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Nonredox Reactions between Dihydrogen Sulfide and *cis*-$\mathrm{Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2}$ (R = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$; dppm = $\mathrm{Ph_2PCH_2PPh_2}$). Isolation and Characterization of Bis(μ-hydrosulfido) and μ-*gem*-Dithiolato Complexes of Dirhenium(II)

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Nonredox reactions occur upon the exposure of *cis*-$\mathrm{Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2}$ (R = Me, Et; dppm = $\mathrm{Ph_2PCH_2PPh_2}$) to gaseous $\mathrm{H_2S}$ in the presence of $\mathrm{HBF_4{\cdot}Et_2O}$ to give either *cis*-$\mathrm{Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2}$, when THF or $\mathrm{CHCl_3}$ is used as the solvent, or the *gem*-dithiolato complexes *cis*-$\mathrm{Re_2(\mu\text{-}S_2CR^1R^2)Cl_2(\mu\text{-dppm})_2}$ and *cis*-$\mathrm{Re_2(\mu\text{-}S_2CHR^2)Cl_2(\mu\text{-dppm})_2}$ in the presence of ketones ($\mathrm{R^1R^2CO}$) and aldehydes ($\mathrm{R^2CHO}$). These are the first examples of compounds in which the Re–Re triply bonded $\mathrm{Re(\mu\text{-}SH)_2Re}$ and $\mathrm{Re(\mu\text{-}S_2CR^1R^2)Re}$ moieties are present. The *gem*-dithiolato dirhenium complexes have been isolated in the following instances: μ-$\mathrm{S_2CR^1R^2}$ with $\mathrm{R^1 = R^2 = CH_3}$, $\mathrm{CD_3}$, $\mathrm{C_2H_5}$ or $\mathrm{C_6H_5}$, $\mathrm{R^1 = CH_3}$ when $\mathrm{R^2 = C_2H_5}$, *n*-$\mathrm{C_3H_7}$, or *i*-$\mathrm{C_3H_7}$, and $\mathrm{R^1, R^2 = -(CH_2)_5-}$ or $\mathrm{-(CH_2)_4-}$; μ-$\mathrm{S_2CHR^2}$ with $\mathrm{R^2 = H, CH_3}$, or $\mathrm{C_2H_5}$. Single-crystal X-ray structural characterizations of *cis*-$\mathrm{Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2}$ (**1**) and *cis*-$\mathrm{Re_2(\mu\text{-}S_2CMe_2)Cl_2(\mu\text{-dppm})_2}$ (**2a**) show that both complexes possess very similar cradlelike geometries and retain very short Re–Re interactions; the Re–Re distances of 2.2577 (5) Å for **1** and 2.2544 (6) Å for **2a** accord with retention of the electron-rich Re–Re triple bond. Data for a crystal of composition $\mathrm{Re_2(SH)_2Cl_2(dppm)_2{\cdot}0.5CH_2Cl_2}$ at +20 °C are as follows: monoclinic space group $P2_1/c$, $a = 23.280\ (3)$ Å, $b = 13.040\ (2)$ Å, $c = 16.582\ (3)$ Å, $\beta = 94.43\ (2)°$, $V = 5018\ (2)$ Å^3, and $Z = 4$. The structure was refined to $R = 0.033$ ($R_w = 0.037$) for 5275 data with $I > 3\sigma(I)$. Data for a crystal of composition $\mathrm{Re_2(S_2CMe_2)Cl_2(dppm)_2{\cdot}CH_2Cl_2}$ at +20 °C are as follows: monoclinic space group $P2_1/n$, $a = 13.093\ (5)$ Å, $b = 23.807\ (9)$ Å, $c = 18.832\ (4)$ Å, $\beta = 106.29\ (2)°$, $V = 5634\ (6)$ Å^3, and $Z = 4$. The structure was refined to $R = 0.053$ ($R_w = 0.069$) for 5555 data with $I > 3\sigma(I)$.

Introduction

The use of $\mathrm{H_2S}$ as a source of dihydrogen and organosulfur compounds has attracted a flurry of interest,[1] although the isolation of well-defined transition-metal complexes of $\mathrm{H_2S}$ have proven to be especially challenging,[2,3] and it is only very recently that the first $\mathrm{H_2S}$ complex has been structurally characterized.[3] One class of compounds whose reactivity toward $\mathrm{H_2S}$ has not previously been described are those dimetal complexes that contain metal–metal multiple bonds based upon a $\sigma^2\pi^4\delta^a\delta^{*b}$ configuration (a = 0, 1, or 2; b = 0, 1, or 2 when a = 2).[4] Since such complexes can exhibit multielectron redox characteristics and should be quite reactive toward $\mathrm{H_2S}$, we have set out to examine the potential for the development of new metal–sulfur chemistry within this class of compound. We have found that the dirhenium(II) compounds $\mathrm{Re_2X_4(\mu\text{-dppm})_2}$ (X = Cl, Br; dppm = $\mathrm{Ph_2PCH_2PPh_2}$)[5] react rapidly with gaseous $\mathrm{H_2S}$ to afford the dirhenium(III) complexes $\mathrm{Re_2(\mu\text{-}H)(\mu\text{-}SH)X_4(\mu\text{-dppm})_2}$.[6] We now describe the behavior of the dirhenium(II) complexes *cis*-$\mathrm{Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2}$ (R = Me or Et) toward $\mathrm{H_2S}$.[7] These systems behave differently from $\mathrm{Re_2X_4(\mu\text{-dppm})_2}$ in that the reactions are nonredox in nature and the dirhenium(II) core is retained in the final products.

Experimental Section

Starting Materials. The compounds *cis*-$\mathrm{Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2}$ (R = $\mathrm{CH_3}$ or $\mathrm{C_2H_5}$) were prepared according to the literature procedures.[8,9] All solvents were obtained from commercial sources and were used as received. Syntheses and product workups were performed with the use of an atmosphere of dry nitrogen, and solvents were deoxygenated prior to use.

