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Redox Reactions of the Dirhenium(II) Complexes $Re_2X_4(dppm)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$). The Reductive Coupling of Nitriles with Retention of a Metal-Metal-Bonded Dirhenium Unit

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The dirhenium(II) complexes $[Re_2X_3(\mu\text{-dppm})_2(NCR)_2]PF_6$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$; R = Me, Et, *i*-Pr, *t*-Bu, Ph) react with nitriles to give the green, paramagnetic complexes $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]PF_6$ in which the $HN_2C_2R_2$ ligand has been formed from the reductive coupling of two nitriles. The lability of the nitrile ligands RCN has been demonstrated by the conversion of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ into $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCR')]PF_6$ upon reaction with R′CN (R′ = *i*-Pr, Ph). Experiments in which CD_3CN is used in place of CH_3CN showed that the source of hydrogen in the $HN_2C_2Me_2$ ligand is the acetonitrile ligand itself; this hydrogen is very labile and readily exchanges with deuterium. The complexes $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]PF_6$ are readily oxidized to the red, diamagnetic salts $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)](PF_6)_2$ by $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$/acetone or $NOPF_6/CH_2Cl_2$; these compounds display well-defined ^1H and $^{31}P\{^1H\}$ NMR spectra. The structural identity of these complexes was confirmed by an X-ray structure analysis of the complex $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)](PF_6)_{0.8}(Br)_{0.2}\cdot{}^1/_2(C_2H_5)_2O\cdot(CH_3)_2CO$ (**1**) at −150 °C. This complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 13.150$ (3) Å, $b = 21.227$ (5) Å, $c = 12.592$ (2) Å, $\alpha = 99.53$ (2)°, $\beta = 113.35$ (2)°, $\gamma = 74.72$ (2)°, $V = 3106$ (2) Å^3, and $Z = 2$. The structure was refined to $R = 0.066$ ($R_w = 0.092$) for 6019 data with $I > 3.0\sigma(I)$. The dirhenium cation of **1** possesses an edge-shared bioctahedral structure in which the two octahedra are bridged by a bromide ligand and a nitrogen atom of the coupled $HN_2C_2Me_2$ ligand. The $[Re_2Br_3(\mu\text{-dppm})_2]$ unit has a cis arrangement of bromide ligands on one side of the molecule and a trans disposition of the dppm ligands. The Re–Re distance is 2.666 (1) Å. The structure solution was complicated by the occurrence of a disorder involving the MeCN and $HN_2C_2Me_2$ ligands. Attempts to grow crystals of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NC\text{-}i\text{-Pr})]PF_6$ from 1,2-dichloroethane/diethyl ether led to the formation of the complex $[Re_2Cl_3(\mu\text{-}HN_2C_2Me\{CHO\})(\mu\text{-dppm})_2(NC\text{-}i\text{-Pr})]PF_6\cdot C_2H_4Cl_2\cdot H_2O$ (**2**) in which one of the methyl groups of the coupled nitrile ligand had been oxidized to an aldehyde. Crystal data for **2** at −140 °C are as follows: triclinic space group $P\bar{1}$, $a = 13.001$ (2) Å, $b = 13.795$ (5) Å, $c = 19.834$ (8) Å, $\alpha = 103.30$ (3)°, $\beta = 104.43$ (2)°, $\gamma = 97.66$ (2)°, $V = 3283$ (4) Å^3, and $Z = 2$. The structure was refined to $R = 0.051$ ($R_w = 0.061$) for 5667 data with $I > 3.0\sigma(I)$. The dirhenium cation in **2** has a structure very similar to that in **1** and a Re–Re distance of 2.640 (1) Å. The disorder problem that was problematic with the structure refinement of **1** was no longer present in **2**. The metallacycle derived from the coupling of two acetonitrile ligands can best be considered in terms of contributions from deprotonated diimine and ene–diamine ligand forms.

Introduction

We have been investigating the reactivity of the triply bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) toward carbon monoxide, alkyl and aryl isocyanides, and organic nitriles with a view to establishing the stability of the dimetal core toward these sterically undemanding ligands. Up to three of these ligands can coordinate with preservation of the dinuclear structure.[1-3] Of special note is the ability of these complexes to react with CO to give the complexes $[Re_2(\mu\text{-X})(\mu\text{-CO})(\mu\text{-dppm})_2X_2(CO)_2]PF_6$ in which there is an all-cis arrangement of CO ligands. Although there are close C···C contacts between the CO ligands (2.38 Å)[2,4,5] and in spite of the redox activity of the dirhenium unit,[6] we have yet to induce reductive coupling of the CO ligands in these complexes. However, we have now encountered an interesting case involving the reductive coupling of nitriles by the complexes $Re_2X_4(\mu\text{-dppm})_2$, in which the dimetal unit is retained and the resulting coupled nitrile ligands exhibit a novel $\mu_2\text{-}\eta^2$ bonding mode. The important aspects of this chemistry are described herein.[7]

Experimental Section

Starting Materials. The compounds $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br),[8,9] $Re_2Cl_4(\mu\text{-dppm})_2$,[10] and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$[11] were prepared by standard procedures. Using the method described previously for the synthesis of $[Re_2X_3(\mu\text{-dppm})_2(NCR)_2]PF_6$ (X = Cl; R = Me, Et, Ph),[12] we prepared additional bis(nitrile) complexes of this type in the case of R = *i*-Pr and *t*-Bu for X = Cl and R = Me and Et for X = Br.[13,14] All other reagents and solvents were obtained from commercial sources. Potassium hexafluorophosphate was recrystallized from water prior to use. Acetonitrile, propionitrile, and isobutyronitrile were distilled from CaH_2 prior to use while the other nitriles were used as received. All solvents were deoxygenated with $N_2(g)$ prior to use.

Reaction Procedures. All reactions were performed under a dry nitrogen atmosphere using standard vacuum-line techniques.

A. Reactions of $[Re_2X_3(\mu\text{-dppm})_2(NCR)_2]PF_6$ (X = Cl, Br; R = Me, Et, *i*-Pr, *t*-Bu, Ph) with Nitriles. (i) $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$. (a) The bis(acetonitrile) complex $[Re_2Cl_3(\mu\text{-dppm})_2(NCMe)_2]PF_6$ (0.100 g, 0.068 mmol) was refluxed in acetonitrile (15 mL, 287 mmol) for 3 days. The dark green mixture was evaporated to dryness and the solid then extracted with dichloromethane (25 mL). The product was precipitated from the extract by the slow addition of diethyl ether (50 mL). The green product was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.056 g (55%). Anal. Calcd for

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(1) Price, A. C.; Walton, R. A. *Polyhedron* **1987**, *6*, 729. This review cites several earlier papers.

(2) Fanwick, P. E.; Price, A. C.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 3920.

(3) Fanwick, P. E.; Price, A. C.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2601.

(4) This distance resembles the short C···C contact found in $Nb(CO)_2(dmpe)_2Cl$, a complex that, like its tantalum analogue, can be induced to undergo a reductive coupling of its carbonyl ligands.[5]

(5) (a) Bianconi, P. A.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 311. (b) Bianconi, P. A.; Vrtis, R. N.; Rao, Ch. P.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *Organometallics* **1987**, *6*, 1968.

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

(7) For a preliminary report, see: Esjornson, D.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 3066.

(8) Barder, T. J.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 2510; *Inorg. Synth.* **1985**, *23*, 116.

(9) Cotton, F. A.; Curtis, N. F.; Johnson, B. F. G.; Robinson, W. R. *Inorg. Chem.* **1965**, *4*, 326.

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

(11) Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971**, *10*, 1559.

(12) Barder, T. J.; Cotton, F. A.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 1258.

(13) The highly insoluble complex that is formed by the reaction of $(n\text{-}Bu_4N)_2Re_2Br_8$ with dppm in refluxing acetonitrile and which we had originally formulated as "α-$[ReBr_2(dppm)]_n$",[14] is in reality $[Re_2Br_3(\mu\text{-dppm})_2(NCMe)_2]Br$. It undergoes anion exchange with PF_6^- to afford $[Re_2Br_3(\mu\text{-dppm})_2(NCMe)_2]PF_6$.

(14) Ebner, J. R.; Tyler, D. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 833.

$C_{56}H_{54}Cl_3F_6N_3P_5Re_2$: C, 44.35; H, 3.59; Cl, 7.01. Found: C, 44.36; H, 3.55; Cl, 6.99.

(b) The propionitrile complex $[Re_2Cl_3(\mu\text{-dppm})_2(NCEt)_2]PF_6$ (0.316 g, 0.211 mmol) was refluxed in acetonitrile (20 mL, 383 mmol), and the product was worked up as in preparation A(i)(a); yield 0.228 g (71%). The product was identified as $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ on the basis of its spectroscopic and electrochemical properties.

The following four compounds were prepared by using a procedure analogous to that described in procedure A(i)(a). Reaction times and product yields are given for each.

(ii) $[Re_2Cl_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppm})_2(NCEt)]PF_6$: 3 days; 58%. *Anal.* Calcd for $C_{59}H_{60}Cl_3F_6N_3P_5Re_2$: C, 45.46; H, 3.88. Found: C, 44.97; H, 4.19.

This complex was isolated as its chloride salt, $[Re_2Cl_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppm})_2(NCEt)]Cl$, when $Re_2Cl_4(\mu\text{-dppm})_2$ was used in place of $[Re_2Cl_3(\mu\text{-dppm})_2(NCEt)_2]PF_6$. The same reaction conditions and workup as described in procedure A(i)(a) were otherwise used; yield 56%. The identity of this product was established by cyclic voltammetry on a solution in 0.1 M TBAH–CH_2Cl_2, which showed processes characteristic of the $[Re_2Cl_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppm})_2(NCEt)]^+$ cation ($E_{1/2}(ox) = +0.21$ V and $E_{1/2}(red) = -0.79$ V) together with $E_{p,a} \simeq +1.1$ V for Cl^-.

