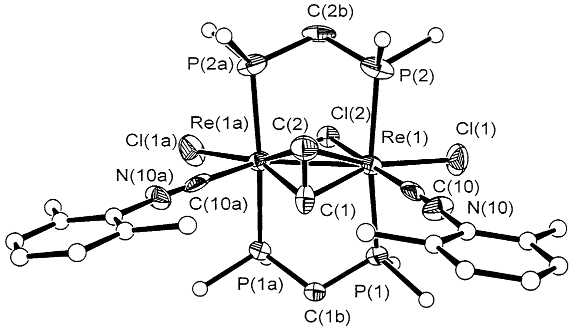

Figure 5. ORTEP[25] representation of the structure of the dirhenium cation $[Re_2Cl_3(\mu\text{-dppm})_2(\mu{:}\eta^2,\eta^2\text{-HCCH})(CNXyl)_2]^+$ as present in **11**. Thermal ellipsoids are drawn at the 50% probability level. The phenyl rings of the dppm ligands have been omitted for clarity because of the disorder involving some of the carbon atoms as discussed in the Experimental Section. The carbon atoms of the phenyl rings that are bound to the P atoms in the dppm ligands are shown as circles of arbitrary radius, as are the carbon atoms of the xylyl groups. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Re(1a) 2.7928(8), Re(1)−Cl(2) 2.472(3), Re(1)−C(1) 2.086(13), Re(1)−C(2) 2.133(14), Re(1)−C(10) 1.976(14), Re(1)−Cl(1) 2.402(3), C(1)−C(2) 1.27(2), C(10)−N(10) 1.189(16); Re(1)−Cl(2)−Re(1a) 68.78(9), Re(1)−C(1)−Re(1a) 84.0(6), Re(1)−C(2)−Re(1a) 81.8(6), Re(1)−C(10)−N(10) 177.9(10), C(10)−N(10)−C(11) 177.7(13).

seen in the ^1H NMR spectra of these complexes, while only a resonance for a bridging acetylene ligand is present in the spectra of **9** and **11** (Table 2). In complexes that contain both terminally bound and bridging HCCH ligands, the resonance for the former is the most downfield one of the two and usually has the appearance of an apparent triplet ($^3J_{P-H} \sim 4-8$ Hz). In the case of the ^1H NMR spectrum of **3**, similar results are obtained in C_6D_6 (Table 2), CD_2Cl_2, and $CDCl_3$. The appearance of the η^2-HCCH proton resonance (which is an AA′XX′ pattern) is very similar to that reported for the edge-sharing bioctahedral complex $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{-CO})(CNXyl)(\eta^2\text{-HCCH})]PF_6$,[11b] but the chemical shift in the latter complex ($\delta = +13.4$ in CD_2Cl_2) and those reported for the coordinatively unsaturated complexes of the type $[Re_2X_3(\mu\text{-dppm})_2(L)(\eta^2\text{-HCCH})]Y$ (X = Cl, Br; L = CO, *t*-BuNC, XylNC; Y = PF_6, O_3SCF_3) (δ in the range $+9.7$ to $+10.4$)[12,15] are all downfield of the ^1H resonance for η^2-HCCH ligand in **3** and **5**−**8** (Table 2). On the basis of these earlier studies,[11b,12,15] which showed that the η^2-HCCH ligand is bound perpendicular to the equatorial plane that contains the dirhenium unit, we can expect a similar rigid structure in solution for **3**−**8**; limited solubility properties of the complexes at low temperatures have thwarted our efforts to pursue temperature range studies. Finally, we note that the $^{13}C\{^1H\}$ NMR spectrum of a sample of **3** (with $H^{13}C^{13}CH$-labeled acetylene) shows resonances at $\delta = +96.3$ (triplet) and δ +67.1 (multiplet) in C_6D_6; similar measurements on a sample of **7** in CD_2Cl_2 gave these resonances at $\delta = +85.2$ and $\delta = +75.0$, respectively. These chemical shifts can be compared with data reported for $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}H^{13}C^{13}CH)]PF_6$, which shows a triplet further downfield at $\delta = +143.2$.[12]

Concluding Remarks

The reactions of $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br) with acetylene lead to bis(acetylene) complexes (Scheme 1), and we find no evidence for reductive coupling under the experimental conditions that we used. This contrasts with chemistry reported for compounds that contain the $(M{\equiv}M)^{6+}$ cores (M = Mo, W) in which μ-alkyne complexes are readily encountered, as well as reactions that lead to reductive coupling and alkylidyne formation through M≡M/C≡C bond metathesis.[1−3,6−10] In previous studies in which we examined the reactions of $Re_2Cl_4(\mu\text{-dppm})_2(CO)$,[12] $Re_2Cl_4(\mu\text{-dppm})_2(CNR)$,[15] and $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$[11] with terminal alkynes (including acetylene), the first two species afforded η^2-alkyne complexes of the type $[Re_2Cl_3(\mu\text{-dppm})_2(L)(\eta^2\text{-HCCR})]^+$ (L = CO, CNR)[12,15] but failed to incorporate a second alkyne ligand, a reaction which might have been expected to give rise to compounds of types **9**−**11** (Scheme 1). However, the edge-sharing bioctahedral complexes $Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_3(L)$ (L = CO, CNXyl) react with terminal alkynes in a fashion such that reductive coupling between the μ-CO ligand and RCCH leads to formation of a stable 3-metallafuran ring.[11] In the present work, the reactions of CO and RNC with the preformed bis(acetylene) complexes **3** and **4** and with the tris(acetylene) complex **8** (Scheme 1) do not lead to the formation of any such reductively coupled products. Instead, the two terminally bound η^2-HCCH ligands of **8** are sufficiently labile that they are easily displaced by CO and XylNC.

Clearly, the reaction course for these dirhenium(II) complexes is critically dependent on an interplay of electronic and steric factors and we are not yet in a position to predict when reductive coupling reactions will occur, even though the ready accessibility of the pair of electrons in the δ^* orbital of the electron-rich triple bond of $(Re{\equiv}Re)^{4+}$ compounds[1] makes them potentially ideal reagents for this purpose. In view of the redox activity of this core, it may well be that the sterically more encumbering environment present in these fairly rigid $[Re_2(\mu\text{-dppm})_2]^{4+}$ systems prevents reductive coupling from occurring, in contrast to the behavior in the less crowded and more flexible electron-poor triply bonded compounds such as those of the type $M_2(OR)_6$.[2,6,8,9] In this same regard, we note that while bis(alkyne) adducts of $W_2(\mu\text{-}O_2C\text{-}t\text{-Bu})_4$ have been isolated, reductive coupling does not occur.[5]

In future work we will investigate the thermal behavior of the bis(acetylene) complex **3** and its derivatives in both the solid-state and solution to explore whether reductive coupling can be initiated under more focusing conditions. In addition, we plan to examine the reactions of $Re_2Cl_4(\mu\text{-dppm})_2$ (**1**) with a variety of other alkynes. Preliminary studies have shown that 1-pentyne and 1-hexyne, for example, react with **1** but NMR spectroscopy indicates that this chemistry is more complex than that observed with acetylene and several species are formed.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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