A. Synthesis of *cis*-$\mathrm{Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2}$. (i) From *cis*-$\mathrm{Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2}$. A suspension of *cis*-$\mathrm{Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2}$ (0.30 g, 0.22 mmol) in 6 mL of deoxygenated THF (or $\mathrm{CHCl_3}$) was treated with 0.15 mL of $\mathrm{HBF_4{\cdot}Et_2O}$ (or 0.15 mL of $\mathrm{HPF_6{\cdot}H_2O}$) and a slow stream of gaseous $\mathrm{H_2S}$ bubbled through the resulting mixture for ca. 3 min which was then stirred for 5 h. The green precipitate was filtered off, washed with diethyl ether (3 × 5 mL), and dried under

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(1) See, for example, the following representative studies. (a) Crabtree, R. H.; Davis, M. W.; Mellen, M. F.; Michelcic, J. M. *Inorg. Chim. Acta* **1983,** *72,* 223. (b) Osakada, K.; Yamamoto, T.; Yamamoto, A. *Inorg. Chim. Acta* **1984,** *90,* L5. (c) Mueting, A. M.; Boyle, P.; Pignolet, L. H. *Inorg. Chem.* **1984,** *23,* 44. (d) Lee, C.-L.; Besenyei, G.; James, B. R.; Nelson, D. A.; Lilga, M. A. *J. Chem. Soc., Chem. Commun.* **1985,** 1175. (e) Osakada, K.; Yamamoto, T.; Yamamoto, A.; Takenaka, A.; Sasada, Y. *Inorg. Chim. Acta* **1985,** *105,* L9. (f) Bottomley, F.; Drummond, D. F.; Egharevba, G. O.; White, P. S. *Organometallics* **1986,** *5,* 1620. (g) Lee, C.-L.; Chisholm, J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chim. Acta* **1986,** *121,* L7. (h) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1986,** *25,* 4617. (i) Besenvei, G.; Lee, C.-L.; Gulinski, J.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chem.* **1987,** *26,* 3622. (j) Mueting, A. M.; Boyle, P.; Wagner, R.; Pignolet, L. H. *Inorg. Chem.* **1988,** *27,* 271. (k) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990,** *112,* 2022. (l) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990,** *112,* 6426. (m) Antonelli, D. M.; Cowie, M. *Inorg. Chem.* **1990,** *29,* 3339. (n) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991,** *113,* 5904. (o) Cecconi, F.; Innocenti, P.; Midollini, S.; Moneti, S.; Vacca, A.; Ramirez, J. A. *J. Chem. Soc., Dalton Trans.* **1991,** 1129.

(2) (a) Vahrenhamp, H. *Angew. Chem., Int. Ed. Engl.* **1975,** *14,* 322 and references cited therein. (b) Herberhold, M.; Suss, G. *Angew. Chem., Int. Ed. Engl.* **1976,** *15,* 366. (c) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976,** *98,* 689. (d) Herberhold, M.; Suss, G. *J. Chem. Res., Synopses* **1977,** 246. (e) Harris, P. J.; Knox, S. A. R.; McKinney, R. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978,** 1009. (f) Urban, G.; Sunkel, K.; Beck, W. *J. Organomet. Chem.* **1985,** *290,* 329. (g) Raab, K.; Beck, W. *Chem. Ber.* **1985,** *118,* 3830. (h) Amarasekera, J.; Rauchfuss, T. B. *Inorg. Chem.* **1989,** *28,* 3875.

(3) (a) Sellman, D.; Lechner, P.; Knoch, F.; Moll, M. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 552. (b) Sellman, D.; Lechner, P.; Knoch, F.; Moll, M. *J. Am. Chem. Soc.* **1992,** *114,* 922 and references cited therein.

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

(5) Walton, R. A. *Polyhedron* **1989,** *8,* 1689.

(6) Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *J. Cluster Sci.*, in press.

(7) A preliminary report has been published. Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1992,** 375.

(8) Cutler, A. R.; Derringer, D. R.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1988,** *110,* 5024.

(9) Derringer, D. R.; Buck, E. A.; Esjornson, S. M. V.; Fanwick, P. E.; Walton, R. A. *Polyhedron* **1990,** *9,* 743.

0020-1669/92/1331-3663$03.00/0

vacuum; yield 0.28 g (97%). Anal. Calcd for $C_{50}H_{46}Cl_2P_4Re_2S_2$: C, 46.98; H, 3.64. Found: C, 47.04; H, 3.77.

This reaction was also carried out in the absence of added acid. A suspension of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (0.10 g, 0.08 mmol) in deoxygenated THF (4 mL) was exposed to a stream of H_2S for 2 min. The resulting mixture was stirred at room temperature for 36 h and the brown-green precipitate filtered off and washed with diethyl ether (2 × 3 mL). ^{1}H NMR spectroscopy and cyclic voltammetry showed that this product was a mixture of $Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2$ (ca. 85%) and starting material (ca. 15%).

(ii) From *cis*-$Re_2(\mu\text{-}O_2CC_2H_5)_2Cl_2(\mu\text{-dppm})_2$. The reaction between *cis*-$Re_2(\mu\text{-}O_2CC_2H_5)_2Cl_2(\mu\text{-dppm})_2$, $HBF_4{\cdot}Et_2O$, and H_2S in THF was carried out as in section A(i) to afford $Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2$ in almost quantitative yield (98%).

B. Synthesis of Complexes of the Type *cis*-$Re_2(\mu\text{-}S_2CR^1R^2)Cl_2(\mu\text{-dppm})_2$. (i) $R^1 = R^2 = CH_3$. A mixture of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (0.10 g, 0.074 mmol), deoxygenated acetone (4 mL), and $HBF_4{\cdot}Et_2O$ (0.07 mL) was exposed to a stream of gaseous H_2S for ca. 5 min and then stirred at room temperature for 20 h. The green precipitate was filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum; yield 0.080 g (82%). Anal. Calcd for $C_{53}H_{50}Cl_2P_4Re_2S_2$: C, 48.28; H, 3.83. Found: C, 48.58; H, 4.28. The product can be purified further by recrystallization from CH_2Cl_2–pentane mixtures.

The complex *cis*-$Re_2(\mu\text{-}O_2CC_2H_5)_2Cl_2(\mu\text{-dppm})_2$ can be used as the starting material in place of the acetate with similar results; yield 82%.

(ii) $R^1 = R^2 = CD_3$. A procedure similar to that in section B(i) but with $(CD_3)_2CO$ in place of $(CH_3)_2CO$ gave the title complex; yield 81%. Anal. Calcd for $C_{53}H_{44}D_6Cl_2P_4Re_2S_2$: C, 48.06; H, 4.27. Found: C, 47.71; H, 4.30.

(iii) $R^1 = CH_3$, $R^2 = C_2H_5$. The use of 2-butanone in place of acetone and a procedure similar to that in section B(i) gave the desired complex following the usual workup procedure; yield 83%. Anal. Calcd for $C_{56}H_{57}Cl_2O_{0.5}P_4Re_2S_2$ (i.e. $Re_2[S_2C(CH_3)(C_2H_5)]Cl_2(dppm)_2{\cdot}0.5(C_2H_5)_2O$): C, 49.11; H, 4.35; Cl, 5.18. Found: C, 49.38; H, 4.36; Cl, 5.71. The presence of a small amount of lattice diethyl ether was confirmed by ^{1}H NMR spectroscopy.