(iii) $[Re_2Cl_3(\mu\text{-}HN_2C_2\{i\text{-}Pr\}_2)(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]PF_6$: 4 days; 62%. Anal. Calcd for $C_{62}H_{66}Cl_3F_6N_3P_5Re_2$: C, 46.52; H, 4.16; Cl, 6.64. Found: C, 45.16; H, 4.30; Cl, 6.91. The microanalytical data are consistent with a very small amount of lattice CH_2Cl_2 being present in the crystals of this product.

(iv) $[Re_2Cl_3(\mu\text{-}HN_2C_2Ph_2)(\mu\text{-dppm})_2(NCPh)]PF_6$: 2 days; 57%. Anal. Calcd for $C_{71}H_{60}Cl_3F_6N_3P_5Re_2$: Cl, 5.88. Found: Cl, 6.25. This complex did not give a satisfactory carbon microanalysis. Nonetheless, its spectroscopic and electrochemical properties were in accord with a pure product and agreed well with comparable data for the other complexes of this type.

(v) $[Re_2Cl_3(\mu\text{-}HN_2C_2\{t\text{-}Bu\}_2)(\mu\text{-dppm})_2(NC\text{-}t\text{-}Bu)]PF_6$: 1 week; 39%. This reaction was especially slow and considerable quantities of unreacted starting material remained even after reflux for 1 week. Since this complex was obtained in very small quantities, it was only characterized on the basis of its electrochemical properties and IR and electronic absorption spectra.

(vi) $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$. This complex was prepared from the bis(propionitrile) derivative $[Re_2Br_3(\mu\text{-dppm})_2(NCEt)_2]PF_6$ by using procedure A(i)(b) and a reaction time of 2 days; yield 71%. Anal. Calcd for $C_{56}H_{54}Br_3F_6N_3P_5Re_2$: C, 40.76; H, 3.29. Found: C, 41.17; H, 3.68.

(vii) $[Re_2Br_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppm})_2(NCEt)]PF_6$. This complex was prepared via procedure A(i)(a) and a reaction time of 3 days; yield 57%. Anal. Calcd for $C_{59}H_{60}Br_3F_6N_3P_5Re_2$: C, 41.88; H, 3.57. Found: C, 42.32; H, 4.02.

B. Oxidations of $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]PF_6$. (i) $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)](PF_6)_2$. (a) A mixture of the green complex $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ (0.221 g, 0.146 mmol) and $NOPF_6$ (0.324 g, 0.185 mmol) in 10 mL of dichloromethane was stirred for 2 h. The excess $NOPF_6$ was removed by filtration. The red product precipitated upon the addition of ca. 40 mL of diethyl ether to the filtrate. The solid was filtered off and dissolved in a solution of ca. 1 g of KPF_6 in 15 mL of acetone. The resulting mixture was filtered, and ca. 40 mL of diethyl ether was added to the filtrate. The desired product was extracted from the resulting precipitate by using 20 mL of dichloromethane. The final product was precipitated by the addition of diethyl ether and recrystallized from an acetone/diethyl ether mixture; yield 0.204 g (84%). Anal. Calcd for $C_{56}H_{54}Cl_3F_{12}N_3P_6Re_2$: C, 40.48; H, 3.28. Found: C, 40.63; H, 3.66.

(b) Modification of the forgoing procedure by the use of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in acetone as the oxidizing medium in place of $NOPF_6$ in dichloromethane gave the title complex in 81% yield. Several recrystallizations from acetone/diethyl ether mixtures were found to be necessary in order to free the product from small amounts of unreacted $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$.

The following four complexes were prepared by using procedures analogous to procedures B(i)(a) and B(i)(b). The oxidant and the yield are given for each.

(ii) $[Re_2Cl_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppm})_2(NCEt)](PF_6)_2$: $NOPF_6$; 92%. Anal. Calcd for $C_{59}H_{60}Cl_3F_{12}N_3P_6Re_2$: C, 41.59; H, 3.55. Found: C, 39.95; H, 3.59.

(iii) $[Re_2Cl_3(\mu\text{-}HN_2C_2\{i\text{-}Pr\}_2)(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)](PF_6)_2$: $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$; 54%. Anal. Calcd for $C_{62}H_{66}Cl_3F_{12}N_3P_6Re_2$: C, 42.65; H, 3.81. Found: C, 41.56; H, 4.00.

(iv) $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)](PF_6)_2\cdot 0.75(C_2H_5)_2O$: $NOPF_6$; 86%. Anal. Calcd for $C_{59}H_{61.5}Br_3F_{12}N_3O_{0.75}P_6Re_2$: C, 38.29; H, 3.35. Found: C, 38.37; H, 3.74. The ^1H NMR spectrum of this complex (recorded in DMSO-d_6) confirmed the presence of diethyl ether in the correct stoichiometric proportion.

(v) $[Re_2Br_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppm})_2(NCEt)](PF_6)_2$: $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$; 84%. Anal. Calcd for $C_{59}H_{60}Br_3F_{12}N_3P_6Re_2$: C, 38.57; H, 3.29. Found: C, 38.37; H, 3.58.

C. Preparation of $[Re_2X_8]^{2-}$ Salts of the $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]^{2+}$ Cations. (i) $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]Re_2Cl_8$. This complex was prepared with the use of a procedure analogous to that described in procedure C(ii); yield 84%. Anal. Calcd for $C_{56}H_{54}Cl_{11}N_3P_4Re_4$: C, 33.17; H, 2.68. Found: C, 33.11; H, 2.91.

(ii) $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]Re_2Br_8$. A solution of $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)](PF_6)_2$ (0.079 g, 0.044 mmol) in acetone (30 mL) was carefully layered with a solution of $(n\text{-}Bu_4N)_2Re_2Br_8$ (0.083 g, 0.056 mmol) in acetone (30 mL). After 2 days, $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]Re_2Br_8\cdot(CH_3)_2CO$ had precipitated. The product was collected by filtration and washed with diethyl ether; yield 0.085 g (75%). Anal. Calcd for $C_{59}H_{60}Br_{11}N_3OP_4Re_4$: C, 27.52; H, 2.37. Found: C, 27.66; H, 2.50. The presence of acetone was confirmed by IR spectroscopy (ν(CO) at 1710 cm^{-1}). The complex was too insoluble for quantitative ^1H NMR spectral intensity measurements, although the presence of acetone was noted ($\delta \simeq 2.0$ in CD_2Cl_2).

D. Reactions of $(n\text{-}Bu_4N)_2Re_2X_8$ with Acetonitrile. (i) An Alternate Route to $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)](PF_6)_2$. A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.304 g, 0.266 mmol), dppm (0.385 g, 1.00 mmol), and KPF_6 (0.554 g, 3.01 mmol) was refluxed in acetonitrile for 4 days. The mixture was filtered and the filtrate evaporated to dryness. The red product was extracted into dichloromethane (ca. 50 mL) and filtered. A sufficient volume of diethyl ether was added to the filtrate to precipitate the red product, which was filtered off and dried. It was purified by recrystallization from dichloromethane/diethyl ether; yield 0.318 g (72%). This complex had spectroscopic and electrochemical properties identical with those of the samples prepared as in B(i)(a).

(ii) An Alternative Route to $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$. Upon substituting $(n\text{-}Bu_4N)_2Re_2Br_8$ for $(n\text{-}Bu_4N)_2Re_2Cl_8$ in procedure D(i), the dark green complex $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ was isolated rather than the dicationic species as in the case of the chloride; yield 83%.

Attempts to prepare other nitrile derivatives by this method led to mixtures of the monocationic and dicationic species that were not easily separated.

E. Deuterium Exchange Reactions. (i) Preparation of $[Re_2Cl_3(\mu\text{-}DN_2C_2\{CD_3\}_2)(\mu\text{-dppm})_2(NCCD_3)]PF_6$. Reaction A(i)(b) was carried out with CD_3CN in place of acetonitrile. The resulting deuteriated product showed a ν(N–D) mode in its IR spectrum (halocarbon mull) at 2487 (w) cm^{-1}.

(ii) Preparation of $[Re_2Cl_3(\mu\text{-}DN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$. This complex was prepared by refluxing $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ (0.100 g) in acetonitrile (5 mL) to which 3 drops of D_2O had been added. The IR spectrum (halocarbon mull) of the resulting product showed ν(N–D) at 2494 (w) cm^{-1}. The identical product was also obtained if a small quantity of D_2O was introduced into the reaction mixture during the synthesis of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$.

F. Reactions of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$. (i) Preparation of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]PF_6$. The acetonitrile complex $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ (0.232 g, 0.153 mmol) was refluxed in isobutyronitrile (10 mL, 110 mmol) for 24 h. The mixture was evaporated to dryness and the crude product recrystallized from dichloromethane/diethyl ether; yield 0.165 g (70%). Anal. Calcd for $C_{58}H_{58}Cl_3F_6N_3P_5Re_2$: C, 45.10; H, 3.78. Found: C, 44.13; H, 3.89.

This complex was oxidized to $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)](PF_6)_2$ by $NOPF_6$ in dichloromethane with the use of a procedure similar to procedure B(i): yield 74%.

(ii) Preparation of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCPh)]PF_6$. This complex was prepared by a procedure similar to procedure F(i) with a reaction time of 18 h; yield 50%. The identity of this product was based upon its spectroscopic and electrochemical properties.

(iii) Reactions with Isocyanides. Attempts to replace the acetonitrile ligand in $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ by reaction of this complex with excess *tert*-butyl or xylyl isocyanides in acetone or dichloromethane at room temperature or under reflux conditions were unsuccessful.

