# Reductive Coupling of Carbon Monoxide with Alkynes Leading to a Novel Case of Carbon–Oxygen Bond Formation. The First Examples of 3-Metallafuran Complexes

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*Received November 12, 1993*[⊗]

The edge-sharing bioctahedral dirhenium complexes $Re_2(\mu\text{-}X)(\mu\text{-}CO)X_3(L)(\mu\text{-}dppm)_2$ (X = Cl when L = CO, xylNC; X = Br when L = CO; dppm = $Ph_2PCH_2PPh_2$) react with terminal alkynes RCCH (R = H, *n*-Pr, *n*-Bu, Ph, *p*-tol) at room temperature in the presence of $TlPF_6$ to afford the novel series of diamagnetic complexes $[Re_2(\mu\text{-}X)(\mu\text{-}COC(R)CH)X_2(L)(\mu\text{-}dppm)_2]PF_6$ in which the reductive coupling of a bridging CO ligand and the alkyne leads to carbon–oxygen bond formation and the generation of a 3-metallafuran ring. The reactions are regioselective to give the R substituent in the 5-position. These complexes were found to undergo anion-exchange reactions when L = xylNC to afford the analogous $BF_4^-$ and $BPh_4^-$ salts. They can be reduced to their neutral congeners $Re_2(\mu\text{-}X)(\mu\text{-}COC(R)CH)(L)(\mu\text{-}dppm)_2$ by cobaltocene. In the case of the reaction between $Re_2(\mu\text{-}Cl)(\mu\text{-}CO)Cl_3(CNxyl)(\mu\text{-}dppm)_2$ and acetylene, the reaction intermediate $[Re_2Cl_3(CO)(\eta^2\text{-}HCCH)(CNxyl)(\mu\text{-}dppm)_2]PF_6$ has been prepared and characterized spectroscopically. A combination of NMR spectroscopy and representative single-crystal X-ray structure determination has been used to confirm the structures of the coupled species and the connectivity within the 3-metallafuran rings. The identities of $[Re_2(\mu\text{-}Cl)(\mu\text{-}COCHCH)Cl_2(CO)(\mu\text{-}dppm)_2]PF_6$ (**3a**) and $[Re_2(\mu\text{-}Cl)(\mu\text{-}COC(p\text{-}tol)CH)Cl_2(CNxyl)(\mu\text{-}dppm)_2]BF_4$ (**5h**) have been established by X-ray crystallography. Crystal data for **3a**: space group *Cc* (No. 9) with $a = 19.396(2)$ Å, $b = 15.495(2)$ Å, $c = 20.001(7)$ Å, $\beta = 99.66(2)°$, $V = 5926(4)$ Å$^3$, and $Z = 4$. The structure was refined to $R = 0.025$ ($R_w = 0.031$) for 3390 data with $I > 3.0\sigma(I)$. Crystal data for **5h**: space group *C*2/*c* (No. 15) with $a = 37.402(8)$ Å, $b = 15.302(4)$ Å, $c = 28.578(8)$ Å, $\beta = 119.06(3)°$, $V = 14\,296(15)$ Å$^3$, and $Z = 8$. The structure was refined to $R = 0.066$ ($R_w = 0.085$) for 5158 data with $I > 3.0\sigma(I)$. In these structures the Re–Re distances are very similar (2.565(1) Å for **3a** and 2.558(1) Å for **5h**).

## Introduction

In an earlier series of studies we showed the existence of an extensive reaction chemistry between the triply bonded dirhenium(II) compounds $Re_2X_4(\mu\text{-}dppm)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) and carbon monoxide, organic isocyanides, and organic nitriles.[1] Among our more important findings was the discovery that these complexes could serve as templates to bring about the reductive coupling of nitriles (RCN) through C–C bond formation to produce salts of the $[Re_2(\mu\text{-}X)(\mu\text{-}HN_2C_2R_2)X_2(NCR)(\mu\text{-}dppm)_2]^+$ cations.[2]

The binding of CO to $Re_2X_4(\mu\text{-}dppm)_2$ occurs in a stepwise fashion to form $Re_2(\mu\text{-}X)X_3(CO)(\mu\text{-}dppm)_2$, $Re_2(\mu\text{-}X)(\mu\text{-}CO)X_3(CO)(\mu\text{-}dppm)_2$, and $[Re_2(\mu\text{-}X)(\mu\text{-}CO)X_2(CO)_2(\mu\text{-}dppm)_2]^+$.[3–5] The monocationic tricarbonyl species exhibits a reversible reduction chemistry which has permitted the isolation of its neutral and monoanionic congeners. However, in spite of the relatively close approach of the CO ligands to one another in these species (the C···C contacts are ~2.3 Å),[5] we were unable to effect the reductive coupling of CO in the electron-rich monoanions $[Re_2(\mu\text{-}X)(\mu\text{-}CO)X_2(CO)_2(\mu\text{-}dppm)_2]^-$. Consequently, we have turned our attention to mixed CO–alkyne systems, where we hoped that the chances for successfully coupling CO with other organic substrates might be greater. During the course of these studies, we have recently synthesized and structurally characterized multiply bonded dirhenium(II) complexes of the type $[Re_2Cl_3(\mu\text{-}dppm)_2(CO)(\eta^2\text{-}RCCR')]PF_6$, where RCCR′ represents a terminal or internal alkyne,[6] but we were not successful in initiating the coupling of CO with RCCR′. However, when we resorted to the use of the dicarbonyl complexes $Re_2(\mu\text{-}X)(\mu\text{-}CO)X_3(CO)(\mu\text{-}dppm)_2$ (X = Cl (**1a**), Br (**1b**))[3,4] and the mixed carbonyl–isocyanide complex $Re_2(\mu\text{-}Cl)(\mu\text{-}CO)Cl_3(CNxyl)(\mu\text{-}dppm)_2$ (**2**)[4] in place of $Re_2(\mu\text{-}X)X_3(CO)(\mu\text{-}dppm)_2$, we discovered that the bridging CO ligand and a variety of terminal alkyne ligands readily undergo reductive coupling under mild reaction conditions to afford a novel series of dirhenium complexes in which an unusual 3-metallafuran ring has been generated through *carbon–oxygen* bond formation. While there is an extensive literature on metallacyclic complexes that contain a

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[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1994.

(1) For a summary of much of this chemistry see: Walton, R. A. *Polyhedron* **1989,** *8,* 1689 and references cited therein.

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0276-7333/94/2313-1235$04.50/0

2-metallafuran ring,[7,8] we are not aware of any previous reports on 3-metallafuran complexes. This chemistry is of further note since it demonstrates the ability of the electron-rich triple bond to serve as a template at which to initiate novel organometallic reductive-coupling chemistry. A preliminary report on some aspects of this chemistry has been communicated.[9]

## Experimental Section

**Starting Materials.** The compounds $\mathrm{Re_2(\mu\text{-}X)(\mu\text{-}CO)X_3(CO)(\mu\text{-}dppm)_2}$ (**1a**, X = Cl; **1b**, X = Br),[3] $\mathrm{Re_2(\mu\text{-}Cl)Cl_3(^{13}CO)(\mu\text{-}dppm)_2}$,[3] $\mathrm{Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}CO)Cl_3(^{13}CO)(\mu\text{-}dppm)_2}$,[3] and $\mathrm{Re_2(\mu\text{-}Cl)(\mu\text{-}CO)Cl_3(CNxyl)(\mu\text{-}dppm)_2}$ (**2**)[4] were prepared according to the literature procedures. $\mathrm{Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}CO)Cl_3(CNxyl)(\mu\text{-}dppm)_2}$ was synthesized from the reaction between $\mathrm{Re_2(\mu\text{-}Cl)Cl_3(^{13}CO)(\mu\text{-}dppm)_2}$ and 1 equiv of xylNC in acetone solution.[4] Carbon monoxide, both unlabeled and $^{13}$C labeled (99.1%), and acetylene were obtained from Matheson Gas Products. All other alkynes were obtained from the Aldrich Chemical Co. Xylyl isocyanide (2,6-dimethylphenyl isocyanide) was purchased from Fluka Chemicals, while cobaltocene and thallium(I) hexafluorophosphate were obtained from Strem Chemicals. 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.