(iv) $R^1 = R^2 = C_2H_5$. A quantity of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (0.100 g, 0.074 mmol) was suspended in a H_2S-saturated solution that contained THF (3 mL), 3-pentanone (1 mL), and $HBF_4{\cdot}Et_2O$ (0.10 mL). This resulting mixture was stirred at room temperature for 24 h. The green precipitate was filtered off, washed very carefully with cold THF (ca. 1 mL) drop by drop, and then with diethyl ether (3 × 5 mL), and finally dried under vacuum; yield 0.063 g (63%). The product was recrystallized from CH_2Cl_2–pentane. Anal. Calcd for $C_{55.5}H_{55}Cl_3P_4Re_2S_2$ (i.e. $Re_2[S_2C(C_2H_5)_2]Cl_2(dppm)_2{\cdot}0.5CH_2Cl_2$): C, 47.99; H, 4.00. Found: C, 47.76; H, 4.18. The presence of lattice CH_2Cl_2 was confirmed by ^{1}H NMR spectroscopy (in $CDCl_3$).

(v) $R^1 = CH_3$, $R^2 = n\text{-}C_3H_7$. This complex was prepared from *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ and 2-pentanone with the use of a procedure similar to that in section B(i); yield 70%. Anal. Calcd for $C_{57}H_{49}Cl_2O_{0.5}P_4Re_2S_2$ (i.e. $Re_2[S_2C(CH_3)(C_3H_7)]Cl_2(dppm)_2{\cdot}0.5(C_2H_5)_2O$): C, 49.48; H, 4.31. Found: C, 49.50; H, 4.34. The presence of a small amount of lattice diethyl ether was confirmed by ^{1}H NMR spectroscopy.

(vi) $R^1 = CH_3$, $R^2 = i\text{-}C_3H_7$. The use of 3-methyl-2-butanone and a procedure similar to that in section B(i) gave the title complex; yield 66%. Anal. Calcd for $C_{55}H_{44}Cl_2P_4Re_2S_2$: C, 49.06; H, 4.19. Found: C, 49.50; H, 4.34.

(vii) $R^1 = R^2 = C_6H_5$. The reaction between *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (0.100 g, 0.074 mmol), benzophenone (0.500 g, 2.74 mmol), $HBF_4{\cdot}Et_2O$ (0.10 mL), and gaseous H_2S was carried out in THF as described in section B(iv); yield 0.054 g (50%). This product was recrystallized from CH_2Cl_2–pentane. Anal. Calcd for $C_{64}H_{56}Cl_4P_4Re_2S_2$ (i.e. $Re_2[S_2C(C_6H_5)_2]Cl_2(dppm)_2{\cdot}CH_2Cl_2$): C, 50.32; H, 3.78. Found: C, 50.00; H, 3.45. The presence of lattice CH_2Cl_2 was confirmed by ^{1}H NMR spectroscopy (in $CDCl_3$).

C. Synthesis of the Complexes *cis*-$Re_2[\mu\text{-}S_2\overline{C(CH_2)_nC}H_2]Cl_2(\mu\text{-dppm})_2$. (i) $n = 4$. A mixture of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (0.100 g, 0.074 mmol), CH_2Cl_2 (2 mL), cyclohexanone (1.5 mL), and $HBF_4{\cdot}Et_2O$ (0.10 mL) was subjected to a flow of gaseous H_2S for 3 min and then stirred for 30 h. The green solid was filtered off, washed with diethyl ether (3 × 5 mL), and then dried under vacuum; yield 0.063 g (62%). Anal. Calcd for $C_{57}H_{56}Cl_4P_4Re_2S_2$ (i.e. $Re_2[S_2(C_6H_{10})]Cl_2(dppm)_2{\cdot}CH_2Cl_2$): C, 47.43; H, 3.92. Found: C, 46.55; H, 3.94. The presence of lattice CH_2Cl_2 was confirmed by ^{1}H NMR spectroscopy (in $CDCl_3$).

Table I. Crystallographic Data for $Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2{\cdot}0.5CH_2Cl_2$ (**1**) and $Re_2(\mu\text{-}S_2CMe_2)Cl_2(\mu\text{-dppm})_2{\cdot}CH_2Cl_2$ (**2a**)

	1	**2**
chem formula	$Re_2Cl_3S_2P_4C_{50.5}H_{47}$	$Re_2Cl_4S_2P_4C_{54}H_{52}$
fw	1320.72	1403.25
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	23.280 (3)	13.093 (5)
b, Å	13.040 (2)	23.807 (9)
c, Å	16.582 (3)	18.832 (4)
β, deg	94.43 (2)	106.29 (2)
V, Å^3	5018 (2)	5634 (6)
Z	4	4
T, °C	20	20
λ, Å (Mo Kα)	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.748	1.654
μ(Mo Kα), cm^{-1}	52.63	47.61
transm coeff	1.00–0.71	1.00–0.60
R^a	0.033	0.053
$R_w{}^b$	0.037	0.069

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

(ii) $n = 3$. A procedure similar to that in section C(i) was used with cyclopentanone (1.5 mL) in place of cyclohexanone. Anal. Calcd for $C_{55.5}H_{53}Cl_4P_4Re_2S_2$ (i.e. $Re_2[S_2(C_5H_8)]Cl_2(dppm)_2{\cdot}0.5CH_2Cl_2$): C, 48.06; H, 3.86. Found: C, 48.12; H, 3.77. The presence of lattice CH_2Cl_2 was confirmed by ^{1}H NMR spectroscopy (in $CDCl_3$).

D. Synthesis of the Complexes *cis*-$Re_2(\mu\text{-}S_2CHR^2)Cl_2(\mu\text{-dppm})_2$. (i) $R^2 = H$. A quantity of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (0.100 g, 0.074 mmol) was suspended in a mixture of deoxygenated CH_2Cl_2 (3 mL), formaldehyde (1 mL), and $HBF_4{\cdot}Et_2O$ (0.10 mL). This resulting mixture was treated with gaseous H_2S for 5 min and then stirred at room temperature for 24 h. The green precipitate was filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum; yield 0.037 g (39%). Anal. Calcd for $C_{52}H_{48}Cl_4P_4Re_2S_2$ (i.e. $Re_2(S_2CH_2)Cl_2(dppm)_2{\cdot}CH_2Cl_2$): C, 45.44; H, 3.39. Found: C, 45.55; H, 3.55. The presence of lattice CH_2Cl_2 was confirmed by ^{1}H NMR spectroscopy (in $CDCl_3$).

(ii) $R^2 = CH_3$. This complex was prepared from *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (0.100 g, 0.074 mmol) as described in section D(i) but with acetaldehyde (2 mL) in place of formaldehyde and THF (3 mL) as the reaction solvent; yield 0.069 g (62%). Anal. Calcd for $C_{52}H_{48}Cl_2P_4Re_2S_2$: C, 47.88; H, 3.72. Found: C, 47.51; H, 4.10.