Preparations of Single Crystals. X-ray quality crystals of what we anticipated would be $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ (see procedure A(vi)) were grown by diffusion of diethyl ether vapor into an acetone solution of the complex. The structure solution indicated that the crystal was that of a complex of stoichiometry $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)_2(\mu\text{-dppm})_2(NCMe)](PF_6)_{0.8}(Br)_{0.2}\cdot{}^1/_2\text{-}$

Table I. Crystallographic Data for $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)](PF_6)_{0.8}(Br)_{0.2}\cdot{}^1/_2(C_2H_5)_2O\cdot(CH_3)_2CO$ (**1**) and $[Re_2Cl_3(\mu\text{-}HN_2C_2Me\{CHO\})(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]PF_6\cdot C_2H_4Cl_2\cdot H_2O$ (**2**)

	1	**2**
chem formula	$Re_2Br_{3.2}P_{4.8}F_{4.8}O_{1.5}N_3C_{61}C_{65}$	$Re_2Cl_5P_5F_6O_2N_3C_{60}H_{62}$
a, Å	13.150 (3)	13.001 (2)
b, Å	21.227 (5)	13.795 (5)
c, Å	12.592 (2)	19.834 (8)
α, deg	99.53 (2)	103.30 (3)
β, deg	113.35 (2)	104.43 (2)
γ, deg	74.72 (2)	97.66 (2)
V, Å^3	3106 (2)	3283 (4)
Z	2	2
fw	1732.23	1675.71
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T, °C	−150	−140
λ, Å	Mo Kα (0.71073)	Mo Kα (0.71073)
ρ_{calcd}, g cm^{-3}	1.852	1.695
μ(Mo Kα), cm^{-1}	63.88	41.18
transmissn coeff	1.000–0.749	1.000–0.492
R^a	0.066	0.051
$R_w{}^b$	0.092	0.061

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

$(C_2H_5)_2O\cdot(CH_3)_2CO$ (**1**). Many attempts to grow crystals of the complex $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]PF_6$ (see procedure F(i)) were carried out, but in only one instance was a batch of suitable crystals obtained. A small crop of red plates was obtained upon slow diffusion of diethyl ether into a solution of this complex in dichloroethane. During the structure refinement, it became apparent that this crystal was not representative of the original bulk sample. It was concluded to be that of a complex of stoichiometry $[Re_2Cl_3(\mu\text{-}HN_2C_2Me\{CHO\})(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]PF_6\cdot C_2H_4Cl_2\cdot H_2O$ (**2**).

X-ray Crystallographic Procedures. The structures of $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)](PF_6)_{0.8}(Br)_{0.2}\cdot{}^1/_2(C_2H_5)_2O\cdot(CH_3)_2CO$ (**1**) and $[Re_2Cl_3(\mu\text{-}HN_2C_2Me\{CHO\})(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]PF_6\cdot C_2H_4Cl_2\cdot H_2O$ (**2**) were determined by application of general procedures that are described more fully elsewhere.[15] The basic crystallographic parameters for **1** and **2** are listed in Table I. The cell constants are based on 25 reflections with $16.5 < \theta < 21.2°$ for **1** and $20.0 < \theta < 23.0°$ for **2**. Three standard reflections were measured after every 5000 s of beam exposure during data collection. In the case of **1**, a linear decay correction was applied to allow for an overall decay of 8% in the standards. For **2** it was necessary to allow for an anisotropic decay correction; we used the decay correction program CHORT (part of the Enraf-Nonius SDP package). Calculations were performed on a PDP 11/34 computer (for **1**) or MicroVAX computer (for **2**) using the Enraf-Nonius structure determination package.

(i) $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)](PF_6)_{0.8}(Br)_{0.2}\cdot{}^1/_2(C_2H_5)_2O\cdot(CH_3)_2CO$ (1). Since the dark green crystals of **1** were not stable at room temperature due to loss of lattice solvent, the structure determination was carried out at low temperature. A single crystal of dimensions 0.20 × 0.11 × 0.08 mm was mounted on a glass fiber with vacuum grease and cooled to −150 °C in a cold stream of gaseous N_2 with an Enraf-Nonius Type 524 temperature controller. The crystal was found to belong to the triclinic space group $P\bar{1}$. The heavy atoms were located and refined from an initial Patterson map. It was apparent early on that the terminally bound acetonitrile ligand was disordered with the $\mu\text{-}HN_2C_2Me_2$ ligand. The structure was refined accordingly, with the disorder model as shown in Figure S1, which also gives the full atomic numbering scheme for the disordered cation. An ORTEP representation of half the disorder is shown in Figure 1.

Details of the modeling of the anion disorder, involving a mixture of PF_6^- and Br^- with occupancies of 0.8 and 0.2, respectively, and the lattice solvent disorder are available as supplementary material. The largest peak in the final difference Fourier map (1.91 e/Å^3) did not appear to be of any chemical significance.

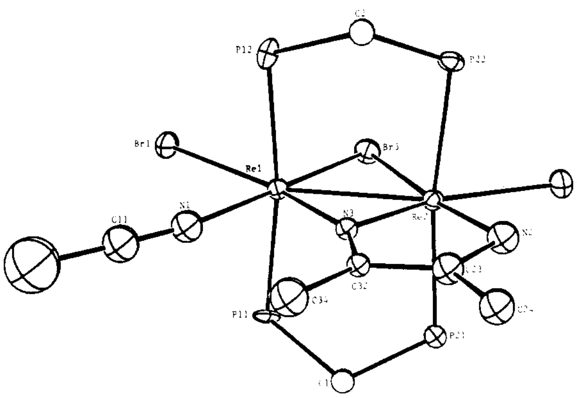

Figure 1. ORTEP view of the structure of the $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]^+$ cation of **1** with the phenyl carbon atoms of the dppm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level except for the methylene carbon atoms which are shown as circles of arbitrary radius. This view represents half of the disorder associated with the cation. The full disorder is shown in Figure S1.

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters for Non-Phenyl Ring Atoms of the $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]^+$ Cation of **1** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
Re(1)	0.49622 (6)	0.27956 (4)	0.12729 (6)	0.98 (2)
Re(2)	0.30200 (6)	0.28092 (4)	−0.05427 (6)	0.98 (2)
Br(1)	0.6416 (2)	0.3430 (1)	0.2759 (2)	1.83 (5)
Br(2)	0.1177 (2)	0.3479 (1)	−0.1935 (2)	1.94 (5)
Br(3)	0.3631 (2)	0.3862 (1)	0.0485 (2)	1.60 (5)
P(11)	0.4087 (4)	0.2860 (2)	0.2691 (4)	1.1 (1)
P(12)	0.6102 (4)	0.2657 (2)	0.0082 (4)	1.1 (1)
P(21)	0.1934 (4)	0.2754 (2)	0.0633 (4)	1.1 (1)
P(22)	0.3878 (4)	0.2782 (2)	−0.1959 (4)	1.2 (1)
N(1)	0.609 (1)	0.2005 (9)	0.211 (1)	2.1 (4)*
N(2)	0.244 (1)	0.2018 (9)	−0.151 (1)	2.1 (3)*
N(3)	0.421 (1)	0.2094 (7)	0.029 (1)	1.0 (3)*
C(1)	0.289 (1)	0.2436 (8)	0.200 (1)	0.0 (3)*
C(2)	0.532 (2)	0.2319 (9)	−0.139 (2)	1.3 (4)*
C(11)	0.686 (4)	0.166 (2)	0.276 (4)	3 (1)*
C(12)	0.785 (6)	0.123 (3)	0.359 (6)	6 (2)*
C(13)	0.572 (3)	0.141 (2)	0.152 (3)	1.7 (8)*
C(14)	0.639 (4)	0.074 (2)	0.200 (4)	3 (1)*
C(21)	0.188 (4)	0.170 (2)	−0.232 (4)	3 (1)*
C(22)	0.128 (5)	0.123 (3)	−0.326 (6)	6 (2)*
C(23)	0.320 (3)	0.143 (2)	−0.098 (3)	1.9 (8)*
C(24)	0.289 (3)	0.076 (2)	−0.162 (4)	2.1 (9)*
C(31)	0.466 (3)	0.147 (2)	0.057 (4)	2.1 (9)*
C(32)	0.417 (3)	0.147 (2)	0.003 (3)	1.0 (7)*
C(33)	0.417 (3)	0.089 (2)	−0.014 (3)	1.8 (8)*
C(34)	0.500 (4)	0.089 (2)	0.063 (4)	2.6 (9)*

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Values marked with an asterisk are for isotropically refined atoms. Data for the phenyl ring carbon atoms, the lattice solvent molecule atoms, and the atoms of the PF_6^- anion are available as supplementary material.

An empirical absorption correction was applied.[16] The linear absorption coefficient was 63.88 cm^{-1}. No correction was made for extinction. The least squares program minimized the function $\sum w(|F_o| - |F_c|)^2$, where *w* is a weighting factor defined as $w = 1/\sigma^2(F_o)$. Because of the various disorder problems, only the Re, Br, P, and F atoms were refined anisotropically, and corrections for anomalous scattering were applied.[17] All other non-hydrogen atoms were refined isotropically. Hydrogens were not included in the least-squares refinement. The final residuals were $R = 0.066$ and $R_w = 0.092$ for 6019 data with $I > 3\sigma(I)$.

Positional parameters and their errors for the non-phenyl group atoms of the dirhenium cation of **1** are listed in Table II. Important intra-

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(15) Fanwick, P. E.; Harwood, W. S.; Walton, R. A. *Inorg. Chim. Acta* **1986**, *122*, 7.

(16) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.