**Syntheses. A. Synthesis of $\mathbf{[Re_2(\mu\text{-}Cl)(\mu\text{-}COC(R)CH)Cl_2(CO)(\mu\text{-}dppm)_2]PF_6}$. (i) R = H (3a).** A solution of **1a** (0.100 g, 0.075 mmol) and $\mathrm{TlPF_6}$ (0.030 g, 0.086 mmol) in $\mathrm{CH_2Cl_2}$ (15 mL) was treated with a slow stream of gaseous acetylene for 2 min. The resulting mixture was then stirred at room temperature for 2 h (this reaction time is critical), and the white precipitate (TlCl) was filtered off. The brown filtrate was evaporated to dryness. The residue was extracted into 3 mL of $\mathrm{CH_2Cl_2}$, and diethyl ether (40 mL) was added to induce the precipitation of the title complex. After a period of ca. 10 min the precipitate was filtered off, washed with diethyl ether (10 mL), and dried under vacuum; yield 0.080 g (72%). Anal. Calcd for $\mathrm{C_{55}H_{48}Cl_5F_6O_2P_5Re_2}$ (i.e. $\mathrm{[Re_2Cl_3(COCHCH)(CO)(\mu\text{-}dppm)_2]PF_6{\cdot}CH_2Cl_2}$): C, 42.36; H, 3.11. Found: C, 42.52; H, 3.07. The presence of a small amount of lattice $\mathrm{CH_2Cl_2}$ was confirmed by $^1$H NMR spectroscopy. IR spectrum: $\nu$(CO) 2032 (s) cm$^{-1}$.

The $^{13}$C-labeled derivative $\mathrm{[Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}COCHCH)Cl_2(^{13}CO)(\mu\text{-}dppm)_2]PF_6}$ was prepared from $\mathrm{Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}CO)Cl_3(^{13}CO)(\mu\text{-}dppm)_2}$ (0.050 g, 0.037 mmol) by use of a procedure similar to that described above; yield 0.040 g (73%). IR spectrum: $\nu$($^{13}$CO) 1986 (s) cm$^{-1}$. $^{13}$C{$^1$H} NMR ($\mathrm{CD_2Cl_2}$): $\delta$ 331.5 (s, bridging alkylidyne carbon), 188.6 (s, $CO_t$).

**(ii) R = *n*-Pr (3b).** A mixture of **1a** (0.100 g, 0.075 mmol), $\mathrm{TlPF_6}$ (0.03 g, 0.086 mmol), and 0.07 mL of 1-pentyne was reacted in 15 mL of $\mathrm{CH_2Cl_2}$ for 5 h at room temperature, and the white precipitate (TlCl) was filtered off. The brown filtrate was reduced to ca. 3 mL, and excess diethyl ether (40 mL) was added to induce precipitation of the product. After a period of ca. 10 min, the precipitate was filtered off, washed with diethyl ether (10 mL), and then dried under vacuum; yield 0.071 g (62%). IR spectrum: $\nu$(CO) 2032 (s) cm$^{-1}$.

The bromo analog $\mathrm{[Re_2(\mu\text{-}Br)(\mu\text{-}COC(}n\mathrm{\text{-}Pr)CH)Br_2(CO)(\mu\text{-}dppm)_2]PF_6}$ was synthesized by a procedure similar to that described above with the use of **1b** in place of **1a**; yield 64%. IR spectrum: $\nu$(CO) 2034 (s) cm$^{-1}$. The cyclic voltammogram of a solution of this complex in 0.1 M TBAH–$\mathrm{CH_2Cl_2}$ was very similar to that of **3b** with $E_{1/2}$(ox) = +1.42 V, $E_{1/2}$(red)(1) = +0.08 V, and $E_{1/2}$(red)(2) = −0.91 V vs Ag/AgCl.

**(iii) R = *n*-Bu (3c).** The use of 1-hexyne (0.08 mL) and a procedure analogous to that described in part A(ii) gave the title complex; yield 0.073 g (63%). Anal. Calcd for $\mathrm{C_{61}H_{62}Cl_3F_6O_3P_5Re_2}$ (i.e. $\mathrm{[Re_2Cl_3(COC(}n\mathrm{\text{-}Bu)CH)(CO)(\mu\text{-}dppm)_2]PF_6{\cdot}(C_2H_5)_2O}$: C, 46.05; H, 3.93. Found: C, 46.60; H, 4.09. IR spectrum: $\nu$(CO) 2035 (s) cm$^{-1}$.

**(iv) R = Ph (3d).** The use of phenylacetylene (0.10 mL) and a procedure analogous to that described in part A(ii) gave the title complex; yield 0.077 g (66%). IR spectrum: $\nu$(CO) 2027 (s) cm$^{-1}$.

**(v) R = *p*-tol (3e).** The use of *p*-tolylacetylene (0.10 mL) and a procedure analogous to that described in part A(ii) gave the title complex; yield 0.079 g (67%). IR spectrum: $\nu$(CO) 2032 (s) cm$^{-1}$.

**B. Synthesis of $\mathbf{Re_2(\mu\text{-}Cl)(\mu\text{-}COC(}\boldsymbol{n}\mathbf{\text{-}Pr)CH)Cl_2(CO)(\mu\text{-}dppm)_2}$.** A mixture of $\mathrm{[Re_2(\mu\text{-}Cl)(\mu\text{-}COC(}n\mathrm{\text{-}Pr)CH)Cl_2(CO)(\mu\text{-}dppm)_2]PF_6}$ (**3b**) (0.040 g, 0.026 mmol) and $\mathrm{(\eta^5\text{-}C_5H_5)_2Co}$ (0.007 g, 0.037 mmol) in acetone (4 mL) was stirred at room temperature for 5 h. The yellow-brown precipitate was filtered off, washed with diethyl ether (5 × 5 mL), and dried under vacuum; yield 0.030 g (84%). IR spectrum: $\nu$(CO) 1983 (s) cm$^{-1}$.

**C. Synthesis of $\mathbf{[Re_2Cl_3(CO)(\eta^2\text{-}HCCH)(CNxyl)(\mu\text{-}dppm)_2]PF_6}$ (4).** A mixture of **2** (0.050 g, 0.035 mmol) and $\mathrm{TlPF_6}$ (0.020 g, 0.057 mmol) in $\mathrm{CH_2Cl_2}$ (7 mL) was exposed to ca. 100 mL of gaseous acetylene. This resulting mixture was stirred at room temperature for 7 h, and the orange-brown precipitate was filtered off. The brown-orange product was extracted into 100 mL of $\mathrm{CH_2Cl_2}$ to separate it from the insoluble TlCl, and the extract was then reduced in volume to ca. 10 mL. A quantity of *n*-pentane (60 mL) was added to the solution, which was then chilled to 0 °C for 1 h to induce precipitation. The orange-brown complex was filtered off using a fine-porosity frit and washed with diethyl ether (10 mL); yield 0.041 g (74%). Anal. Calcd for $\mathrm{C_{62}H_{55}Cl_3F_6NOP_5Re_2}$: C, 47.19; H, 3.52. Found: C, 46.63; H, 3.60. IR spectrum: $\nu$(CN) 2138 (s), $\nu$(CO) 1880 (m-s) cm$^{-1}$.

The $^{13}$C-labeled compound $\mathrm{[Re_2Cl_3(^{13}CO)(\eta^2\text{-}HCCH)(CNxyl)(\mu\text{-}dppm)_2]PF_6}$ was prepared from $\mathrm{Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}CO)Cl_3(CNxyl)(\mu\text{-}dppm)_2}$ by use of a procedure analogous to that described above; yield 0.040 g (72%). IR spectrum: $\nu$(CN) 2139 (s), $\nu$(CO) 1837 (m-s) cm$^{-1}$. $^{13}$C{$^1$H} NMR ($\mathrm{CD_2Cl_2}$) $\delta$ 193.3 (t, CO).

**D. Synthesis of $\mathbf{[Re_2(\mu\text{-}Cl)(\mu\text{-}COC(R)CH)Cl_2(CNxyl)(\mu\text{-}dppm)_2]X}$ (5). (i) R = H, X = $\mathbf{PF_6}$ (5a). Method a.** A solution of **2** (0.050 g, 0.035 mmol) and $\mathrm{TlPF_6}$ (0.020 g, 0.057 mmol) in $\mathrm{CH_2Cl_2}$ (7 mL) was treated with a slow stream of gaseous acetylene for 1 min. The resulting mixture was then stirred at room

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temperature for 2 days, and the white precipitate (TlCl) was filtered off. The green filtrate was evaporated to dryness. The residue was dissolved in 2 mL of $CH_2Cl_2$, and diethyl ether (25 mL) was added to induce the precipitation of the title complex. After a period of ca. 15 min the precipitate was filtered off, washed with diethyl ether (10 mL), and dried under vacuum; yield 0.042 g (76%). Anal. Calcd for $C_{63}H_{57}Cl_5F_6NOP_5Re_2$ (i.e. $[Re_2Cl_3(COCHCH)(CNxyl)(\mu\text{-dppm})_2]PF_6{\cdot}CH_2Cl_2$): C, 45.51; H, 3.46. Found: C, 45.24; H, 3.57. The presence of a small amount of lattice $CH_2Cl_2$ was confirmed by $^1H$ NMR spectroscopy. IR spectrum: $\nu$(CN) 2162 (s) $cm^{-1}$.