(iii) $R^2 = C_2H_5$. With the use of a procedure similar to that described in section D(i) and propionaldehyde (1.0 mL) in THF (3 mL), this complex was obtained after the usual workup; yield 61%. Its identity was established through a comparison of its spectroscopic and electrochemical properties with those exhibited by other complexes of this type.

E. Reactions of $Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2$ with Ketones and Dihydrogen Sulfide. (i) Acetone. A stream of gaseous H_2S was passed through a mixture of *cis*-$Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2$ (0.050 g, 0.039 mmol), $HBF_4{\cdot}Et_2O$ (0.07 mL), and acetone (5 mL) for ca. 5 min. The resulting solution was stirred for 20 h at room temperature and the green precipitate filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum; yield 0.035 g (68%). The product was identified as $Re_2[\mu\text{-}S_2C(CH_3)_2]Cl_2(\mu\text{-dppm})_2$ on the basis of its spectroscopic and electrochemical properties.

(ii) 2-Butanone. A similar reaction to that in section E(i) was carried out but with 2-butanone (2 mL) in place of acetone; yield 69%. The product was identified as $Re_2[\mu\text{-}S_2C(CH_3)(C_2H_5)]Cl_2(\mu\text{-dppm})_2$.

(iii) 3-Pentanone. With a mixture of THF (3 mL) and 3-pentanone (1 mL) in place of acetone, a procedure similar to that in section E(i) afforded the green complex $Re_2[\mu\text{-}S_2C(C_2H_5)_2]Cl_2(\mu\text{-dppm})_2$ which was washed carefully with 1 mL of cold THF and then with diethyl ether (3 × 5 mL); yield 48%.

(iv) 2-Pentanone. The use of 2-pentanone (3 mL) gave $Re_2[\mu\text{-}S_2C(CH_3)(C_3H_7)]Cl_2(\mu\text{-dppm})_2$ when a procedure similar to that in section E(i) was used; yield 67%.

Preparation of Single Crystals for Structure Determinations. Crystals of composition $Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2{\cdot}0.5CH_2Cl_2$ (**1**) and $Re_2(\mu\text{-}S_2CMe_2)Cl_2(\mu\text{-dppm})_2{\cdot}CH_2Cl_2$ (**2a**) were grown by the slow diffusion of *n*-pentane into dichloromethane solutions of these complexes.

X-ray Crystallography. The structures of **1** and **2a** were determined at +20 °C by application of standard procedures. The basic crystallographic parameters for these complexes are listed in Table I. The cell constants are based on 25 reflections with 20 < θ < 23° for **1** and 20 <

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Phenyl Group Atoms and Nonlattice Solvent Molecule Atoms of $Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2\cdot0.5CH_2Cl_2$ (**1**)[a]

atom	*x*	*y*	*z*	*B*
Re(1)	0.24353 (2)	0.14712 (3)	0.08723 (2)	2.091 (7)
Re(2)	0.22876 (2)	−0.01089 (3)	0.13731 (2)	2.166 (7)
Cl(1)	0.2538 (1)	0.2742 (2)	−0.0256 (1)	3.85 (6)
Cl(2)	0.2115 (1)	−0.1977 (2)	0.1348 (2)	4.10 (6)
S(1)	0.2908 (1)	−0.0003 (2)	0.0230 (1)	3.11 (5)
S(2)	0.1634 (1)	0.0450 (2)	0.0210 (1)	3.19 (5)
P(11)	0.3314 (1)	0.1907 (2)	0.1640 (1)	2.35 (5)
P(12)	0.1800 (1)	0.2410 (2)	0.1669 (1)	2.33 (5)
P(21)	0.3109 (1)	−0.0205 (2)	0.2331 (1)	2.40 (5)
P(22)	0.1578 (1)	0.0267 (2)	0.2306 (1)	2.38 (5)
C(B1)	0.3348 (4)	0.1112 (7)	0.2558 (5)	2.5 (2)
C(B2)	0.1641 (4)	0.1634 (7)	0.2551 (5)	2.6 (2)

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

$\theta < 22°$ for **2a**. Three standard reflections were measured after 5000 s of beam time during data collection; there were no systematic variations in intensity. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. The crystals were found to belong to the monoclinic space group $P2_1/c$ (for **1**) or $P2_1/n$ (for **2a**). 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.

The structures were solved by the use of the Patterson heavy-atom method which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were identified in succeeding difference Fourier syntheses. Both crystals were found to contain a molecule of lattice CH_2Cl_2 located about a general position. In the case of **1** the lattice solvent was refined as a disordered CH_2Cl_2 molecule at half occupancy. The hydrogen atoms of the dppm ligands of **1** and **2a** and methyl groups of the *gem*-dithiolate ligand of **2a** were included at fixed positions which were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. We assumed that the value of *B*(H), i.e. the isotropic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, their positions were not refined. The hydrogen atoms of the two hydrosulfido ligands of **1** were tentatively located in difference maps and were so refined; one of these atoms (H(1)) refined with a large thermal parameter. The structures were refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where *w* is the weighting factor defined as $w = 1/\sigma^2(F_o)$. All non-hydrogen atoms of the dirhenium complexes were refined anisotropically; corrections for anomalous scattering were applied to these atoms.[11]

Positional parameters and their errors for all atoms, except the phenyl group atoms and those of the lattice CH_2Cl_2 molecules, are listed in Tables II and III. Important intramolecular bond distances and angles are given in Tables IV and V. Full details of the crystal data, data collection parameters, and all structural parameters are available as supplementary material.

Table III. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Phenyl Group Atoms and Nonlattice Solvent Molecule Atoms of $Re_2(\mu\text{-}S_2CMe_2)Cl_2(\mu\text{-dppm})_2\cdot CH_2Cl_2$[a]

atom	*x*	*y*	*z*	*B*
Re(1)	0.54615 (4)	0.23084 (2)	0.46571 (3)	2.00 (1)
Re(2)	0.68012 (4)	0.22183 (2)	0.41305 (3)	2.13 (1)
Cl(1)	0.4448 (3)	0.2281 (2)	0.5602 (2)	3.78 (9)
Cl(2)	0.8596 (3)	0.1964 (2)	0.4020 (2)	4.6 (1)
S(1)	0.7283 (3)	0.2461 (2)	0.5467 (2)	2.94 (8)
S(2)	0.6474 (3)	0.1426 (1)	0.4883 (2)	2.44 (8)
P(11)	0.4081 (3)	0.1881 (2)	0.3693 (2)	2.15 (7)
P(12)	0.5043 (3)	0.3280 (2)	0.4395 (2)	2.67 (8)
P(21)	0.5886 (3)	0.1793 (2)	0.2972 (2)	2.34 (8)
P(22)	0.6821 (3)	0.3160 (2)	0.3657 (2)	2.79 (8)
C(11)	0.742 (1)	0.1713 (6)	0.5727 (8)	3.1 (3)
C(12)	0.854 (1)	0.1489 (7)	0.583 (1)	4.6 (4)
C(13)	0.703 (1)	0.1596 (7)	0.6398 (7)	4.0 (4)
C(1B)	0.447 (1)	0.1923 (6)	0.2824 (7)	2.3 (3)
C(2B)	0.550 (1)	0.3473 (6)	0.3592 (8)	3.2 (3)