(17) (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 III. Important Bond Distances (Å) and Bond Angles (deg) for **1**[a]

Distances			
Re(1)-Re(2)	2.6656 (8)	P(12)-C(2)	1.86 (5)
Re(1)-Br(1)	2.580 (2)	P(12)-C(1211)	1.77 (1)
Re(1)-Br(3)	2.540 (2)	P(12)-C(1221)	1.82 (2)
Re(1)-P(11)	2.449 (3)	P(21)-C(1)	1.79 (3)
Re(1)-P(12)	2.447 (4)	P(21)-C(2111)	1.81 (1)
Re(1)-N(1)	2.04 (1)	P(21)-C(2121)	1.85 (2)
Re(1)-N(3)	1.98 (1)	P(22)-C(2)	1.80 (5)
Re(2)-Br(2)	2.571 (2)	P(22)-C(2211)	1.85 (1)
Re(2)-Br(3)	2.545 (2)	P(22)-C(2221)	1.82 (1)
Re(2)-P(21)	2.463 (4)	N(1)-C(11)	1.18 (3)
Re(2)-P(22)	2.446 (3)	N(2)-C(23)	1.45 (4)
Re(2)-N(2)	2.03 (1)	N(3)-C(32)	1.32 (4)
Re(2)-N(3)	1.96 (1)	C(11)-C(12)	1.49 (5)
P(11)-C(1)	1.86 (3)	C(23)-C(24)	1.58 (4)
P(11)-C(1111)	1.85 (2)	C(23)-C(32)	1.41 (5)
P(11)-C(1121)	1.80 (2)	C(32)-C(34)	1.49 (4)

Angles			
Re(2)-Re(1)-Br(1)	148.87 (4)	P(22)-Re(2)-N(3)	93.5 (4)
Re(2)-Re(1)-Br(3)	58.48 (4)	N(2)-Re(2)-N(3)	79.2 (5)
Re(2)-Re(1)-P(11)	93.80 (9)	Re(1)-Br(3)-Re(2)	63.22 (4)
Re(2)-Re(1)-P(12)	94.06 (9)	Re(1)-P(11)-C(1)	107 (1)
Re(2)-Re(1)-N(1)	127.8 (3)	Re(1)-P(11)-C(1111)	121.3 (5)
Re(2)-Re(1)-N(3)	47.1 (4)	Re(1)-P(11)-C(1121)	113.0 (6)
Br(1)-Re(1)-Br(3)	90.59 (5)	C(1)-P(11)-C(1111)	104 (1)
Br(1)-Re(1)-P(11)	89.60 (9)	C(1)-P(11)-C(1121)	106 (1)
Br(1)-Re(1)-P(12)	85.47 (9)	C(1111)-P(11)-C(1121)	104.0 (8)
Br(1)-Re(1)-N(1)	83.3 (3)	Re(1)-P(12)-C(2)	109 (2)
Br(1)-Re(1)-N(3)	163.6 (4)	Re(1)-P(12)-C(1211)	123.0 (5)
Br(3)-Re(1)-P(11)	90.55 (9)	Re(1)-P(12)-C(1221)	112.0 (5)
Br(3)-Re(1)-P(12)	96.54 (9)	C(2)-P(12)-C(1211)	104 (2)
Br(3)-Re(1)-N(1)	172.6 (3)	C(2)-P(12)-C(1221)	104 (2)
Br(3)-Re(1)-N(3)	105.5 (4)	C(1211)-P(12)-C(1221)	103.0 (7)
P(11)-Re(1)-P(12)	171.4 (1)	Re(2)-P(21)-C(1)	109 (1)
P(11)-Re(1)-N(1)	85.3 (3)	Re(2)-P(21)-C(2111)	122.4 (5)
P(11)-Re(1)-N(3)	93.0 (4)	Re(2)-P(21)-C(2121)	111.6 (5)
P(12)-Re(1)-N(1)	87.1 (3)	C(1)-P(21)-C(2111)	106 (1)
P(12)-Re(1)-N(3)	89.8 (4)	C(1)-P(21)-C(2121)	103 (1)
N(1)-Re(1)-N(3)	80.8 (5)	C(2111)-P(21)-C(2121)	103.1 (7)
Re(1)-Re(2)-Br(2)	148.45 (4)	Re(2)-P(22)-C(2)	108 (2)
Re(1)-Re(2)-Br(3)	58.30 (4)	Re(2)-P(22)-C(2211)	119.4 (5)
Re(1)-Re(2)-P(21)	94.20 (9)	Re(2)-P(22)-C(2221)	115.2 (5)
Re(1)-Re(2)-P(22)	93.92 (7)	C(2)-P(22)-C(2211)	107 (2)
Re(1)-Re(2)-N(2)	126.8 (3)	C(2)-P(22)-C(2221)	104 (2)
Re(1)-Re(2)-N(3)	47.7 (4)	C(2211)-P(22)-C(2221)	102.5 (7)
Br(2)-Re(2)-Br(3)	90.17 (5)	Re(1)-N(1)-C(11)	164 (2)
Br(2)-Re(2)-P(21)	87.41 (9)	Re(2)-N(2)-C(23)	109 (2)
Br(2)-Re(2)-P(22)	87.77 (7)	Re(1)-N(3)-Re(2)	85.3 (5)
Br(2)-Re(2)-N(2)	84.8 (3)	Re(1)-N(3)-C(32)	151 (2)
Br(2)-Re(2)-N(3)	163.7 (4)	P(11)-C(1)-P(21)	112 (2)
Br(3)-Re(2)-P(21)	95.69 (9)	P(12)-C(2)-P(22)	111 (3)
Br(3)-Re(2)-P(22)	91.98 (7)	N(1)-C(11)-C(12)	179 (2)
Br(3)-Re(2)-N(2)	174.3 (3)	N(2)-C(23)-C(24)	116 (2)
Br(3)-Re(2)-N(3)	106.0 (4)	N(2)-C(23)-C(32)	120 (3)
P(21)-Re(2)-P(22)	171.0 (1)	C(24)-C(23)-C(32)	124 (3)
P(21)-Re(2)-N(2)	86.7 (3)	N(3)-C(32)-C(23)	108 (3)
P(21)-Re(2)-N(3)	89.0 (4)	N(3)-C(32)-C(34)	128 (3)
P(22)-Re(2)-N(2)	85.2 (3)	C(23)-C(32)-C(34)	124 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. The distances and angles are for half of the disorder; data for the other half are included in the supplementary material.

Table IV. Positional Parameters and Equivalent Isotropic Displacement Parameters for Non-Phenyl Ring Atoms of the $[Re_2Cl_3(\mu\text{-}HN_2C_2Me\{CHO\})(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]^+$ Cation of **2** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
Re(1)	0.24655 (4)	0.69331 (4)	0.30140 (3)	1.54 (1)
Re(2)	0.13008 (5)	0.82484 (4)	0.26273 (3)	1.84 (1)
Cl(1)	0.3773 (3)	0.6582 (3)	0.3991 (2)	2.35 (8)
Cl(2)	0.0635 (3)	0.9785 (3)	0.2958 (2)	3.2 (1)
Cl(3)	0.2415 (3)	0.8491 (2)	0.3854 (2)	1.92 (8)
P(11)	0.0991 (3)	0.5999 (3)	0.3313 (2)	2.06 (9)
P(12)	0.4014 (3)	0.7662 (3)	0.2676 (2)	1.79 (8)
P(21)	−0.0374 (3)	0.7391 (3)	0.2786 (2)	2.14 (9)
P(22)	0.2762 (3)	0.9259 (3)	0.2348 (2)	2.18 (9)
O(2)	0.061 (1)	0.230 (1)	−0.0126 (8)	6.9 (4)
N(1)	0.260 (1)	0.5534 (9)	0.2461 (7)	2.8 (3)
N(2)	0.046 (1)	0.8092 (9)	0.1599 (7)	3.0 (3)
N(3)	0.1512 (8)	0.6929 (7)	0.2079 (6)	1.5 (2)*
C(1)	−0.032 (1)	0.604 (1)	0.2711 (8)	2.3 (4)
C(2)	0.358 (1)	0.839 (1)	0.2022 (7)	1.9 (3)
C(11)	0.275 (1)	0.472 (1)	0.2264 (9)	3.5 (4)
C(12)	0.283 (1)	0.363 (1)	0.200 (1)	4.0 (5)
C(13)	0.297 (2)	0.343 (1)	0.122 (1)	5.0 (5)
C(14)	0.377 (2)	0.340 (1)	0.256 (1)	5.4 (5)
C(21)	0.047 (1)	0.721 (1)	0.1094 (8)	3.0 (4)
C(22)	0.007 (2)	0.295 (1)	0.969 (1)	4.6 (5)
C(31)	0.109 (1)	0.655 (1)	0.1389 (8)	2.6 (4)
C(32)	0.124 (1)	0.555 (1)	0.0950 (9)	3.6 (4)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. The value marked with an asterisk is for an isotropically refined atom.

molecular bond distances and angles are in Table III. Tables giving full details of the crystal data and data collection parameters (Table S1), atomic positional parameters (Table S2), thermal parameters (Table S3), and complete listings of bond distances (Table S4) and bond angles (Table S5) are available as supplementary material, as well as a figure (Figure S1) that shows the full atomic numbering scheme of the disordered model for the dirhenium cation. The quality of the crystals and the difficulties in modeling the disorders is reflected in the relatively high standard deviations associated with some of the bond distances and angles and in the isotropic thermal parameters obtained for some of the atoms, e.g. the C(1) carbon of one of the dppm ligands.