The $^{13}C$-labeled derivative $[Re_2(\mu\text{-Cl})(\mu\text{-}^{13}COCHCH)Cl_2(CNxyl)(\mu\text{-dppm})_2]PF_6$ was prepared from $Re_2(\mu\text{-Cl})(\mu\text{-}^{13}CO)Cl_3(CNxyl)(\mu\text{-dppm})_2$ by a procedure analogous to that described above; yield 0.040 g (72%). IR spectrum: $\nu$(CN) 2160 (s) $cm^{-1}$.

**Method b.** A quantity of $[Re_2Cl_3(CO)(\eta^2\text{-HCCH})(CNxyl)(\mu\text{-dppm})_2]PF_6$ (**4**) (0.030 g, 0.019 mmol) was placed in $CH_2Cl_2$ (10 mL), and the mixture was stirred at room temperature for 2 days. The resulting green solution was evaporated to dryness. The residue was dissolved in $CH_2Cl_2$ (2 mL), and diethyl ether (25 mL) was added to induce the precipitation of the title complex. The green solid was filtered off, washed with diethyl ether (10 mL), and dried under vacuum; yield 0.025 g (83%).

**(ii) R = *n*-Pr, X = $PF_6$ (5b).** A mixture of **2** (0.100 g, 0.069 mmol), $TlPF_6$ (0.040 g, 0.114 mmol), and 0.08 mL of 1-pentyne was reacted in 10 mL of $CH_2Cl_2$ for 10 h at room temperature, and the white precipitate (TlCl) was filtered off. The brown-green filtrate was reduced to ca. 3 mL, and excess diethyl ether (60 mL) was added to induce precipitation of the title complex. After a period of 1 h, the precipitate was filtered off, washed with diethyl ether (10 mL), and dried under vacuum; yield 0.098 g (88%). Anal. Calcd for $C_{65}H_{61}Cl_3F_6NOP_5Re_2$: C, 48.19; H, 3.80. Found: C, 47.61; H, 3.72. IR spectrum: $\nu$(CN) 2159 (s) $cm^{-1}$.

**(iii) R = *n*-Bu, X = $PF_6$ (5c).** The use of 1-hexyne (0.08 mL) and a procedure similar to that described in part D(ii) gave the title complex; yield 0.100 g (89%). Anal. Calcd for $C_{66}H_{63}Cl_3F_6NOP_5Re_2$: C, 48.51; H, 3.89. Found: C, 48.16; H, 3.87. IR spectrum: $\nu$(CN) 2162 $cm^{-1}$.

**(iv) R = Ph, X = $PF_6$ (5d).** The use of phenylacetylene (0.07 mL) and a procedure similar to that described in part D(ii) gave the title complex; yield 0.083 g (73%). IR spectrum: $\nu$(CN) 2147 (s) $cm^{-1}$.

**(v) R = Ph, X = $BF_4$ (5e).** The $[BF_4]^-$ salt was prepared by the use of a procedure similar to that described in part D(ii) 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 the mixture stirred at room temperature for 20 min. The resulting solution was reduced to ca. 2 mL, and diethyl ether (50 mL) was added to induce precipitation of the complex. The brown-green powder was filtered off and washed with diethyl ether (3 × 10 mL); yield 0.032 g (59%). IR spectrum: $\nu$(CN) 2151 (s), $\nu$(B–F) 1058 (s, br) $cm^{-1}$.

**(vi) R = Ph, X = $BPh_4$ (5f).** A mixture of **5d** (0.040 g, 0.024 mmol) and $NaBPh_4$ (0.063 g, 0.180 mmol) in acetone (15 mL) was stirred at room temperature for 20 h. The solution was reduced in volume to ca. 3 mL and an excess of diethyl ether (ca. 50 mL) added to induce precipitation. After a period of 1 h, the brown-green solid was filtered off, washed with diethyl ether (10 mL), and dried under vacuum; yield 0.041 g (93%). This product was recrystallized from $CH_2Cl_2$–pentane. Anal. Calcd for $C_{92}H_{79}BCl_3NOP_4Re_2$: C, 60.44; H, 4.36. Found: C, 60.50; H, 4.38. IR spectrum: $\nu$(CN) 2152 (s) $cm^{-1}$.

**(vii) R = *p*-tol, X = $PF_6$ (5g).** The use of *p*-tolylacetylene (0.07 mL) and a procedure similar to that described in part D(ii) gave the title complex; yield 0.101 g (87%). Anal. Calcd for $C_{69}H_{61}Cl_3F_6NOP_5Re_2$: C, 49.68; H, 3.69. Found: C, 49.16; H, 3.80. IR spectrum: $\nu$(CN) 2162 (s) $cm^{-1}$.

**(viii) R = *p*-tol, X = $BF_4$ (5h).** This salt was prepared by the use of a procedure very similar to that described for **5e** in part D(v). IR spectrum: $\nu$(CN) 2159 (m-s), $\nu$(B-F) 1056 (s, br) $cm^{-1}$.

**E. Synthesis of $Re_2(\mu\text{-Cl})(\mu\text{-COC(R)CH})Cl_2(CNxyl)(\mu\text{-dppm})_2$. (i) R = Ph.** A mixture of $[Re_2(\mu\text{-Cl})(\mu\text{-COC(Ph)CH})Cl_2(CNxyl)(\mu\text{-dppm})_2]PF_6$ (**5d**; 0.030 g, 0.018 mmol) and $(\eta^5\text{-}C_5H_5)_2Co$ (0.004 g, 0.021 mmol) in acetone (3 mL) was stirred at room temperature for 2 h. The yellow-brown precipitate was filtered off and washed with diethyl ether (5 × 5 mL); yield 0.022 g (81%). IR spectrum: $\nu$(CN) 2101 (s) $cm^{-1}$.

**Table 1. Crystallographic Data for $[Re_2(\mu\text{-Cl})(\mu\text{-COCHCH})Cl_2(CO)(\mu\text{-dppm})_2]PF_6$ (3a) and $[Re_2(\mu\text{-Cl})(\mu\text{-COC}(p\text{-tol})CH)Cl_2(CNxyl)(\mu\text{-dppm})_2]BF_4{\cdot}{}^1/_2H_2O$ (5h)**

| | **3a** | **5h** |
|---|---|---|
| chem formula | $Re_2Cl_3P_5F_6O_2C_{54}H_{46}$ | $Re_2Cl_3P_4F_4O_{1.5}NBC_{69}H_{62}$ |
| fw | 1474.58 | 1618.73 |
| space group | *Cc* (No. 9) | *C*2/*c* (No. 15) |
| *a*, Å | 19.396(2) | 37.402(8) |
| *b*, Å | 15.495(2) | 15.302(4) |
| *c*, Å | 20.001(7) | 28.578(8) |
| $\beta$, deg | 99.66(2) | 119.06(3) |
| *V*, $Å^3$ | 5926(4) | 14 296(15) |
| *Z* | 4 | 8 |
| *T*, °C | 20 | 20 |
| $\lambda$(Mo K$\alpha$), Å | 0.710 73 | 0.710 73 |
| $\rho_{calcd}$, g $cm^{-3}$ | 1.654 | 1.504 |
| $\mu$(Mo K$\alpha$), $cm^{-1}$ | 44.62 | 36.93 |
| transmissn coeff | 1.000–0.759 | 1.000–0.718 |
| $R^a$ | 0.025 | 0.066 |
| $R_w{}^b$ | 0.031 | 0.085 |
| GOF | 1.019 | 1.715 |

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

**(ii) R = *p*-tol.** The use of **5g** (0.030 g, 0.018 mmol) and a procedure analogous to that described in part E(i) gave the title complex; yield 0.020 g (78%). IR spectrum: $\nu$(CN) 2094 (s) $cm^{-1}$.

**Preparation of Single Crystals.** Crystals of $[Re_2(\mu\text{-Cl})(\mu\text{-COCHCH})Cl_2(CO)(\mu\text{-dppm})_2]PF_6$ (**3a**) were grown by layering a dichloromethane solution of this complex with isopropyl ether, while crystals of $[Re_2(\mu\text{-Cl})(\mu\text{-COC}(p\text{-tol})CH)Cl_2(CNxyl)(\mu\text{-dppm})_2]BF_4$ (**5h**) were obtained from a solution of this complex in chloroform that was layered with *n*-pentane.

**X-ray Crystallography.** The structures of **3a** and **5h** were determined at 20 °C by the application of standard procedures. The basic crystallographic parameters for these complexes are listed in Table 1. The cell constants are based on 25 reflections with $18 < \theta < 20°$ for **3a** and $11 < \theta < 15°$ for **5h**. Three standard reflections were measured after 5000 s of beam time during data collection; there were no systematic variations in intensity. Lorentz and polarization corrections were applied to both sets of data. An empirical absorption correction[10] was applied, but no correction for extinction was made. Calculations were performed on a MicroVAX II computer using the Enraf-Nonius structure determination package.