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

Table IV. Some Important Bond Distances (Å) and Bond Angles (deg) for $Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2\cdot0.5CH_2Cl_2$ (**1**)[a]

	Distances		
Re(1)–Re(2)	2.2577 (5)	P(11)–C(B1)	1.838 (9)
Re(1)–Cl(1)	2.525 (2)	P(11)–C(1111)	1.819 (9)
Re(1)–S(1)	2.495 (2)	P(11)–C(1121)	1.833 (9)
Re(1)–S(2)	2.479 (2)	P(12)–C(B2)	1.839 (9)
Re(1)–P(11)	2.392 (2)	P(12)–C(1211)	1.835 (9)
Re(1)–P(12)	2.395 (2)	P(12)–C(1221)	1.836 (9)
Re(2)–Cl(2)	2.469 (2)	P(21)–C(B1)	1.836 (9)
Re(2)–S(1)	2.475 (2)	P(21)–C(2111)	1.845 (9)
Re(2)–S(2)	2.472 (2)	P(21)–C(2121)	1.821 (9)
Re(2)–P(21)	2.392 (2)	P(22)–C(B2)	1.831 (9)
Re(2)–P(22)	2.400 (2)	P(22)–C(2211)	1.818 (9)
S(1)–H(1)	1.5 (2)	P(22)–C(2221)	1.839 (9)
S(2)–H(2)	1.2 (1)		
	Angles		
Re(2)–Re(1)–Cl(1)	153.82 (6)	Re(1)–Re(2)–P(21)	98.94 (6)
Re(2)–Re(1)–S(1)	62.54 (6)	Re(1)–Re(2)–P(22)	100.53 (6)
Re(2)–Re(1)–S(2)	62.73 (6)	Cl(2)–Re(2)–S(1)	98.40 (8)
Re(2)–Re(1)–P(11)	99.75 (6)	Cl(2)–Re(2)–S(2)	100.83 (9)
Re(2)–Re(1)–P(12)	98.37 (6)	Cl(2)–Re(2)–P(21)	94.60 (9)
Cl(1)–Re(1)–S(1)	96.83 (8)	Cl(2)–Re(2)–P(22)	95.33 (8)
Cl(1)–Re(1)–S(2)	97.77 (9)	S(1)–Re(2)–S(2)	75.31 (8)
Cl(1)–Re(1)–P(11)	96.47 (8)	S(1)–Re(2)–P(21)	91.56 (8)
Cl(1)–Re(1)–P(12)	99.87 (8)	S(1)–Re(2)–P(22)	162.62 (8)
S(1)–Re(1)–S(2)	74.85 (9)	S(2)–Re(2)–P(21)	160.97 (8)
S(1)–Re(1)–P(11)	91.30 (8)	S(2)–Re(2)–P(22)	91.71 (8)
S(1)–Re(1)–P(12)	160.29 (8)	P(21)–Re(2)–P(22)	97.92 (8)
S(2)–Re(1)–P(11)	161.18 (8)	Re(1)–S(1)–Re(2)	54.03 (5)
S(2)–Re(1)–P(12)	92.51 (8)	Re(1)–S(1)–H(1)	112 (9)
P(11)–Re(1)–P(12)	97.12 (8)	Re(2)–S(1)–H(1)	105 (9)
Re(1)–Re(2)–Cl(2)	157.44 (6)	Re(1)–S(2)–Re(2)	54.26 (5)
Re(1)–Re(2)–S(1)	63.44 (6)	Re(1)–S(2)–H(2)	98 (6)
Re(1)–Re(2)–S(2)	63.01 (6)	Re(2)–S(2)–H(2)	98 (5)

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

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 $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were performed with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035 B *x*-*y* recorder. All NMR spectra were recorded on CD_2Cl_2 or $CDCl_3$ solutions of the complexes. The $^{31}P\{^1H\}$ spectra were obtained with use of a Varian XL-200A spectrometer operated at 80.98 MHz with 85% H_3PO_4 as an external standard. ^1H NMR and $^{13}C\{^1H\}$ spectra were obtained on a GE QE-300 spectrometer. 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.

Results

The carboxylato complexes *cis*-$Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2$ (R = CH_3 or C_2H_5) can be activated toward reaction with H_2S in the presence of strong acid (eq 1). The green hydrosulfido complex *cis*-$Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2$ (**1**) precipitates in essen-

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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. *Ibid.* Table 2.2B.

Table V. Some Important Bond Distances (Å) and Bond Angles (deg) for $Re_2(\mu\text{-}S_2CMe_2)Cl_2(\mu\text{-dppm})_2\cdot CH_2Cl_2$[a]

Distances

Re(1)–Re(2)	2.2544 (6)	P(11)–C(1111)	1.83 (1)
Re(1)–Cl(1)	2.501 (3)	P(11)–C(1121)	1.83 (1)
Re(1)–S(1)	2.471 (3)	P(12)–C(2B)	1.83 (1)
Re(1)–S(2)	2.457 (3)	P(12)–C(1211)	1.85 (1)
Re(1)–P(11)	2.399 (3)	P(12)–C(1221)	1.81 (1)
Re(1)–P(12)	2.397 (3)	P(21)–C(1B)	1.817 (9)
Re(2)–Cl(2)	2.491 (3)	P(21)–C(2111)	1.82 (1)
Re(2)–S(1)	2.485 (3)	P(21)–C(2121)	1.83 (1)
Re(2)–S(2)	2.469 (3)	P(22)–C(2B)	1.86 (1)
Re(2)–P(21)	2.398 (3)	P(22)–C(2211)	1.81 (1)
Re(2)–P(22)	2.415 (3)	P(22)–C(2221)	1.83 (1)
S(1)–C(11)	1.84 (1)	C(11)–C(12)	1.52 (2)
S(2)–C(11)	1.85 (1)	C(11)–C(13)	1.51 (2)
P(11)–C(1B)	1.85 (1)		