(ii) $[Re_2(\mu\text{-}HN_2C_2Me\{CHO\})(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]PF_6\cdot C_2H_4Cl_2\cdot H_2O$. The structure of this complex, like that of **1**, was determined at low temperature (−140 °C). The crystal was found to belong to the triclinic space group $P\bar{1}$. The type of disorder that plagued the dirhenium cation of **1** was no longer present in **2**, thereby simplifying the structure refinement. However, the structure determination proved to be nonroutine in two important respects. Most importantly, during the latter stages of the refinement of that portion of the dirhenium cation which contained the coupled acetonitrile ligands, difference maps revealed a region of electron density (ca. 5 e/Å^3) at a bonding distance (ca. 1.2 Å) to what we had anticipated would be the exocyclic "methyl" group (C(22)). This exocyclic fragment was treated in three ways. First, it was modeled as $-CH_2CH_3$, then as $-CH_2NH_2$, and finally as an aldehyde grouping, $-CHO$.[18] The last choice gave by far the most satisfactory solution, the resulting C(21)-C(22) and C(22)-O(2) distances of 1.50 (2) and 1.28 (3)Å, and the C(21)-C(22)-O(2) angle of 117 (2)° being in good agreement with this supposition. Apparently, this exocyclic methyl group in $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]PF_6$ was oxidized during the recrystallization by a mechanism we do not as yet understand.

A second problem arose in the refinement of several regions of residual electron density that were apparent in the difference Fourier maps but were not at bonding distances to the dirhenium cation or the PF_6^- anion. These were modeled as lattice solvent, primarily 1,2-dichloroethane. One molecule resides on an inversion center, and is therefore constrained to have the fully staggered (or anti) conformation. The other molecule resides on a general position with 50% occupancy. The latter molecule adopts a gauche conformation. Further details relating to the modeling of the lattice solvent disorder are available as supplementary material. A further peak in the difference maps was satisfactorily modeled as the oxygen atom O(1) of a water molecule. The largest unassigned peak (1.7 e/Å^3) in the final Fourier difference map is situated between the oxygen of this water molecule and a carbon atom (C(1000)) of one of the 1,2-dichloroethane molecules. It did not appear to be of any special chemical significance.

An empirical absorption correction was applied.[16] The linear absorption coefficient was 41.18 cm^{-1}. No correction was made for extinction. The Re, Cl, P, C, N, and O atoms of the dirhenium cation and the P and F atoms of the hexafluorophosphate anion were refined anisotropically and corrections for anomalous scattering were applied.[17] The atoms of the lattice solvent molecules were refined isotropically. Hydrogen atoms were not included. The final residuals were $R = 0.051$ and $R_w = 0.061$ for 5667 data with $I > 3\sigma(I)$.

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(18) It was also modeled as a disorder involving the partial occupancy of the methyl site by an ethyl group such that there was a superimposition of the methyl group carbon atom with that of the methylene carbon atom of the ethyl group. This again proved to be unsatisfactory. Incidentally, our rationale for considering this possibility was that the preparation of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]PF_6$ can start from the propionitrile complex $[Re_2Cl_3(\mu\text{-dppm})_2(NCEt)_2]PF_6$ (see procedures A(i)(b) and F(i)). In this event cross-coupling of acetonitrile and propionitrile could result, although we have no independent evidence that it does.

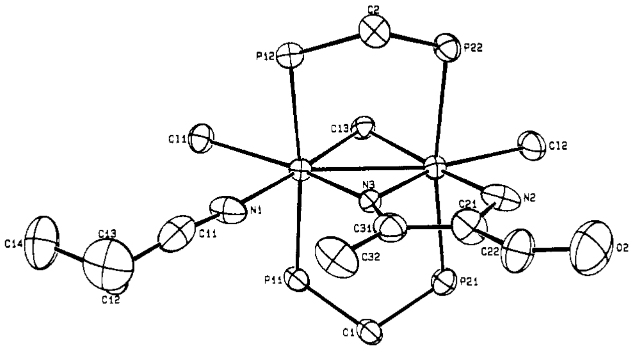

Figure 2. ORTEP view of the structure of the $[Re_2Cl_3(\mu\text{-}HN_2C_2Me\{CHO\})(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]^+$ cation of **2** with the phenyl carbon atoms of the dppm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level for anisotropically refined atoms.

Table V. Important Bond Distances (Å) and Bond Angles (deg) for **2**[a]

Distances			
Re(1)–Re(2)	2.6396 (8)	P(12)–C(1221)	1.82 (1)
Re(1)–Cl(1)	2.427 (4)	P(21)–C(1)	1.84 (1)
Re(1)–Cl(3)	2.417 (3)	P(21)–C(2111)	1.83 (2)
Re(1)–P(11)	2.439 (4)	P(21)–C(2121)	1.83 (1)
Re(1)–P(12)	2.441 (4)	P(22)–C(2)	1.82 (2)
Re(1)–N(1)	2.04 (1)	P(22)–C(2211)	1.81 (1)
Re(1)–N(3)	1.96 (1)	P(22)–C(2221)	1.82 (2)
Re(2)–Cl(2)	2.409 (4)	O(2)–C(22)	1.28 (3)
Re(2)–Cl(3)	2.422 (3)	N(1)–C(11)	1.16 (2)
Re(2)–P(21)	2.462 (4)	N(2)–C(21)	1.39 (2)
Re(2)–P(22)	2.456 (4)	N(3)–C(31)	1.29 (2)
Re(2)–N(2)	2.00 (1)	C(11)–C(12)	1.50 (2)
Re(2)–N(3)	1.99 (1)	C(12)–C(13)	1.56 (3)
P(11)–C(1)	1.84 (1)	C(12)–C(14)	1.56 (3)
P(11)–C(1111)	1.83 (2)	C(21)–C(22)	1.50 (2)
P(11)–C(1121)	1.85 (2)	C(21)–C(31)	1.43 (2)
P(12)–C(2)	1.84 (2)	C(31)–C(32)	1.52 (2)
P(12)–C(1211)	1.80 (2)		
Angles			
Re(2)–Re(1)–Cl(1)	145.61 (8)	Re(1)–P(11)–C(1)	109.9 (6)
Re(2)–Re(1)–Cl(3)	57.04 (8)	Re(1)–P(11)–C(1111)	121.3 (4)
Re(2)–Re(1)–P(11)	92.7 (1)	Re(1)–P(11)–C(1121)	114.5 (6)
Re(2)–Re(1)–P(12)	93.6 (1)	C(1)–P(11)–C(1111)	104.9 (7)
Re(2)–Re(1)–N(1)	132.2 (3)	C(1)–P(11)–C(1121)	102.7 (6)
Re(2)–Re(1)–N(3)	48.5 (3)	C(1111)–P(11)–C(1121)	101.6 (7)
Cl(1)–Re(1)–Cl(3)	88.7 (1)	Re(1)–P(12)–C(2)	110.4 (5)
Cl(1)–Re(1)–P(11)	90.0 (1)	Re(1)–P(12)–C(1211)	113.0 (5)
Cl(1)–Re(1)–P(12)	86.8 (1)	Re(1)–P(12)–C(1221)	122.8 (6)
Cl(1)–Re(1)–N(1)	82.1 (4)	C(2)–P(12)–C(1211)	104.0 (7)
Cl(1)–Re(1)–N(3)	165.6 (3)	C(2)–P(12)–C(1221)	102.3 (6)
Cl(3)–Re(1)–P(11)	91.1 (1)	C(1211)–P(12)–C(1221)	102.2 (7)
Cl(3)–Re(1)–P(12)	95.4 (1)	Re(2)–P(21)–C(1)	109.1 (5)
Cl(3)–Re(1)–N(1)	170.1 (4)	Re(2)–P(21)–C(2111)	123.3 (4)
Cl(3)–Re(1)–N(3)	105.5 (3)	Re(2)–P(21)–C(2121)	109.8 (6)
P(11)–Re(1)–P(12)	172.7 (1)	C(1)–P(21)–C(2111)	104.4 (7)
P(11)–Re(1)–N(1)	85.2 (4)	C(1)–P(21)–C(2121)	104.3 (6)
P(11)–Re(1)–N(3)	92.2 (3)	C(2111)–P(21)–C(2121)	104.3 (7)
P(12)–Re(1)–N(1)	87.9 (4e)	Re(2)–P(22)–C(2)	107.2 (5)
P(12)–Re(1)–N(3)	89.3 (4)	Re(2)–P(22)–C(2211)	121.9 (6)
N(1)–Re(1)–N(3)	83.9 (5)	Re(2)–P(22)–C(2221)	113.6 (6)
Re(1)–Re(2)–Cl(2)	149.4 (1)	C(2)–P(22)–C(2211)	106.6 (6)
Re(1)–Re(2)–Cl(3)	56.85 (8)	C(2)–P(22)–C(2221)	102.6 (8)
Re(1)–Re(2)–P(21)	94.9 (1)	C(2211)–P(22)–C(2221)	103.2 (7)
Re(1)–Re(2)–P(22)	94.7 (1)	Re(1)–N(1)–C(11)	168 (1)
Re(1)–Re(2)–N(2)	122.9 (4)	Re(2)–N(2)–C(21)	116 (1)
Re(1)–Re(2)–N(3)	47.5 (3)	Re(1)–N(3)–Re(2)	84.1 (4)
Cl(2)–Re(2)–Cl(3)	92.6 (1)	Re(1)–N(3)–C(31)	152 (1)
Cl(2)–Re(2)–P(21)	85.1 (1)	Re(2)–N(3)–C(31)	124 (1)
Cl(2)–Re(2)–P(22)	88.0 (1)	P(11)–C(1)–P(21)	107.6 (6)
Cl(2)–Re(2)–N(2)	87.6 (4)	P(12)–C(2)–P(22)	110.0 (8)
Cl(2)–Re(2)–N(3)	162.8 (3)	N(1)–C(11)–C(12)	174 (2)
Cl(3)–Re(2)–P(21)	95.9 (1)	C(11)–C(12)–C(13)	109 (2)
Cl(3)–Re(2)–P(22)	91.6 (1)	C(11)–C(12)–C(14)	108 (1)
Cl(3)–Re(2)–N(2)	176.3 (4)	C(13)–C(12)–C(14)	114 (2)
Cl(3)–Re(2)–N(3)	104.3 (3)	N(2)–C(21)–C(22)	121 (2)
P(21)–Re(2)–P(22)	170.0 (1)	N(2)–C(21)–C(31)	114 (1)
P(21)–Re(2)–N(2)	87.7 (4)	C(22)–C(21)–C(31)	125 (1)
P(21)–Re(2)–N(3)	90.6 (3)	N(3)–C(31)–C(21)	110 (1)
P(22)–Re(2)–N(2)	84.7 (4)	N(3)–C(31)–C(32)	125 (1)
P(22)–Re(2)–N(3)	93.9 (3)	C(21)–C(31)–C(32)	125 (1)
N(2)–Re(2)–N(3)	75.6 (5)	O(2)–C(22)–C(21)	117 (2)

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

Positional parameters and their errors for the non-phenyl group atoms of the cation of **2** are listed in Table IV, while important intramolecular bond distances and angles are listed in Table V. An ORTEP representation of the dirhenium cation of **2** is shown in Figure 2. Tables giving full details of the crystal and data collection parameters (Table S6), atomic positional parameters (Table S7), thermal parameters (Table S8), and complete of bond distances (Table S9) and bond angles (Table S10) are available as supplementary material, as well as a figure (Figure S2) that shows the full atomic numbering scheme for the dirhenium cation of **2**.