The structure of **3a** was solved by the Enraf-Nonius structure solution procedure MolEN. The hydrogen atoms of the dppm ligands were introduced at calculated positions (C–H = 0.95 Å, $B = 1.3B_C$) and were not refined but constrained to ride on their C atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; corrections for anomalous scattering were applied to all anisotropically refined atoms.[11] Early in the refinement procedure it became apparent that a disorder existed of a kind which is very similar to one that we had encountered previously[2] in the case of the structure determination of a salt of the $[Re_2(\mu\text{-Br})(\mu\text{-HN}_2C_2Me_2)Br_2(NCMe)(\mu\text{-dppm})_2]^+$ cation. The structure of **3a** was refined accordingly, with the full disorder model as shown in Figure S1. The disordered atoms O(1), O(2), C(1A), and C(2A) were refined with multiplicities of 0.5. An ORTEP representation of half the disorder is shown in Figure 1. The structure refinement was otherwise routine, although

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(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. Reference 11a, Table 2.2B.

the rather large anisotropic displacement parameters associated with F atoms of the $[PF_6]^-$ anion signified the presence of high thermal motion or an unresolved disorder problem. The final residuals for **3a** were $R = 0.025$ ($R_w = 0.031$) and GOF = 1.019; for the other enantiomorph, $R = 0.034$ ($R_w = 0.044$) and GOF = 1.431. The highest peak in the final difference Fourier was 0.53 e/Å$^3$.

The structure of a crystal of **5h** was determined as described for **3a**. The refinement of the dirhenium cation proceeded satisfactorily. Corrections for anomalous scattering were applied to all anisotropically refined atoms.[11] Hydrogen atoms were not included in the refinement. Unfortunately, a satisfactory refinement of the $[BF_4]^-$ anion eluded us; this is most likely a consequence of it being badly disordered. While we located four regions of electron density in the difference map that we tentatively attributed to the B atom and three of the F atoms, we were unable to locate the fourth F atom in the coordination sphere. The large thermal parameters associated with these atoms as well as marked disparities in the resulting "B–F" bond distances and angles revealed obvious inadequacies in our model. Alternatives, including that of a planar $BO_3$ unit, which could have arisen from hydrolysis of $[BF_4]^-$ to $[H_2BO_3]^-$,[12] were also considered, but none gave a clearly better solution. Since variations in these models did not affect in any significant way the structure of the dirhenium unit, we terminated the structure refinement at this stage.[13] The highest peak in the final difference Fourier (2.15 e/Å$^3$) was close to the anion. A peak that was located about an inversion center was modeled as a disordered water oxygen at half-occupancy.

Important intramolecular bond distances and angles for the cation of **5h** are given in Table 2. Full details of the crystal data, data collection parameters, and all structural parameters for **3a** and **5h** 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 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 $E_{1/2} = +0.47$ vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were performed with a BAS Inc. Model CV-27 instrument in conjunction with a BAS Model RXY recorder. The $^{31}P\{^1H\}$ NMR 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. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were obtained on a GE QE-300 spectrometer operated at 300 and 75.61 MHz, respectively. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent.

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory. Microanalyses of representative examples of complexes of types **3** and **5** were obtained. The instability of the reduced compounds $Re_2(\mu\text{-}Cl)(\mu\text{-}COC(R)CH)Cl_2(CNxyl)(\mu\text{-}dppm)_2$ (R = Ph or *p*-tol) prevented us from obtaining acceptable and reproducible C and H microanalyses.

**Table 2. Important Bond Distances (Å) and Bond Angles (deg) for the Dirhenium Cation of 5h**[a]

| | | | |
|---|---|---|---|
| Distances | | | |
| Re(1)–Re(2) | 2.558(1) | C(1)–C(2) | 1.27(3) |
| Re(1)–Cl(B) | 2.466(6) | C(2)–C(21) | 1.45(4) |
| Re(1)–Cl(11) | 2.429(6) | C(11)–C(12) | 1.42(5) |
| Re(1)–P(11) | 2.471(7) | C(11)–C(16) | 1.41(5) |
| Re(1)–P(12) | 2.449(7) | C(12)–C(13) | 1.48(6) |
| Re(1)–C(4) | 1.99(2) | C(12)–C(121) | 1.47(6) |
| Re(1)–C(10) | 2.01(3) | C(13)–C(14) | 1.51(8) |
| Re(2)–Cl(2) | 2.406(7) | C(14)–C(15) | 1.52(7) |
| Re(2)–Cl(B) | 2.480(6) | C(15)–C(16) | 1.44(6) |
| Re(2)–P(21) | 2.466(7) | C(16)–C(161) | 1.48(5) |
| Re(2)–P(22) | 2.469(7) | C(21)–C(22) | 1.39(4) |
| Re(2)–C(1) | 2.10(3) | C(21)–C(26) | 1.38(4) |
| Re(2)–C(4) | 1.88(2) | C(22)–C(23) | 1.40(5) |
| O(3)–C(2) | 1.48(3) | C(23)–C(24) | 1.39(6) |
| O(3)–C(4) | 1.27(3) | C(24)–C(25) | 1.43(5) |
| N(10)–C(10) | 1.13(3) | C(24)–C(27) | 1.62(5) |
| N(10)–C(11) | 1.39(4) | C(25)–C(26) | 1.45(4) |
| Angles | | | |
| Re(2)–Re(1)–Cl(B) | 59.1(1) | Re(1)–Re(2)–Cl(2) | 152.7(2) |
| Re(2)–Re(1)–Cl(11) | 148.9(2) | Re(1)–Re(2)–Cl(B) | 58.6(1) |
| Re(2)–Re(1)–P(11) | 94.4(2) | Re(1)–Re(2)–P(21) | 96.0(2) |
| Re(2)–Re(1)–P(12) | 94.4(2) | Re(1)–Re(2)–P(22) | 95.3(2) |
| Re(2)–Re(1)–C(4) | 46.7(7) | Re(1)–Re(2)–C(1) | 122.6(7) |
| Re(2)–Re(1)–C(10) | 124.8(7) | Re(1)–Re(2)–C(4) | 50.6(7) |
| Cl(B)–Re(1)–Cl(11) | 89.8(2) | Cl(2)–Re(2)–Cl(B) | 94.3(2) |
| Cl(B)–Re(1)–P(11) | 95.5(2) | Cl(2)–Re(2)–P(21) | 85.6(2) |
| Cl(B)–Re(1)–P(12) | 89.1(2) | Cl(2)–Re(2)–P(22) | 86.3(2) |
| Cl(B)–Re(1)–C(4) | 105.8(7) | Cl(2)–Re(2)–C(1) | 84.7(7) |
| Cl(B)–Re(1)–C(10) | 175.3(7) | Cl(2)–Re(2)–C(4) | 156.5(7) |
| Cl(11)–Re(1)–P(11) | 87.0(2) | Cl(B)–Re(2)–P(21) | 89.7(2) |
| Cl(11)–Re(1)–P(12) | 85.5(2) | Cl(B)–Re(2)–P(22) | 99.7(2) |
| Cl(11)–Re(1)–C(4) | 164.3(7) | Cl(B)–Re(2)–C(1) | 175.0(7) |
| Cl(11)–Re(1)–C(10) | 86.3(7) | Cl(B)–Re(2)–C(4) | 109.1(7) |
| P(11)–Re(1)–P(12) | 171.2(2) | P(21)–Re(2)–P(22) | 168.0(2) |
| P(11)–Re(1)–C(4) | 89.8(7) | P(21)–Re(2)–C(1) | 85.4(7) |
| P(11)–Re(1)–C(10) | 86.9(7) | P(21)–Re(2)–C(4) | 96.4(8) |
| P(12)–Re(1)–C(4) | 96.1(7) | P(22)–Re(2)–C(1) | 85.1(7) |
| P(12)–Re(1)–C(10) | 88.0(7) | P(22)–Re(2)–C(4) | 87.6(8) |
| C(4)–Re(1)–C(10) | 78(1) | C(1)–Re(2)–C(4) | 72(1) |
| Re(1)–Cl(B)–Re(2) | 62.3(2) | C(1)–C(2)–C(21) | 132(3) |
| C(2)–O(3)–C(4) | 107(2) | Re(1)–C(4)–Re(2) | 82.8(9) |
| C(10)–N(10)–C(11) | 170(3) | Re(1)–C(4)–O(3) | 146(2) |
| Re(2)–C(1)–C(2) | 117(2) | Re(2)–C(4)–O(3) | 131(2) |
| O(3)–C(2)–C(1) | 114(2) | Re(1)–C(10)–N(10) | 178(2) |
| O(3)–C(2)–C(21) | 115(2) | | |

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

## Results

The multiply bonded dirhenium complexes $Re_2(\mu\text{-}Cl)(\mu\text{-}CO)Cl_3(CO)(\mu\text{-}dppm)_2$ (**1a**) and $Re_2(\mu\text{-}Cl)(\mu\text{-}CO)Cl_3(CNxyl)(\mu\text{-}dppm)_2$ (**2**) react at room temperature with terminal alkynes, in the presence of the halide labilizing reagent $TlPF_6$, to afford compounds of types **3** and **5**, in which the CO and RCCH ligands have reductively coupled and produced a novel 3-metallafuran ring (see Scheme 1).[14] The reactions of acetylene with the $^{13}C$-labeled derivatives of **1a** and **2**, $Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}CO)Cl_3(^{13}CO)(\mu\text{-}dppm)_2$ and $Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}CO)Cl_3(CNxyl)(\mu\text{-}dppm)_2$, have been used as routes to the labeled compounds $[Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}COCHCH)Cl_2(L)(\mu\text{-}dppm)_2]PF_6$, where L = $^{13}CO$, xylNC.