Angles

Re(2)–Re(1)–Cl(1)	160.74 (7)	Cl(2)–Re(2)–S(2)	100.5 (1)
Re(2)–Re(1)–S(1)	63.27 (7)	Cl(2)–Re(2)–P(21)	93.7 (1)
Re(2)–Re(1)–S(2)	63.02 (6)	Cl(2)–Re(2)–P(22)	94.9 (1)
Re(2)–Re(1)–P(11)	98.09 (6)	S(1)–Re(2)–S(2)	68.40 (9)
Re(2)–Re(1)–P(12)	99.35 (7)	S(1)–Re(2)–P(21)	159.94 (9)
Cl(1)–Re(1)–S(1)	100.21 (9)	S(1)–Re(2)–P(22)	97.59 (9)
Cl(1)–Re(1)–S(2)	102.87 (9)	S(2)–Re(2)–P(21)	94.40 (9)
Cl(1)–Re(1)–P(11)	95.17 (9)	S(2)–Re(2)–P(22)	160.56 (9)
Cl(1)–Re(1)–P(12)	92.0 (1)	P(21)–Re(2)–P(22)	96.3 (1)
S(1)–Re(1)–S(2)	68.81 (9)	Re(1)–S(1)–Re(2)	54.12 (6)
S(1)–Re(1)–P(11)	157.11 (9)	Re(1)–S(1)–C(11)	91.4 (3)
S(1)–Re(1)–P(12)	96.3 (1)	Re(2)–S(1)–C(11)	91.3 (3)
S(2)–Re(1)–P(11)	91.36 (9)	Re(1)–S(2)–Re(2)	54.48 (6)
S(2)–Re(1)–P(12)	160.43 (9)	Re(1)–S(2)–C(11)	91.7 (4)
P(11)–Re(1)–P(12)	99.98 (9)	Re(2)–S(2)–C(11)	91.7 (4)
Re(1)–Re(2)–Cl(2)	158.21 (8)	S(1)–C(11)–S(2)	98.0 (5)
Re(1)–Re(2)–S(1)	62.62 (7)	S(1)–C(11)–C(12)	113.0 (8)
Re(1)–Re(2)–S(2)	62.50 (6)	S(1)–C(11)–C(13)	111.8 (8)
Re(1)–Re(2)–P(21)	100.85 (6)	S(2)–C(11)–C(12)	111.7 (8)
Re(1)–Re(2)–P(22)	99.47 (7)	S(2)–C(11)–C(13)	110.5 (8)
Cl(2)–Re(2)–S(1)	99.4 (1)	C(12)–C(11)–C(13)	111 (1)

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

$$cis\text{-}Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2 + 2H_2S \rightarrow cis\text{-}Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2 + 2RCO_2H \quad (1)$$

tially quantitative yield when THF or $CHCl_3$ is used as the solvent. This same reaction course ensues in the absence of added acid, but the reaction is much slower. Presumably, the H_2S-saturated solutions are sufficiently acidic to facilitate the slow release of RCO_2H with concomitant coordination of HS^-.

When acetone is used in place of THF and $CHCl_3$ as the solvent, the nonredox reaction proceeds to give the green *gem*-dithiolato complex *cis*-$Re_2(\mu\text{-}S_2CMe_2)Cl_2(\mu\text{-dppm})_2$. The use of other ketones and aldehydes in place of acetone leads to a range of *gem*-dithiolato complexes *cis*-$Re_2(\mu\text{-}S_2CR^1R^2)Cl_2(\mu\text{-dppm})_2$ (see eq 2), so this is a simple and quite general route to species of this type.

The reactions of **1** with acetone, 2-butanone, 3-pentanone, and 2-pentanone in the presence of $HBF_4\cdot Et_2O$ and H_2S also provide a route to the appropriate *gem*-dithiolato complexes **2a**, **2c**, **2d**, and **2e**, respectively. However, these reactions do not proceed in the absence of either H_2S or $HBF_4\cdot Et_2O$.

The structure of **1** was established by single-crystal X-ray analysis on a crystal of composition $Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2\cdot 0.5CH_2Cl_2$. An ORTEP representation of the structure is shown in Figure 1. The important details of the crystallographic and structural parameters are given in Tables I, II, and IV.

The Nujol mull IR spectrum of **1** shows a sharp, weak, but clearly defined ν(S–H) mode at 2451 cm^{-1}. However, the ^1H spectrum (CD_2Cl_2) of **1** does not reveal a clearly discernible S–*H* resonance even when the solution is cooled to −80 °C; well-resolved phenyl resonances occur between δ +7.8 and +6.8, while the $-CH_2-$ resonances of the dppm ligands are multiplets at δ +6.34 and δ +5.04. While the $^{31}P\{^1H\}$ NMR spectrum shows two fairly close but broad resonances of approximate equal intensity at δ −6.5 and δ −3.8, in accord with the retention of pairs of chemically inequivalent dppm phosphorus atoms in solution, as is the case in the solid-state structure (Figure 1), a reasonable alternative interpretation could be the presence of two isomers in which the hydrogen atoms of the μ-SH ligands project either toward the same side or opposite sides of the molecule.[12] The cyclic voltammogram of a solution of **1** in 0.1 M TBAH–CH_2Cl_2 consists of an oxidation at $E_{1/2}$ = +0.71 V (ΔE_p = 70 mV; $i_{p,a} = i_{p,c}$ when the switching potential is +0.9 V) and an irreversible reduction at −1.62 V vs Ag/AgCl. When the CV scan is extended to more positive potentials, an irreversible oxidation is found at $E_{1/2}$ = +1.3 V vs Ag/AgCl.

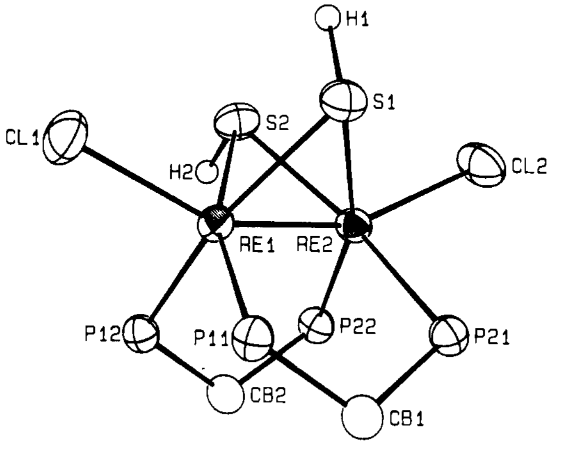

Figure 1. ORTEP representation of the structure of the molecule $Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2$ (**1**) with the phenyl group atoms of the dppm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level.

$$cis\text{-}Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2 + 2H_2S + R^1R^2CO \xrightarrow{H^+} \underset{\mathbf{2,\,3}}{cis\text{-}Re_2(\mu\text{-}S_2CR^1R^2)Cl_2(\mu\text{-dppm})_2} + 2RCO_2H + H_2O \quad (2)$$