Physical Measurements. Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol or halocarbon mulls with IBM Instruments IR/32 and Perkin-Elmer 1800 Fourier transform spectrometers. Electronic absorption spectra were recorded on IBM Instruments 9420 UV–visible (900–200 nm) and Hewlett Packard HP8451A (820–190 nm) spectrophotometers. Electrochemical experiments were carried out by using a Bioanalytical Systems Inc. Model CV-1A instrument 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 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, which was used as an internal standard. Conductivity measurements were performed on ca. 10^{-3} M acetone solutions by using an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. ^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. $^{31}P\{^1H\}$ spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock using aqueous 85% H_3PO_4 as an external standard. X-Band ESR spectra of dichloromethane solutions were recorded at ca. −160 °C with the use of a Varian E-109 spectrometer. Magnetic susceptibility measurements were performed by Dr. Thomas J. Smith, Kalamazoo College, using a Cahn/Ventron Faraday Susceptibility Balance. The complex $Hg[Co(NCS)_4]$ was used as the calibrant, and diamagnetic corrections were estimated from Pascal's constants.

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

Results and Discussion

(a) Synthesis of $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]PF_6$ (X = Cl, Br). The reductive coupling of acetonitrile ligands has been accomplished by heating the preformed bis(acetonitrile) complex $[Re_2Cl_3(\mu\text{-dppm})_2(NCMe)_2]PF_6$[12] in acetonitrile for 3 days. A dark green complex of stoichiometry $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ is the resulting product (yield ca. 55%). The bis(propionitrile) complex can be reacted with refluxing acetonitrile to give the same product, thereby establishing the lability of the nitrile ligands in the *bis*(nitrile) starting materials to complete nitrile exchange. The generality of this reaction has been established through the isolation of analogous products arising from the coupling of propionitrile, isobutyronitrile, trimethylacetonitrile, and benzonitrile, as well as the corresponding bromo complexes in the case of the acetonitrile and propionitrile derivatives. Since these reactions are very sluggish when carried out at room temperature, the reflux conditions that we used represent a compromise between reasonable product yield (at least 50%) and reaction times that were deemed not to be excessively long (ca. 3 days). Attempts to better control the reactions by using stoichiometric amounts of the nitrile ligand (1–2 equiv) in a reaction solvent such as 1,2-dichloroethane led to little or no reaction. Use of the neat nitrile was necessary for reasonable product yields and reaction times.

In the case of the propionitrile-coupled species $[Re_2Cl_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppm})_2(NCEt)]^+$, we showed that it is also generated by the direct reaction of $Re_2Cl_4(\mu\text{-dppm})_2$ with refluxing propionitrile. This result is not surprising since the bis(nitrile) complexes $[Re_2X_3(\mu\text{-dppm})_2(NCR)_2]PF_6$ are themselves formed directly from $Re_2X_4(\mu\text{-dppm})_2$.[12]

While we found no evidence for any detectable amounts of *cross-nitrile coupling*, for example, in the reaction of $[Re_2Cl_3(\mu\text{-dppm})_2(NCEt)_2]PF_6$ with acetonitrile, we did establish the lability of the uncoupled nitrile ligand in $[Re_2X_3(\mu\text{-}$

Table VI. Cyclic Voltammetric Data and Spectroscopic Properties for $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR')]PF_6$

complex			voltammetric half-wave potentials,[a] V		IR,[c] cm^{-1}		ESR[d]
R	R′	X	$E_{1/2}(ox)$[b]	$E_{1/2}(red)$[b]	ν(N—H)	ν(C≡N)	g_{av}
Me	Me	Cl	+0.19 (110)	-0.80 (110)	3354 w	2286 vw	2.12
Et	Et	Cl	+0.21 (110)	-0.79 (110)	3354 w	≃2280 vw	2.08
i-Pr	*i*-Pr	Cl	+0.25 (110)	-0.77 (110)	3344 w	*e*	2.12
t-Bu	*t*-Bu	Cl	+0.20 (100)	-0.81 (100)	3341 vw	*e*	*f*
Ph	Ph	Cl	+0.32 (80)	-0.64 (80)	3346 vw	*e*	2.13
Me	Me	Br	+0.25 (110)	-0.72 (110)	3350 w	2287 vw	2.13
Et	Et	Br	+0.28 (110)	-0.70 (110)	3345 m-w	*e*	2.14
Me	*i*-Pr	Cl	+0.18 (110)	-0.79 (120)	3349 vw	*e*	*f*
Me	Ph	Cl	+0.19 (110)	-0.77 (120)	3352 vw	2247 vw	2.13

[a] Versus Ag/AgCl. Recorded on solutions in 0.1 M TBAH–CH_2Cl_2 by the use of a Pt-bead electrode. Data obtained at v = 200 mV s^{-1}. [b] Numbers in parentheses are ΔE_p (i.e., $E_{p,a} - E_{p,c}$). [c] Nujol mulls. [d] X-Band ESR spectra recorded at -160 °C on dichloromethane solutions. [e] Not observed. [f] Not measured.

$HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]PF_6$ to nitrile exchange. This was shown in the case of the reactions of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ with isobutyronitrile and benzonitrile, which yielded $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCR)]PF_6$ (R = *i*-Pr or Ph) in good yield.

(b) Spectroscopic and Other Properties of $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]PF_6$. The nine complexes of this general type have very similar electrochemical and spectroscopic properties, important details of which are listed in Table VI. Cyclic voltammetric (CV) measurements on solutions of the complexes in 0.1 M TBAH–CH_2Cl_2 show the existence of a reversible one-electron oxidation ($E_{1/2}(ox)$) between +0.19 and +0.32 V vs Ag/AgCl, and a one-electron reduction ($E_{1/2}(red)$) between -0.64 and -0.80 V vs Ag/AgCl. The dicationic one-electron-oxidized product can be accessed by bulk electrolysis or with the use of a one-electron chemical oxidant (see section d). Solutions of the complexes in acetone ($\simeq 1 \times 10^{-3}$ M) were shown to have conductivities typical of those expected for 1:1 electrolytes[19] in this solvent with Λ_m values in the range 113 to 126 Ω^{-1} cm^2 mol^{-1}. The electronic absorption spectra of these complexes, measured in dichloromethane, were strikingly similar to one another, implying that they have essentially identical electronic structures. The spectrum of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$, which is representative of this group of complexes, exhibits the following absorption bands (λ_{max} values (nm); molar extinction coefficients (M^{-1} cm^{-1}) in parentheses): 800 (910), 720 sh, 650 (2330), 478 (5570), ≃450 sh, 393 (11 300). Data for the other complexes are available in Table S11.

The most useful diagnostic feature in the IR spectra of the complexes (recorded as Nujol mulls) is the ν(N–H) mode of the coupled nitrile ligands. This is seen as a weak (generally sharp) absorption close to 3350 cm^{-1}. It shifts to 2494 cm^{-1} in the deuteriated product $[Re_2Cl_3(\mu\text{-}DN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$. The ν(C≡N) mode of the coordinated, uncoupled, nitrile ligand is seen as a very weak band in the spectra of some of these complexes (Table VI).

The paramagnetism of these complexes is indicated by the appearance of broad, poorly defined resonances in their ^1H NMR spectra and confirmed by magnetic susceptibility and ESR spectral measurements. The magnetic moments of the three complexes $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ and $[Re_2X_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppm})_2(NCEt)]PF_6$ (X = Cl, Br) were within experimental error the same (μ_{eff} = 2.0, 2.0, and 1.9 (±0.1) μ_B, respectively). The X-band ESR spectra of dichloromethane solutions of most of the complexes were recorded at low temperature (−160 °C). Each displayed a fairly isotropic but very broad signal centered at $g \simeq 2.1$ (Table VI) that showed complex hyperfine structure. In all instances, the signals had a spectral width of ca. 3.3 kG. A representative spectrum is available in the supplementary material (Figure S3). The complexity of the hyperfine structure presumably reflects coupling of the unpaired electron to the dirhenium core, the coupled nitrile ring system, and, perhaps, the phosphorus atoms. The striking similarity between the spectra of analogous chloride and bromide complexes indicates that there is little contribution from the halide ligands to the HOMO.