The reactions that lead to **3** are complete in ca. 5 h, except in the case of **3a**, for which a shorter reaction time (2 h) is required to ensure the purity of the product. Complexes of type **3** were isolated in yields of 60–75%. The synthesis of **5** in high yield (generally >80%) requires

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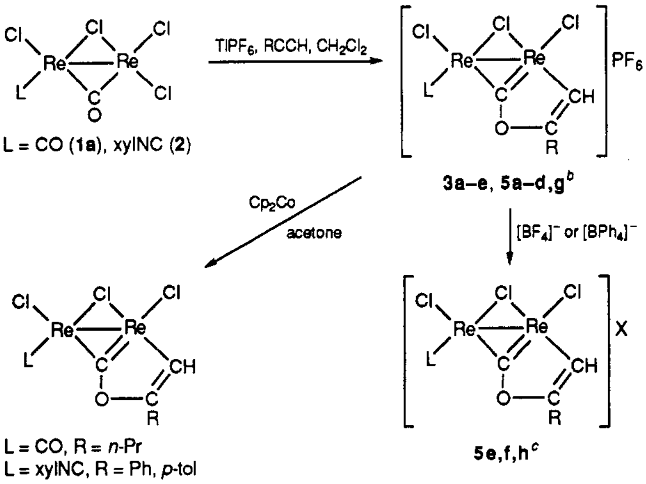
[12] We have no independent chemical evidence to support this possibility, since the crop of crystals from which one was selected for this particular structure determination had properties entirely in accord with those found for all other samples of the $[BF_4]^-$ salt.

[13] Although we also collected a complete data set on a crystal of complex **5b** (i.e. $[Re_2(\mu\text{-}Cl)(\mu\text{-}COC(n\text{-}Pr)CH)Cl_2(CNxyl)(\mu\text{-}dppm)_2]PF_6$), the $[PF_6]^-$ anion was even more badly disordered than the anion in **5h**. However, this structure determination showed conclusively that the chemical connectivity within the dirhenium cation was exactly the same as that present in **5h**. The Re–Re distance (~2.56 Å) is very simialr to that of **5h**.

[14] These compounds can also be described in 2-metalated 3-oxa-1-metallacyclopenta-1,4-diene complexes.

**Scheme 1. Summary of the Reactions of 1a and 2 with Alkynes to produce 3-Metallafuran Complexes**[a]



[a] The $\mu$-dppm ligands have been omitted for clarity. [b] L = CO, R = H (**3a**), *n*-Pr (**3b**), *n*-Bu (**3c**), Ph (**3d**), *p*-tol (**3e**); L = xylNC, R = H (**5a**), *n*-Pr (**5b**), *n*-Bu (**5c**), Ph (**5d**), *p*-tol (**5g**). [c] L = xylNC, R = Ph, X = $BF_4$ (**5e**), $BPh_4$ (**5f**); L = xylNC, R = *p*-tol, X = $BF_4$ (**5h**).

**Table 3. Electrochemical and $^{31}P\{^1H\}$ NMR Spectral Data for Complexes of the Type $[Re_2(\mu\text{-}Cl)(\mu\text{-}COC(R)CH)Cl_2(L)(\mu\text{-dppm})_2]X$**

| | | | | CV half-wave potential, V[a] | | | |
|---|---|---|---|---|---|---|---|
| complex | R | L | X | $E_{1/2}$-(ox) | $E_{1/2}$-(red)(1) | $E_{1/2}$-(red)(2) | $^{31}P\{^1H\}$ NMR, $\delta^{b,c}$ |
| **3a** | H | CO | $PF_6$ | +1.56 | +0.10 | −0.90 | −12.0, −15.4 |
| **3b** | *n*-Pr | CO | $PF_6$ | +1.40 | +0.05 | −0.94 | −12.9, −16.4 |
| **3c** | *n*-Bu | CO | $PF_6$ | +1.40 | +0.04 | −0.95 | −12.8, −16.4 |
| **3d** | Ph | CO | $PF_6$ | +1.32 | +0.11 | −0.89 | −13.1, −15.3 |
| **3e** | *p*-tol | CO | $PF_6$ | +1.26 | +0.10 | −0.89 | −13.2, −16.1 |
| **5a** | H | xylNC | $PF_6$ | +1.28 | −0.17 | −1.13 | −12.2, −13.6 |
| **5b** | *n*-Pr | xylNC | $PF_6$ | +1.13 | −0.22 | −1.19 | −12.9, −14.4 |
| **5c** | *n*-Bu | xylNC | $PF_6$ | +1.14 | −0.22 | −1.18 | −12.7, −14.4 |
| **5d** | Ph | xylNC | $PF_6$ | +1.12[d] | −0.13 | −1.07 | −12.8[e] |
| **5e** | Ph | xylNC | $BF_4$ | +1.11[d] | −0.14 | −1.10 | −12.8[e] |
| **5f** | Ph | xylNC | $BPh_4$[f] | +1.10[d] | −0.15 | −1.10 | −12.9[e] |
| **5g** | *p*-tol | xylNC | $PF_6$ | +1.06[d] | −0.14 | −1.17 | −13.3[g] |
| **5h** | *p*-tol | xylNC | $BF_4$ | +1.06[d] | −0.15 | −1.11 | −12.6[g,h] |

[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. In all cases $i_{p,a} \approx i_{p,c}$ and $E_{p,a} - E_{p,c}$ values are in the range 60–80 mV. [b] Spectra recorded in $CD_2Cl_2$ unless otherwise indicated. [c] Spectra have the appearance of AA′BB′ patterns; the chemical shifts quoted are those of the most intense components. [d] Irreversible oxidation also present at more positive potentials ($E_{p,a}$ value between +1.58 and +1.69 V vs Ag/AgCl with a sweep rate of 200 mV/s). [e] Spectrum has the appearance of a broad singlet. [f] The $[BPh_4]^-$ anion is characterized by an irreversible oxidation at $E_{p,a}$ = +0.91 V vs. Ag/AgCl when $v$ = 200 mV/s. [g] Spectrum has the appearance of a single symmetrical multiplet. [h] Spectrum recorded in $CDCl_3$.

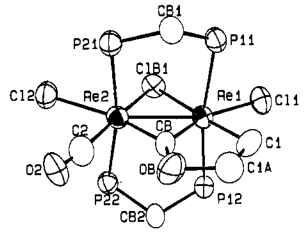


**Figure 1.** ORTEP representation of the structure of the $[Re_2(\mu\text{-}Cl)(\mu\text{-}COCHCH)Cl_2(CO)(\mu\text{-dppm})_2]^+$ cation as present in complex **3a** with the phenyl group atoms of the dppm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level. This representation shows half of the disorder involving the metallafuran ring.

longer reaction times (usually ca. 10 h). For the preparation of **5a** a reaction time of 2 days was used; much shorter reaction times (ca. 5 h) allowed for the isolation of the intermediate $\eta^2$-acetylene complex $[Re_2Cl_3(CO)(\eta^2\text{-}HCCH)(CNxyl)(\mu\text{-dppm})_2]PF_6$ (**4**). Anion exchange reactions can be used to obtain the analogous $[BF_4]^-$ and $[BPh_4]^-$ salts, as demonstrated by the preparation of **5e,f,h** (Scheme 1). Conductivity measurements on acetone solutions of **3a,b** and **5a,b** (ca. 1 × $10^{-3}$ M) show behavior typical of 1:1 electrolytes ($\Lambda_m$ = 104–120 $\Omega^{-1}$ $cm^2$ $mol^{-1}$).[15]

The reaction of the complex $Re_2(\mu\text{-}Br)(\mu\text{-}CO)Br_3(CO)(\mu\text{-dppm})_2$ (**1b**) with 1-pentyne to give $[Re_2(\mu\text{-}Br)(\mu\text{-}COC(n\text{-}Pr)CH)Br_2(CO)(\mu\text{-dppm})_2]PF_6$ demonstrates that a similar chemistry can, if desired, be developed for the analogous bromo species. The properties of this complex (see Experimental Section, part A(ii)) are in very close accord with those of the corresponding chloride **3b**.