2: **a**, $R^1 = R^2 = CH_3$; **b**, $R^1 = R^2 = CD_3$;
c, $R^1 = CH_3$, $R^2 = C_2H_5$; **d**, $R^1 = R^2 = C_2H_5$;
e, $R^1 = CH_3$, $R^2 = n\text{-}C_3H_7$;
f, $R^1 = CH_3$, $R^2 = i\text{-}C_3H_7$;
g, $R^1 = R^2 = C_6H_5$; **h**, $R^1, R^2 = -(CH_2)_5-$;
i, $R^1, R^2 = -(CH_2)_4-$

3: **a**, $R^1 = R^2 = H$; **b**, $R^1 = H$, $R^2 = CH_3$;
c, $R^1 = H$, $R^2 = C_2H_5$

The 12 *gem*-dithiolate complexes **2** and **3** that have been prepared possess very similar spectroscopic and electrochemical properties (Table VI). With the exception of **3b** and **3c**, these complexes show a singlet in their $^{31}P\{^1H\}$ NMR spectra; the spectra of **3b** and **3c** appear as AA′BB′ patterns ($J_{PP} \approx$ 54 Hz). The cyclic voltammetric properties of these complexes resemble the behavior described for **1** and show two oxidations and a reduction. However, in the case of **2** and **3** the reduction appears to much more reversible ($i_{p,c} \approx i_{p,a}$). The ^1H NMR spectra are fully in

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(12) Even with the presence of a single isomeric form possessing the structure shown in Figure 1, the two sets of inequivalent P nuclei may not have significantly different chemical shifts. However, we have not yet been able to investigate the possibility of isomeric forms of **1** being present because of the very poor solubility properties of this complex and the difficulty of obtaining satisfactory VT-^{31}P NMR spectra. We thank a referee for suggesting the possibility of isomers.

Table VI. Selected Electrochemical and Spectral Data for *gem*-Dithiolate Complexes of Dirhenium of the Type $Re_2(\mu\text{-}S_2CR^1R^2)Cl_2(\mu\text{-dppm})_2$

			CV half-wave potentials, V[a]			$^{31}P\{^1H\}$
complex	R^1	R^2	$E_{p,a}$	$E_{1/2}(ox)$	$E_{1/2}(red)$	NMR, δ[b]
2a	CH_3	CH_3	+1.41	+0.64	−1.57	−10.1
2b	CD_3	CD_3	+1.45	+0.65	−1.58	−10.1
2c	CH_3	C_2H_5	+1.37	+0.61	−1.62	−10.2
2d	C_2H_5	C_2H_5	+1.40	+0.62	−1.60	−10.5
2e	CH_3	*n*-C_3H_7	+1.38	+0.61	−1.64	−10.2
2f	CH_3	*i*-C_3H_7	+1.42	+0.62	−1.62	−10.7
2g	C_6H_5	C_6H_5	+1.38	+0.64	−1.57	−10.1
2h	$-(CH_2)_5-$		+1.40	+0.63	−1.58	−10.4
2i	$-(CH_2)_4-$		+1.40	+0.63	−1.60	−9.0
3a	H	H	+1.44	+0.68	−1.53	−6.7
3b	H	CH_3	+1.44	+0.63	−1.57	−6.8, −8.8[c]
3c	H	C_2H_5	+1.45	+0.64	−1.58	−6.9, −9.0[c]

[a] Measured on 0.1 M TBAH–CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode with a scan rate (ν) 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 $E_{p,a} - E_{p,c}$ are in the range 60–100 mV for $E_{1/2}(ox)$ and 90–120 mV for $E_{1/2}(red)$. [b] Spectra recorded in CD_2Cl_2. These spectra are singlets unless otherwise noted. [c] Spectrum has the appearance of an AA′BB′ pattern; the chemical shifts quoted are those of the most intense components.

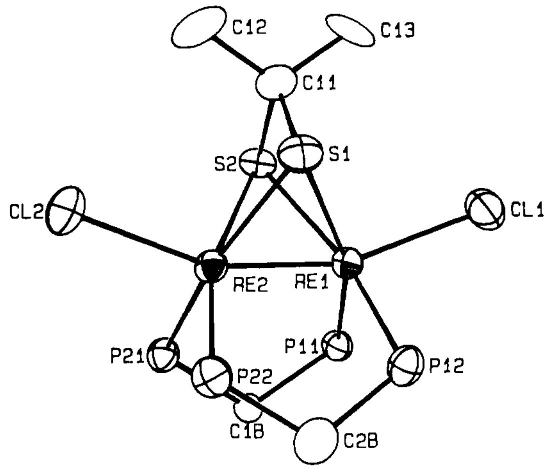

Figure 2. ORTEP representation of the structure of the molecule $Re_2(\mu\text{-}S_2CMe_2)Cl_2(\mu\text{-dppm})_2$ (**2a**) with the phenyl group atoms of the dppm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level.

accord with the stoichiometries of the complexes but are otherwise unexceptional (see Table S13). A close relationship between the structures of these complexes is implied by the similarity of their properties. The structure of **2a** has been determined by an X-ray analysis on a crystal of composition $Re_2(\mu\text{-}S_2CMe_2)Cl_2(dppm)_2 \cdot CH_2Cl_2$. The structure of the dirhenium complex is shown in Figure 2, while the crystallographic and structural parameters are given in Tables I, III, and V.

Discussion

The reactions of *cis*-$Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2$ with H_2S to afford *cis*-$Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2$ and the *gem*-dithiolate complexes **2** and **3** provide an easy entry into the chemistry of compounds that contain the previously unknown metal–metal-bonded $Re(\mu\text{-}SH)_2Re$ and $Re(\mu\text{-}S_2CR^1R^2)Re$ moieties. Presumably, access to an even wider range of complexes of types **2** and **3** is possible by this same route, the only limitation being the availability of the appropriate ketone or aldehyde. Our work demonstrates the effectiveness of the triply bonded dirhenium unit *cis*-$Re_2(\mu\text{-dppm})_2$ as a template for new metal–sulfur chemistry. Our initial choice of the cis isomer of $Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2$, rather than the equally accessible trans isomer, was dictated by our previous finding[8,9] that the trans isomers readily convert to the more thermodynamically favored cis forms.