(c) X-ray Structural Results. The structure of the $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]^+$ cation in **1** is that of an edge-sharing bioctahedron. In addition to the trans disposition of dppm ligands, the ORTEP representation (Figure 1) shows that the three bromide ligands occupy mutually cis positions on one side of the molecule in the equatorial plane. The bridgehead methylene carbon atoms C(1) and C(2) are folded over on the side of the molecule that contains the acetonitrile ligand and the five-membered metallacyclic ring formed from the coupling of two acetonitrile ligands. Related structures involving this same geometry for the $[Re_2X_3(\mu\text{-dppm})_2]$ fragment (X = Cl, Br) have been reported previously for $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$,[2] $[Re_2Cl_3(dppm)_2(CO)_2(NCEt)]PF_6$,[20] and $Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)$.[21] The Re–Re bond distance of 2.666 (1) Å is somewhat longer than that seen in other edge-shared bioctahedral dirhenium complexes of this general type, e.g., $[Re_2Cl_3(dppm)_2(CO)_3]PF_6$ (2.582 (1) Å)[2] and $[Re_2Cl_3(dppm)_2(CO)_2(NCEt)]PF_6$ (2.586 (1) Å).[20] The extent to which this reflects differences in Re–Re bond order is not easily assessed in view of the presence of the unusual coupled nitrile ligand. This point will be discussed further in section e. The other bond distances and angles involving the $[Re_2X_3(\mu\text{-dppm})_2]$ unit (see Table III) are unexceptional[2,20,21] and need not be discussed further. As far as the acetonitrile ligand is concerned, the distance Re(1)–N(1) of 2.04(1) Å compares favorably with the analogous distance of 2.03 (2) Å in the structure of $[Re_2Cl_3(dppm)_2(CO)_2(NCEt)]PF_6$.[20] While the C≡N bond distance N(1)–C(11) for the coordinated nitrile ligand of **1** is longer than that in $[Re_2Cl_3(dppm)_2(CO)_2(NCEt)]PF_6$,[20] this distance is nonetheless within the range observed for other nitrile complexes[22] and agrees well with the corresponding distance in the structure of **2** (vide infra). The extent to which this distance is an artifact of the disorder problem that involves the nitrile and coupled nitrile ligands (see Experimental Section) is difficult to gauge. Interestingly, while a similar explanation can be advanced to account for the rather large deviation from linearity of the Re(1)–N(1)–C(11) unit, the magnitude of which is greater than usual for nitrile complexes,[22] it turns out that this angle (i.e. 164 (2)°) is not that much different from the comparable angle in **2**.

While the structure refined sufficiently well to clearly establish that the coupled nitrile ligand had given rise to a *planar*, five-membered metallacycle, the low precision of the structure stemming from the disorder problem precluded a detailed description of this ring. The shortness of the bridging Re–N bonds (Re(1)–N(3) = 1.98 (1) Å and Re(2)–N(3) = 1.96 (1) Å) imply that these may represent strong Re–amido(N) σ interactions with

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[19] Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

[20] Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 4180.

[21] Anderson, L. B.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Price, A. C.; Reid, A. H.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 2717.

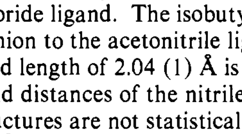
[22] Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1.

contributing N(pπ)–Re(dπ) bonding. Also, the shortness of the bond N(3)–C(32), relative to the other C–C and C–N ring bonds, indicates that the delocalization in this ring is far from uniform. Interestingly, there is an internal consistency in the bond distances and angles for the coupled nitrile ligand within the *halves* of the nitrile disorder (see Tables S4 and S5). Two separate low-temperature data sets were collected on crystals obtained from different preparative samples of **1**, and both showed exactly these same structural features.

The displacement of the acetonitrile ligand in $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ by isobutyronitrile gave a complex cation that no longer exhibited the type of disorder present in the structure of **1**. The resulting complex had the requisite properties for a complex of stoichiometry $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]PF_6$ (see Experimental Section and Table VI), but all attempts to grow suitable X-ray quality crystals failed, *with one exception.* A few crystals that grew from a 1,2-dichloroethene/diethyl ether solution of this complex over a period of several weeks proved to be those of a compound of stoichiometry $[Re_2Cl_3(\mu\text{-}HN_2C_2Me\{CHO\})(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)]PF_6{\cdot}C_2H_4Cl_2{\cdot}H_2O$ (**2**). Although we have not yet established how one of the methyl groups was oxidized, we note that the formation of aldehydes from the oxidation of methyl groups adjacent to alkenes is well-known, e.g. the oxidation of propylene to acrolein.[23] We plan to explore this point further. Nonetheless, the structure determination of **2** confirmed the important details we had established in our structural analysis of **1**. The structure of the dirhenium cation, with the phenyl rings omitted, is shown in Figure 2. Bond distances and angles are listed in Table V.

The $[Re_2Cl_3(\mu\text{-dppm})_2]$ unit, which consists of an all-cis arrangement of chlorides and a trans arrangement of dppm ligands, is isostructural with the comparable unit in the structure of **1**. The Re–Re bond length of 2.640 (1) Å, which is slightly shorter than that in **1**, may reflect the change from bromide to the smaller chloride ligand. The isobutyronitrile ligand is bound in a similar fashion to the acetonitrile ligand present in **1**. The Re(1)–N(1) bond length of 2.04 (1) Å is the same as that in **1**, and the C≡N bond distances of the nitrile ligands (N(1)–C(11)) in these two structures are not statistically different (1.18 (3) Å for **1** vs 1.16 (2) Å for **2**). The same is probably true of the associated Re–N–C angles (labeled Re(1)–N(1)–C(11) in both structures), which are 164 (2)° for **1** and 168 (1)° for **2**, although the larger angle may indeed reflect a closer approach to linearity of the Re–N–C unit.

Within the planar coupled nitrile ligand of **2**, the same pattern of bond distances emerges as for **1**, althouth the greater precision of the structure determination of **2** allows for a more meaningful appraisal of these structural parameters. The shortest distance within the ring is 1.29 (2) Å for N(3)–C(31) and this can be compared with a value of 1.32 (4) Å for the N(3)–C(32) bond in **1**. This distance is characteristic of that encountered with α-diimine complexes of the 1,4-diaza-1,3-butadiene type (RN=C(R′)—C(R′)=NR).[24] However, since the C(21)–C(31) distance of 1.43 (2) Å is shorter than the expected value for a single bond, while the other C–N distance N(2)–C(21) is longer than that of the double bond N(3)–C(31) (1.39 (2) Å vs 1.29 (2) Å), it is reasonable to represent this ring system as having contributions from the singly deprotonated diimine ligand I and the triply deprotonated ene-diamine ligand form II. However, the unsymmetrical nature of the ligand, with N(2)–C(21) being longer than N(3)–C(31), obviously implies that this is an oversimplification, although form I seems to predominate. The C-N fragment N(3)–C(31) can be viewed as a strongly bridging ketimino group with associated very short Re–N bonds. This presumably introduces disparities in the charge distribution within this metallacycle, perhaps through N(pπ)–Re(dπ) overlap, and leads to a disparity in the lengths of N(3)–C(31) and N(2)–C(21).



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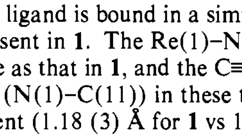

II

(d) Oxidation to the Diamagnetic $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]^{2+}$ Dications. The CV's of $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]PF_6$ in 0.1 M TBAH–CH_2Cl_2 (Table VI) display a reversible one-electron couple with an $E_{1/2}$ value between +0.19 and +0.32 V vs Ag/AgCl, which corresponds to an oxidation of the bulk complex. This oxidation can be accessed chemically with the use of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in acetone or $NOPF_6$ in dichloromethane as oxidants. These oxidations were carried out in the case of R = Me, Et, and *i*-Pr for X = Cl and R = Me and Et for X = Br. In addition, the red acetonitrile complex $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)](PF_6)_2$ was the major product when a mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ and dppm was reacted with acetonitrile in the presence of KPF_6. The related reaction using $(n\text{-}Bu_4N)_2Re_2Br_8$ gave the dark green 1:1 salt $[Re_2Br_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$. In the case of R = Me, these complexes were found to undergo anion exchange with $[Re_2X_8]^{2-}$ to afford the rather insoluble 1:1 salts $[Re_2X_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]Re_2X_8$.

The hexafluorophosphate salts dissolve in acetone to give solutions that have conductivities typical of 1:2 electrolytes (Λ_m in the range 178–190 Ω^{-1} cm^2 mol^{-1} for $C_m \simeq 1 \times 10^{-3}$ M). Like their monocationic analogues, these complexes show diagnostic features in their IR spectra that can be assigned to the ν(N—H) and ν(C≡N) modes of the coupled nitrile and coordinated nitrile ligands, respectively (see Table VII). The electronic absorption spectra of these complexes (recorded in dichloromethane) were very similar to one another (see Table S11). A representative spectrum is that of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)](PF_6)_2$, which displays the following absorption bands (λ_{max} values (nm); molar extinction coefficients (M^{-1} cm^{-1}) in parentheses): 536 (1550), 425 sh, 391 (7570), 335 (5200). The CV properties of these complexes are the same (within experimental error) as those of their 1:1 analogues, except that the couple listed as $E_{1/2}$(ox) in Table VI now corresponds to a reduction of the bulk complex.[25]

The complexes are ESR silent (dichloromethane solutions at −150 °C) in accord with their expected diamagnetism. Their ^{1}H NMR spectra (recorded in CD_2Cl_2) all display similar characteristics, the most important features of which are listed in Table VII. In addition to the resonances associated with the coordinated dppm ligand, the $-CH_2-$ resonance of which occurs as a characteristic ABX_4 pattern centered close to δ +4.5, there is a broad N-*H* resonance associated with the coupled nitrile ligand downfield of the dppm phenyl resonances (Table VII). The remaining features of note in these spectra are the alkyl resonances associated with the coordinated nitrile and the ligand derived from the coupling of the two nitriles. These cover a usually wide chemical shift range, as exemplified by the spectrum of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me)_2(\mu\text{-dppm})_2(NCMe)](PF_6)_2$ in which there are three methyl resonances at δ +1.74, +3.02, and +6.05, all singlets. Our assignment of the acetonitrile resonance (Table VII) has been confirmed by measuring the spectrum of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NC\text{-}i\text{-}Pr)](PF_6)_2$ in which the methyl resonance of coordinated CH_3CN is replaced by those due to the isopropyl group of *i*-PrCN. All other complexes listed in Table VII show these same characteristics, viz., three sets of ethyl resonances in the case of the complexes derived from the coupling of the propionitrile ligands. We are unsure as to why the ^{1}H

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[23] Cullis, C. F.; Fish, A. In *The Chemistry of the Carbonyl Group*; Patai, S., Ed.; Interscience Publ.: London, 1966; pp 108–109.