The IR spectra of **3** and **5** (recorded as Nujol mulls) show $\nu$(CO) and $\nu$(CN) modes in the ranges 2032–2027 and 2162–2147 $cm^{-1}$, respectively, for the terminal carbonyl and xylyl isocyanide ligands. The corresponding $\nu$(CO) and $\nu$(CN) modes of the $^{13}C$-labeled complexes $[Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}COCHCH)Cl_2(^{13}CO)(\mu\text{-dppm})_2]PF_6$ and $[Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}COCHCH)Cl_2(CNxyl)(\mu\text{-dppm})_2]PF_6$ are at 1986 and 2160 $cm^{-1}$, respectively. The first of these is shifted by −46 $cm^{-1}$ relative to the $\nu$(CO) mode in the $^{12}CO$ derivative **3a**. These individual spectroscopic data are given in the Experimental Section. A strong band at 840 $cm^{-1}$, which was observed for all the $[PF_6]^-$ salts, is assigned to the $\nu$(PF) mode of the anion. For the $[BF_4]^-$ salts **5e,h**, the analogous $\nu$(BF) mode was at ca. 1057 $cm^{-1}$.

The cyclic voltammetric (CV) properties of **3** and **5**, which are presented in Table 3, are very similar to one another and reveal one reversible one-electron oxidation and two one-electron reductions. As might be expected, these three processes are all shifted to more negative potentials by between 180 and 280 mV for the xylyl isocyanide complexes **5**, compared to their carbonyl analogues **3**; this is a consequence of the greater $\pi$-acceptor properties of CO (compared to xylNC) which leads to an increase in the positive charge at the dirhenium core. The reversibility of the most accessible reduction ($E_{1/2}$(red)(1) in Table 3) has been demonstrated by the ease of reducing several of these complexes (specifically **3b** and **5d,g**) to their neutral congeners $Re_2(\mu\text{-}Cl)(\mu\text{-}COC(R)CH)Cl_2(L)(\mu\text{-dppm})_2$ through the use of cobaltocene as the reducing agent (Scheme 1). These three complexes were characterized by cyclic voltammetry and IR spectroscopy. Their cyclic voltammetric properties are identical with those of **3b** or **5d,g**, except that the process labeled as $E_{1/2}$(red)(1) in Table 3 now corresponds to a one-electron *oxidation* of the bulk complex. The IR spectra of the three compounds (see Experimental Section) showed that the $\nu$(CO) and $\nu$(CN) bands of the terminal CO and xylNC ligands are shifted to lower frequencies compared to those of their oxidized congeners, in accord with a reduction in the metal oxidation state and an increase in the extent of Re → CO($\pi^*$) and Re → CNxyl($\pi^*$) back-bonding in the reduced species. The shifts are −49, −46, and −68 $cm^{-1}$, respectively, for the reduction products of **3b**, and **5d,g**.

The structural identities of representative members of the two series of compounds of types **3** and **5** were established by single-crystal X-ray structure analyses.

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(15) Geary, W. J. *Coord. Chem. Rev.* 1971, 7, 81.

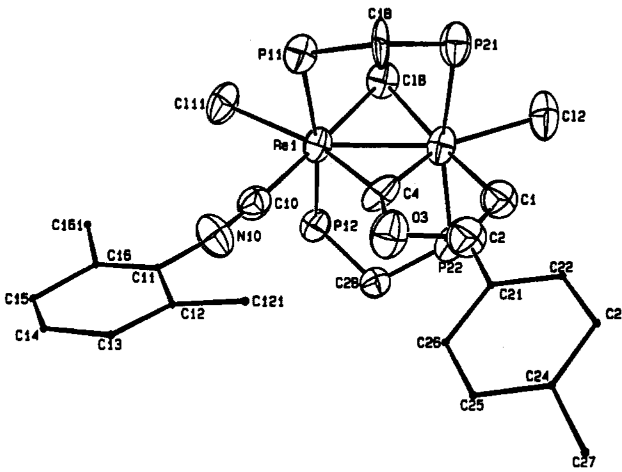

**Figure 2.** ORTEP representation of the $[Re_2(\mu\text{-}Cl)(\mu\text{-}COC(p\text{-}tol)CH)Cl_2(CNxyl)(\mu\text{-}dppm)_2]^+$ cation as present in complex **5h** with the phenyl group atoms of the dppm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level.

**Table 4.** **$^1$H NMR Spectral Data for Complexes of the Type $[Re_2(\mu\text{-}Cl)(\mu\text{-}COC(R)CH)Cl_2(L)(\mu\text{-}dppm)_2]X$**

| complex | R | L | X | $^1$H NMR, $\delta$[a] |
|---|---|---|---|---|
| **3a** | H | CO | $PF_6$ | 3.38 (m, 2H),[b] 4.27 (m, 2H),[b] 7.05–7.85 (m, 42H)[c] |
| **3b** | *n*-Pr | CO | $PF_6$ | 1.01 (t, 3H), 1.12 (m, 2H), 3.36 (m, 2H),[b] 4.02 (br, 2H), 4.23 (m, 2H),[b] 7.05–7.80 (m, 41H)[c] |
| **3c** | *n*-Bu | CO | $PF_6$ | 0.97 (t, 3H), 1.02 (m, 2H), 1.40 (m, 2H), 3.43 (m, 2H),[b] 4.10 (br, 2H), 4.38 (m, 2H),[b] 7.00–7.80 (m, 41H)[c] |
| **3d** | Ph | CO | $PF_6$ | 3.39 (m, 2H),[b] 4.24 (m, 2H),[b] 6.95–7.80 (m, 40H),[c] 8.35 (s, 1H) |
| **3e** | *p*-tol | CO | $PF_6$ | 2.82 (s, 3H), 3.30 (m, 2H),[b] 4.22 (m, 2H),[b] 6.22 (d, 2H), 6.87 (d, 2H), 6.90–6.80 (m, 40H),[c] 8.32 (s, 1H) |
| **5a** | H | xylNC | $PF_6$ | ~2.0 (br, 6H),[d] 3.54 (m, 2H),[b] 4.11 (m, 2H),[b] 6.80–7.85 (m, 45H)[c] |
| **5b** | *n*-Pr | xylNC | $PF_6$ | 1.04 (t, 3H), 1.26 (m, 2H), ~2.0 (vbr, 6H),[d] 3.41 (m, 2H),[b] 3.71 (m, 2H), 4.11 (m, 2H),[b] 6.80–7.85 (m, 43H)[c] |
| **5c** | *n*-Bu | xylNC | $PF_6$ | 1.01 (t, 3H), 1.18 (m, 2H), 1.42 (m, 2H), ~2.0 (vbr, 6H),[d] 3.42 (m, 2H),[b] 3.76 (m, 2H), 4.11 (m, 2H),[b] 6.80–7.85 (m, 43H)[c] |
| **5d** | Ph | xylNC | $PF_6$ | ~2.2 (br, 6H),[d] 3.45 (m, 2H),[b] 4.09 (m, 2H),[b] 6.80–7.85 (m, 48H),[c] 8.21 (s, 1H) |
| **5e** | Ph | xylNC | $BF_4$ | 2.13 (br, 6H),[d] 3.46 (m, 2H),[b] 4.11 (m, 2H),[b] 6.80–7.90 (m, 48H),[c] 8.21 (s, 1H) |
| **5f** | Ph | xylNC | $BPh_4$ | 2.13 (br, 6H),[d] 3.42 (m, 2H),[b] 4.08 (m, 2H),[b] 6.80–7.90 (m, 48H),[c] 8.25 (s, 1H) |
| **5g** | *p*-tol | xylNC | $PF_6$ | ~2.15 (br, 6H),[d] 2.71 (s, 3H),[e] 3.43 (m, 2H),[b] 4.09 (m, 2H),[b] 6.80–7.90 (m, 47H),[c] 8.16 (s, 1H) |
| **5h** | *p*-tol | xylNC | $BF_4$ | ~2.10 (br, 6H),[d] 2.68 (s, 3H),[e] 3.49 (m, 2H),[b] 4.17 (m, 2H),[b] 6.80–7.90 (m, 47H),[c] 8.14 (s, 1H) |

[a] Spectra recorded in $CD_2Cl_2$ except for **5a** and **5h** ($CDCl_3$). The appearance of the spectra and the relative intensities are indicated in parentheses: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. [b] Resonances of the $-CH_2-$ units of the dppm ligands. [c] Resonances of the phenyl ring protons. [d] Resonance for the methyl groups of the xylyl isocyanide ligand. [e] Resonance for the methyl group of the *p*-tolyl ring.

ORTEP representions of the structures of the dirhenium cations present in **3a** and **5h** are shown in Figures 1 and 2, while crystallographic data and important structural parameters are given in Tables 1 and 2. Full details are available as supplementary material.