The structures of **1** and the complexes of types **2** and **3** were established through crystal determinations on **1** and **2a** (Figures 1 and 2). These two structures are remarkably similar, with each possessing a cradlelike geometry,[13] in which two μ-SH ligands or a bridging *gem*-dithiolate ligand have replaced the cis carboxylate bridges of the precursor complex. Excluding the H atoms on the two μ-SH ligands of **1**, both complexes possess virtual C_{2v} symmetry. The Re–Re bond distances (2.2577 (5) Å for **1**, 2.2544 (6) Å for **2a**), are consistent with the retention of the electron-rich Re–Re triple bond[4,5,8,9] in both compounds and, by implication, all other compounds of types **2** and **3**. The remaining structural parameters for **1** and **2a** are also very similar, the comparable Re–Cl, Re–P, and Re–S bond lengths and Re–Re–Cl angles, for example, differing very little between the two structures. The Re–S distances, which are in the ranges 2.472 (2)–2.495 (2) and 2.457 (3)–2.485 (3) Å for **1** and **2a**, respectively, are a little longer than those reported for the dirhenium(III) complexes $Re_2(\mu\text{-}H)(\mu\text{-}SH)Cl_4(\mu\text{-dppm})_2$ (average 2.412 [2] Å)[6] and $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ (dto = 3,6-dithiaoctane) (average 2.349 [22] Å)[14] but much longer than the distances in the μ-sulfido-bridged $[Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_2(CS)(\mu\text{-dpam})_2(NCEt)]PF_6$ (dpam = $Ph_2AsCH_2AsPh_2$) (average 2.252 [12] Å).[15] No metal–metal-bonded dirhenium(II) complexes that contain μ-SH and μ-SR ligands are available in the literature with which to provide a benchmark for a comparison of the Re–S distances in **1** and **2a** since none have been structurally characterized previously.

The formation of the dirhenium(II) complex *cis*-$Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2$ (**1**) from *cis*-$Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2$ contrasts with the oxidative addition of H_2S to $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl or Br) to produce[6] the dirhenium(III) compounds $Re_2(\mu\text{-}H)(\mu\text{-}SH)X_4(\mu\text{-dppm})_2$. In the formation of **1**, and the closely allied *gem*-dithiolate complexes **2** and **3**, the carboxylate groups of the starting material are labilized through protonation to generate the reactive, weakly-solvated *cis*-$[Re_2Cl_2(\mu\text{-dppm})_2]^{2+}$ moiety whose enhanced electrophilic character, compared to the more easily oxidized neutral $Re_2X_4(\mu\text{-dppm})_2$,[5] results in nonredox reactions with H_2S, the actual reaction course being dependent on the solvent used. Although the bis(μ-hydrosulfido) complex **1** is not converted into **2** when reacted with H_2S and ketone, or $HBF_4 \cdot Et_2O$ and ketone, it does convert when a mixture of $HBF_4 \cdot Et_2O$, H_2S, and the ketone is used. This is shown by the conversions of **1** to **2a**, **2c**, **2d**, and **2e** by this means. Since **1** is formed more rapidly than **2**, we believe that it could be an intermediate in the formation of the *gem*-dithiolate complexes; in the preparation of **2**, shorter reaction times than those quoted in the Experimental Section give mixtures of **1** and **2**. However, since **1** does not give **2** when reacted with the ketone *unless both* H_2S *and* $HBF_4 \cdot Et_2O$ are present, the mechanism apparently does not involve the attack of ketone R^1R^2CO upon the $Re(\mu\text{-}SH)_2Re$ unit to give $Re(\mu\text{-}S_2CR^1R^2)Re$ with the elimination of H_2O. Since *gem*-dithiols (along with thioketones or thioaldehydes) are formed by the reactions of H_2S with ketones and aldehydes under acidic and basic conditions,[16] it seems possible that a second (competitive) pathway to the formation of **2** could involve the direct attack of $R^1R^2C(SH)_2$ or $R^2HC(SH)_2$ upon the *cis*-$Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2$ precursor complex.

Complexes in which a methanedithiolato bridge ($\mu\text{-}S_2CH_2$) is present are well documented, and several have been structurally

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(13) (a) Wu, J.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1989**, *111*, 7812. (b) Cotton, F. A.; Dunbar, K. R.; Verbruggen, M. G. *J. Am. Chem. Soc.* **1987**, *109*, 5498.

(14) Heyen, B. J.; Powell, G. L. *Inorg. Chem.* **1990**, *29*, 4574.

(15) Qi, J.-S.; Schrier, P. W.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 258.

(16) (a) Mayer, R.; Giller, G.; Nitzschke, M.; Jentzsch, J. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 370. (b) Mayer, R..; Morgenstern, J.; Fabian, J. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 277.

characterized.[17-19] On the other hand, examples of *gem*-dithiolato ligand bridges of the type μ-$S_2CR^1R^2$ remain surprisingly scarce, although a few examples exist in cyclopentadienyldimolybdenum chemistry in the cases where $R^1 = CH_3$ when $R^2 = OH$,[20] NH_2,[20] CH_3,[17a] or Ph.[17b] While none of these compounds have been structurally characterized by X-ray crystallography, there is one example of a structurally characterized 2,4-dithiametallacyclobutane complex, $(\eta^5$-$C_5Me_5)(Me_3P)Ir(S_2CMe_2)$, that contains a chelating η^2-S_2CMe_2 ligand.[21,22] Our isolation of the complexes **2** and **3** provides the first extensive series of μ-*gem*-dithiolate complexes for the transition elements which incorporate a wide variety of alkyl substituents and which can be prepared in high yield in such a simple and straightforward fashion.

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Supplementary Material Available: For **1** and **2a** tables giving full details of the crystal data and data collection parameters (Tables S1 and S7), positional parameters for the non-hydrogen atoms (Tables S2 and S8) and the hydrogen atoms (Tables S3 and S9), thermal parameters (Tables S4 and S10), and complete listings of bond distances (Tables S5 and S11) and bond angles (Tables S6 and S12) and for complexes of types **2** and **3** a table giving ^1H NMR spectral data (37 pages). Ordering information is given on any current masthead page.

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(17) (a) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329. (b) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234. (c) Birnbaum, J.; Haltiwanger, R. C.; Bernatis, P.; Teachout, C.; Parker, K.; Rakowski DuBois, M. *Organometallics* **1991**, *10*, 1779. (d) Maciejewski Farmer, M.; Haltiwanger, R. C.; Kvietok, F.; Rakowski DuBois, M. *Organometallics* **1991**, *10*, 4066.

(18) Shaver, A.; Filtzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

(19) (a) Adams, R. D.; Golembeski, N. M.; Seleque, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 546. (b) Adams, R. D. *Acc. Chem. Res.* **1983**, *16*, 67.

(20) Coons, D. E.; Laurie, J. C. V.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1987**, *109*, 283.

(21) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2022.

(22) Complexes that contain the η^2-S_2CH_2 ligand are also known, as in the recently characterized $(\eta^5$-$C_5Me_5)Rh(PMe_3)(S_2CH_2)$. Jones, W. D.; Selmeczy, A. D. *Organometallics* **1992**, *11*, 889.