The $^{31}P\{^1H\}$ NMR spectra of the complexes of types **3** and **5** generally reveal well-resolved AA′BB′ coupling patterns in accord with the presence of pairs of inequivalent P atoms. In the case of **5g,h** the spectra have the appearance of a single symmetric multiplet because of the existence of a very small chemical shift difference between the pairs of P atoms. For the three compounds **5d–f** only a singlet was observed (at $\delta$ ca. −12.8), with no resolvable splitting. Apparently, in these cases an even smaller chemical shift difference exists. We have encountered this same phenomenon with some other unsymmetrical compounds that contain the *trans*-$Re_2(\mu\text{-}dppm)_2$ unit.[16] In this situation, the inner lines emerge and grow in intensity at the expense of the outer lines, which eventually become too weak to be observed, and the pattern collapses to a deceptively simple first-order singlet.

The $^1$H NMR spectral data for **3** and **5** are given in Table 4. The Re–$C_\alpha$ protons of the coupled $\mu$-COC(R)-$C_\alpha$H ligands are present as singlets between $\delta$ 8.1 and 8.4 in the spectra of **3d,e** and **5d–h**. For those complexes where R = H or alkyl, this resonance is shifted upfield and becomes obscured by the phenyl group resonances. For the xylyl isocyanide containing compounds (**5a–h**) the methyl groups of the xylyl group are characterized by a broad hump close to $\delta$ ~2 which is in accord with a slowly rotating xylNC ligand. In the case of **5a**, a variable temperature $^1$H NMR spectral study (+30 to −80 °C) showed that this resonance collapses upon lowering the temperature (coalescence temperature ca. −22 °C) and splits into two sharp singlets at $\delta$ 2.91 and 0.83 with an integration of 1:1 at −80 °C.

The $^{13}$C-containing derivative $[Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}COCHCH)Cl_2(^{13}CO)(\mu\text{-}dppm)_2]PF_6$ has singlets at $\delta$ 188.6 and 331.5 in its $^{13}C\{^1H\}$ NMR spectrum, showing the presence of a terminally bonded CO ligand and implying the presence of a bridging alkylidyne carbon[17] that has been generated from the bridging carbonyl ligand of **1a**. The $^{13}C\{^1H\}$ NMR spectrum of the analogous xylyl isocyanide complex $[Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}COCHCH)Cl_2(CNxyl)(\mu\text{-}dppm)_2]PF_6$ shows a similar alkylidyne carbon resonance at $\delta$ 338.7.

The reaction of **2** with acetylene to afford **5a** is sufficiently sluggish that it has allowed for the isolation of an intermediate of composition $[Re_2Cl_3(CO)(\eta^2\text{-}HCCH)(CNxyl)(\mu\text{-}dppm)_2]PF_6$ (**4**) when a reaction time of ca. 5 h is used. The $^{13}$C-labeled derivative $[Re_2Cl_3(^{13}CO)(\eta^2\text{-}HCCH)(CNxyl)(\mu\text{-}dppm)_2]PF_6$ can be prepared from $Re_2(\mu\text{-}Cl)(\mu\text{-}^{13}CO)Cl_3(CNxyl)(\mu\text{-}dppm)_2$. Compound **4** converts in almost quantitative yield to the reductively coupled product **5a** when it is stirred in dichloromethane for ca. 2 days.

The IR spectral properties of **4** (Nujol mull) display a $\nu$(CN) mode at 2138 cm$^{-1}$, a terminal $\nu$(CO) mode at 1880 cm$^{-1}$, and a $\nu$(PF) mode for the $[PF_6]^-$ anion at 836 cm$^{-1}$. For the $^{13}$C-labeled derivative, the IR spectrum shows little change in the $\nu$(CN) mode at 2139 cm$^{-1}$, but the $\nu$(CO) mode shifts to 1837 cm$^{-1}$. Cyclic voltammetric measurements on a 0.1 M TBAH–$CH_2Cl_2$ solution of **4** (sweep rate

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[16] Barder, T. J.; Cotton, F. A.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 1258 and references cited therein.

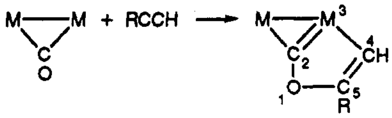
[17] Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5284. Chisholm, M. H.; Huffman, J. C.; Heppert, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5116.

200 mV $s^{-1}$) show that there is a reversible oxidation at $E_{1/2} = +1.03$ V and a reversible reduction at $-0.25$ V vs Ag/AgCl; for these processes $i_{p,a} \approx i_{p,c}$ and $\Delta E_p = 60$ mV. There is also an irreversible reduction at $E_{p,c}$ = ca. $-0.96$ V, followed by a reversible reduction at $E_{1/2} = -1.53$ V ($\Delta E_p = 70$ mV) and, on the positive reverse sweep, an irreversible oxidation at $E_{p,a} = -0.04$ V which is presumably due to a chemical product that is formed following the irreversible reduction at $-0.96$ V. A conductivity measurement (on a $1 \times 10^{-3}$ M acetone solution) confirmed this product to be a 1:1 electrolyte ($\Lambda_m = 125\ \Omega^{-1}\ cm^2\ mol^{-1}$).[15]

The $^1H$ NMR spectra of 4, recorded in $CD_2Cl_2$ and $CD_3CN$, display a complex phenyl region arising from the xylNC and dppm ligands between $\delta$ 6.6 and 8.0 and two multiplets from the bridgehead $-CH_2-$ protons of the dppm ligands centered at $\delta$ 4.0 and 5.1 in $CD_2Cl_2$ ($\delta$ 4.1 and 5.5 in $CD_3CN$). The characteristic acetylene resonance appears as a triplet at $\delta$ 13.4 in $CD_2Cl_2$ and $\delta$ 13.7 in $CD_3CN$ ($^3J_{P-H} = 12.1$ Hz). The relatively poor solubility of 4 in $CD_2Cl_2$ and $CD_3CN$ thwarted our attempts to obtain satisfactory variable-temperature $^1H$ NMR spectra for this complex. The $^{13}C\{^1H\}$ NMR spectrum of the $^{13}C$-containing derivative (recorded in $CD_2Cl_2$) shows a multiplet at $\delta$ 193.3 with $^2J_{P-C} \approx 5.5$ Hz for the $^{13}CO$ ligand. The $^{31}P\{^1H\}$ NMR spectrum of 4 ($CD_2Cl_2$) shows an AA′XX′ coupling pattern with the two multiplets centered at $\delta$ $-13.0$ and $-29.5$.

## Discussion

The occurrence of alkyne–alkyne coupling reactions at the triply bonded dimetal units present in complexes of the type $M_2(OR)_6$ (M = Mo, W) and closely related species,[18] as well as $(\eta^5\text{-}C_5R_5)_2M_2(CO)_4$ (M = Cr, Mo),[19] is now extensively documented.[20,21] Although the coupling of CO with alkynes, with resulting C–C bond formation, has quite often been encountered at unsaturated dimetal centers, the products are in most cases formally the result of the insertion of a single CO ligand into a dimetal–alkyne "cluster" to generate a $-C(O)CR{=}CR-$ unit.[22] In addition, double CO insertion can also occur, as in the case of the conversions of the singly bonded dimetal carbonyl species $Co_2(CO)_8$ and $Mn_2(\mu\text{-dppm})(CO)_8$ to the furanylidene complexes $Co_2(\mu\text{-CO})[\mu\text{-}\overline{CCR{=}CR'C(O)O}](CO)_6$[23] and $Mn_2(\mu\text{-CO})[\mu\text{-}\overline{CCH{=}CRC(O)O}](\mu\text{-dppm})(CO)_6$[7c] in the presence of alkynes. In such cases both C—C *and* C—O bond formation occurs. As far as we are aware, there are no previous instances of the type of CO–alkyne coupling we have observed in the present study in which *carbon–oxygen* bond formation occurs to give a simple 3-metallafuran type of ring:



However, there is a similarity between the CO–alkyne coupling we have observed and the RCN–alkyne coupling that occurs in the reaction between the triply bonded complex $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-HCCH})(py)$ and PhC≡N to form $W_2(O\text{-}t\text{-}Bu)_6[\mu\text{-NC(Ph)CHCH}]$.[24]

These reactions are formally the result of the 1,3-dipolar addition of RC≡CH to M—C—O. The regioselectivity of these reactions to give the substituent R in the 5-position is probably controlled by the steric constraints that are imposed by the phenyl rings of the dppm ligands within the cleftlike pocket where the coupling reaction occurs. This conclusion is supported by our observation that the use of internal alkynes (2-butyne, 2-pentyne, and 3-hexyne) does not lead to the same reaction course. The main difference between the reactions of RCCH with $Re_2(\mu\text{-Cl})(\mu\text{-CO})Cl_3(CO)(\mu\text{-dppm})_2$ (**1a**) and with $Re_2(\mu\text{-Cl})(\mu\text{-CO})Cl_3(CNxyl)(\mu\text{-dppm})_2$ (**2**) was the longer reaction times necessary for the latter complex to produce the coupled product (**5**) in good yield. In the case of the reaction between **2** and HCCH, this permitted the isolation of the intermediate $\eta^2$-alkyne complex $[Re_2Cl_3(CO)(\eta^2\text{-HCCH})(CNxyl)(\mu\text{-dppm})_2]PF_6$ (**4**). Interestingly, the monocarbonyl–alkyne complexes of the type $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-RCCR}')]PF_6$, which are formed[6] upon reacting the monocarbonyl complex $Re_2(\mu\text{-Cl})Cl_3(CO)(\mu\text{-dppm})_2$ with RCCR′, do not react with CO or xylNC to give products in which the CO and RCCR′ ligands are reductively coupled. The stereochemically rigid complexes $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-RCCR}')]PF_6$ have structures where the CO and RCCR′ ligands are bound to different Re atoms and are in an anti arrangement to one another.

Although the X-ray crystal structure determination on $[Re_2(\mu\text{-Cl})(\mu\text{-COCHCH})Cl_2(CO)(\mu\text{-dppm})_2]PF_6$ (**3a**) established the presence of the edge-sharing bioctahedral geometry for the cation and the nature of the metallacyclic ring (Figure 1), the disorder problem that was encountered (see Experimental Section) precluded a meaningful consideration of most of the structural parameters associated with the key Re($\mu$-COCHCH)Re unit. Indeed, because of the disorder this structure solution could not distinguish between the four-atom bridging unit being Re($\mu$-Cl)($\mu$-C)Re or Re($\mu$-Cl)($\mu$-O)Re. However, IR spectroscopy demonstrated that while a terminal CO ligand was still present, the bridging CO ligand must have become incorporated into the metallacyclic ring. $^{13}C\{^1H\}$ NMR spectroscopy of the product that was formed from the reaction of the $^{13}CO$-labeled precursor **1a** with HCCH showed the presence of a bridging alkylidyne carbon ($\delta$ 331.5) and therefore confirmed that the connectivity of

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[18] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 4389. Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806. Chisholm, M. H.; Conroy, B. K.; Huffman, J. C. *Organometallics* **1986**, *5*, 2384. Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C. *Organometallics* **1989**, *8*, 49. Chisholm, M. H.; Eichhorn, B. W.; Huffman, J. C. *Organometallics* **1989**, *8*, 67.

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[20] Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, U.K., 1993; see Chapters 5 and 9.

[21] Winter, M. J. *Adv. Organomet. Chem.* **1989**, *29*, 128–132.

[22] For example, see: Herrmann, W.; Bauer, C.; Schäfer, A. *J. Organomet. Chem.* **1983**, *256*, 147. Dickson, R. S.; Evans, G. S.; Fallon, G. D. *Aust. J. Chem.* **1985**, *38*, 273.

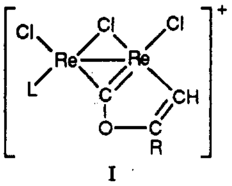
[23] Sternberg, H. W.; Shukys, J. G.; Donne, C. D.; Markby, R.; Friedel, R. A.; Wender, I. *J. Am. Chem. Soc.* **1959**, *81*, 2339. Mills, O. S.; Robinson, G. *Proc. Chem. Soc., London* **1959**, 156. Palyi, G.; Varadi, G.; Vizi-Orosz, A.; Marko, L. *J. Organomet. Chem.* **1975**, *90*, 85. Varad, G.; Vecsei, I.; Otvos, I.; Palyi, G.; Marko, L. *J. Organomet. Chem.* **1979**, *182*, 415.

[24] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6815.

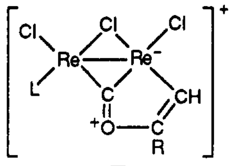
the metallacyclic ring unit is as represented in Figure 1 and Scheme 1.

To eliminate the type of crystallographic disorder that was encountered in **3a**, we determined the crystal structure of the xylyl isocyanide complex $[Re_2(\mu\text{-}Cl)(\mu\text{-}COC(p\text{-tol})CH)Cl_2(CNxyl)(\mu\text{-dppm})_2]BF_4$ (**5h**). Since the spectroscopic and electrochemical properties of complexes of types 3 and 5 are so similar, we had expected a close similarity in structures between these two series of compounds. This was confirmed by the structure determination of **5h**. There is an *all-cis* arrangement of three chloro ligands occupying mutually *cis* positions on one side of the molecule in both structures. The bridgehead methylene carbon atoms of the dppm ligands are folded over on the same side of the molecule that contains the terminal CO or xylNC ligand and the five-membered metallacyclic ring formed from coupling of the bridging CO and the alkyne ligands.

The Re–Re distances in the structures of **3a** and **5h** are essentially identical (2.565(1) and 2.558(1) Å). These distances are somewhat shorter than that present in the nitrile-coupled product $[Re_2(\mu\text{-}Br)(\mu\text{-}HN_2C_2Me_2)Br_2(\mu\text{-dppm})_2(NCMe)]PF_6$ (2.666(1) Å) but are very similar to that present in the bridging alkylidyne complex $Re_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$ of 2.557(1) Å.[25] The shortness of the Re–Re bond in **3a** and **5h** is probably due in part to the strong interaction between the bridging alkylidyne carbon and two rhenium atoms. The Re–P distances in these two structures are very similar (range 2.449(7)–2.488(4) Å), as are the structural parameters associated with the $[ClRe(\mu\text{-}Cl)ReCl]$ unit. Within the coupled $Re(\mu\text{-}COCC)Re$ unit of **5h**, the alkylidyne type bridging carbon atom C(4) appears to be bound asymmetrically to the two rhenium atoms (the distances are 1.99(2) and 1.88(2) Å), with the shorter of the two distances involving the rhenium atom (Re(2)) that is incorporated into the 3-metallafuran ring. The distances Re(2)–C(1), C(1)–C(2), and C(2)–O(3) of 2.10(3), 1.27(3), and 1.48(3) Å, respectively, are in good accord with the 3-metallafuran ring having the resonance form **I** as a major contributing structure. Although the distance C(4)–O(3) (1.27(3) Å) is appreciably longer than the C–O distances of the $\mu$-CO ligands in related dirhenium complexes,[4,5,26] it is, nonetheless, indicative of the retention of appreciable multiple-bond character, and this implies that the structural form **II** also makes a significant contribution. The disparity in the C–O distances within the metallafuran ring suggests that this metallacycle may be susceptible to ring-opening reactions, a possibility that is now under investigation. One reaction we have examined is that between the acetylene complex **3a** and PhCCH in refluxing 1,2-dichloroethane. We found no evidence for alkyne exchange.

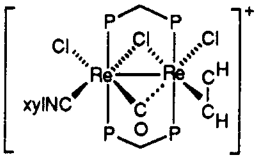


I



II

The isolation of the $\eta^2$-alkyne complex $[Re_2Cl_3(CO)(\eta^2\text{-HCCH})(CNxyl)(\mu\text{-dppm})_2]PF_6$ from the reaction of **2** with acetylene and its subsequent conversion to the coupled product **5a** suggest that it is an intermediate in the conversion of **2** to **5a**. It is the logical species that would be formed upon labilization of the terminal Re–Cl bond which is cis to the bridging carbonyl ligand. We presume that related intermediates are formed in the other reactions. Our ability to isolate **4** pure in such high yield is probably a consequence of the relatively sluggish nature of this particular reaction and the insolubility of the product in the reaction mixture. The low frequency of the $\nu$(CO) mode in the IR spectrum of this complex (1880 cm$^{-1}$) is in accord with the presence of a bridging carbonyl ligand (perhaps semibridging), while the downfield shift of the acetylene resonance in the $^1H$ NMR spectrum ($\delta$ 13.4 in $CD_2Cl_2$) is consistent with the $\eta^2$-HCCH ligand behaving as a four-electron donor in such a metal–metal-bonded dirhenium complex.[6,27] Although we have been unable to isolate suitable crystals of **4** for a single-crystal X-ray structure determination, we suggest that it has the structure shown by **III** on the basis of its spectroscopic properties. Within this structure it is not unreasonable, on electron-counting grounds, to propose the presence of a Re–Re single bond; in the absence of such a bond each Re atom would have a 17-electron count if we assume that acetylene is behaving as a four-electron donor and the CO ligand is only weakly bridging.



III

**Acknowledgment.** Support from the National Science Foundation, through Grant No. CHE91-07578 to R.A.W., is gratefully acknowledged. We also thank the National Science Foundation (Grant No. CHE86-15556) for the purchase of the MicroVAX II computer and diffractometer.

**Supplementary Material Available:** Full details of the crystal data and data collection parameters (Tables S1 and S7), atomic positional parameters (Tables S2, S3, and S8), anisotropic thermal parameters (Tables S4 and S9), bond distances (Tables S5 and S10), and bond angles (Tables S6 and S11) for **3a** and **5h** and a diagram showing the disorder model for the dirhenium cation of **3a** (39 pages). Ordering information is given on any current masthead page.

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