[24] Vrieze, K.; Van Koten, G. *Inorg. Chim. Acta* **1985**, *100*, 79.

[25] The CV's of $[Re_2X_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]Re_2X_8$ in 0.1 M TBAH–CH_2Cl_2 are a composite of the processes that characterize the dications and the $[Re_2X_8]^{2-}$ anions. For example, when X = Cl, the $[Re_2Cl_8]^{2-}$ anion shows the couples $E_{1/2}$(ox) at +1.20 V and $E_{1/2}$(red) at ≃−0.85 V vs Ag/AgCl, the latter of which overlaps with a couple at −0.80 V that is characteristic of the $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]^{2+}$ cation (see Table VI for CV data on the analogous monocation).

Table VII. Spectroscopic Properties for $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR')](PF_6)_2$

complex			IR,[a] cm^{-1}		$^{31}P\{^1H\}$ NMR,[b] δ		^1H NMR,[c] δ			
R	R′	X	ν(N—H)	ν(C≡N)	dppm[d]	PF_6^- [e]	R[f]	R′[f]	N—H	P—CH$_2$—P[g]
Me	Me	Cl	3345 vw	2297 vw	−13.5, −20.8	−144.0	+6.05 s, +3.02 s	+1.74 s	+7.9 s	+4.6, +4.2
Et	Et	Cl	3347 w	2287 vw	−15.4, −24.8	−144.0	4.23 q, −0.05 t +4.70 q, +1.56 t	+2.07 q, +0.44 t	+7.9 s	+4.7, +4.0
i-Pr	*i*-Pr	Cl	3347 w	2277 w	*h*		*h*			
Me	Me	Br	3340 vw	2290 vw	−21.8, −27.6	−143.7	+6.36 s, +3.20 s	+1.82 s	+8.07 s	+4.8, +4.4
Et	Et	Br	3340 vw	2284 vw	−23.8, −32.5	−144.1	+4.45 q, +0.05 t +4.9 q, +1.72 t	+2.18 q, +0.51 t	+8.02 s	+4.9, +4.2
Me	*i*-Pr	Cl	3335 vw	2282 vw	−13.0, −21.8	−143.7	+6.23 s, +2.99 s	+2.45 sp, +0.54 d	+7.88 s	+4.6, +4.3

[a] Nujol mulls. [b] Recorded at room temperature in CH_2Cl_2 with aqueous H_3PO_4 as an external standard. [c] Spectra recorded at room temperature in CD_2Cl_2. Abbreviations are as follows: s = singlet; d = doublet; t = triplet; q = quartet; sp = septet. [d] The spectra are best described as AA′BB′ patterns; chemical shifts are of the most intense components of the pattern. [e] The most intense peak of the seven-line pattern is given. [f] For the ethyl groups, assignment of the pairs of $-CH_2-$ and $-CH_3$ resonances was confirmed by decoupling experiments. [g] The resonances quoted are those of the two most intense inner components of an ABX_4 pattern. [h] Not measured.

resonances for the α-carbons of the two alkyl groups (R) of the coupled ligand appear so far downfield. This may simply reflect diamagnetic anisotropy effects associated with the metallacyclic ring. It is unlikely to be due to a contact shifting arising from the thermal population of a low-lying paramagnetic excited state because temperature range measurements on the two bromide complexes reveal only very small chemical shifts in these spectra as the temperature is lowered from room temperature down to −50 °C.

The $^{31}P\{^1H\}$ spectra of these complexes (Table VII) bear a striking resemblance to one another and to other complexes that contain the $[Re_2X_3(\mu\text{-dppm})_2]$ unit;[26] all can be described in terms of an AA′BB′ pattern.

(e) Concluding Remarks. Although there are a few examples reported in the literature involving the stabilization of reductively coupled nitriles at *mononuclear* transition-metal centers,[27-32] no systems have shown the combination of features displayed by these dirhenium species that represent the most versatile reactions of their type to date. These systems also constitute the first examples where the reductive coupling has occurred at a multiply bonded dimetal core in which the nuclearity of the metal core is preserved. Previously, reactions of the metal–metal-bonded tetrachlorides $[MCl_2Cl_{4/2}]_\infty$ (M = Nb, Ta)[31] and the dinuclear complex $Ta_2(\mu\text{-}Cl)_2(\mu\text{-THT})Cl_4(THT)_2$ (THT = tetrahydrothiophene)[32] with nitriles have been shown to give complexes in which two metal centers are linked by a coupled nitrile ligand but in which there is no metal–metal interaction. The complexes described in the present report possess an interesting analogy to $W_2(\mu\text{-}NC(Ph)CHCH)(O\text{-}i\text{-}Pr)_6$, a complex that is formed through the coupling of benzonitrile and acetylene ligands.[33]

The coupling of two organonitrile molecules by the triply bonded $(Re{\equiv}Re)^{4+}$ core, as is present in $Re_2X_4(\mu\text{-dppm})_2$ and $[Re_2X_3(\mu\text{-dppm})_2(NCR)_2]PF_6$, can be represented formally as redox processes that involve oxidation of the dirhenium core to Re_2^{5+} or Re_2^{7+}, depending upon the description of the resulting $Re_2(\mu\text{-}NC(R)C(R)NH)$ dimetallacycle. We can envision the reactions as first giving the dicationic species $[Re_2X_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]^{2+}$ (these are formally Re_2^{6+} or Re_2^{8+} derivatives depending upon the ligand formulation), which then undergo a one-electron reduction under the reaction conditions to afford the monocations (correspondingly formulated as Re_2^{5+} or Re_2^{7+}). The intramolecular redox process that gives rise to the nitrile coupling is accompanied by the "protonation" of the terminal nitrogen atom of the coupled ligand. Experiments using CD_3CN in place of CH_3CN show that the source of this hydrogen is the acetonitrile ligand itself. This hydrogen is very labile and exchanges with deuterium when the complex is treated with CH_3CN/D_2O.

While the Re–Re distances in the structures of **1** and **2** (2.666 (1) and 2.640 (1) Å, respectively) are very similar to that in the edge-shared bioctahedral species $[Re_2(\mu\text{-}Cl)_2(\mu\text{-dppm})_2Cl_4]^+$ (2.682 (1) Å),[34] a derivative of the Re_2^{5+} core, this does not permit us an easy way to unambiguously distinguish between the oxidation state formalisms Re_2^{5+} and Re_2^{7+}. From the bonding treatment for edge-shared bioctahedral species of this type,[35] it might be anticipated that both cores could have similar metal–metal bond orders (1.5), based upon the predicted ground state configurations $\sigma^2\pi^2\delta^{*2}\delta^2\pi^{*1}$ and $\sigma^2\pi^2\delta^{*2}\delta^1$, respectively.

As far as the mechanism of these reactions is concerned, we are tempted to propose that they proceed by the type of carbonyl–carbyne and isocyanide–aminocarbyne coupling mechanism that Lippard and co-workers[36] have provided such compelling evidence for in their elegant studies on the reductive coupling of carbonyl and isocyanide ligands. In our systems, we are uncertain whether this would involve a nitrile–alkylimido coupling step, but this possibility clearly merits further study. Since the reductive coupling reactions we have reported herein require quite forcing conditions and are rather sluggish and, furthermore, have not yielded any characterizable reaction intermediates, our systems do not appear to be ideal from the standpoint of further mechanistic studies. As an alternative strategy, we are now investigating the reactions of preformed (alkylimido)rhenium(V) complexes such as $Re(NR)X_3(dppbe)$ (X = Cl, Br; dppbe = 1,2-bis(diphenylphosphino)benzene) with nitriles.[37]

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Supplementary Material Available: Tables giving full details of crystal data and data collection parameters (Tables S1 and S6), details of the refinements of the disordered anion and lattice solvent molecules of **1** and the disordered lattice solvent molecules of **2**, complete listings of posi-

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(26) Examples include the isomers of stoichiometry $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(CNxyl)]PF_6$; see ref 3.

(27) DeBoer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1978**, *153*, 53.

(28) Harris, T. V.; Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966.

(29) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.

(30) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551.

(31) (a) Finn, P. A.; King, M. S.; Kilty, P. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 220. (b) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1978**, *17*, 3525.

(32) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094.

(33) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6815.

(34) Dunbar, K. R.; Powell, D.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 2842.

(35) Shaik, S.; Hoffmann, R.; Fisel, R. C.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

(36) Vrtis, R. N.; Rao, Ch. P.; Warner, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2669.

(37) For a preliminary report on the isolation and characterization of these mononuclear complexes, see: Bakir, M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2016.

tional parameters and their errors (Tables S2 and S7), thermal parameters (Tables S3 and S8), bond distances (Tables S4 and S9), bond angles (Tables S5 and S10), and electronic absorption spectral data (Table S11), and figures showing the full atomic number schemes for the monocations of **1** (Figure S1) and **2** (Figure S2) and the X-band ESR spectrum of $[Re_2Cl_3(\mu\text{-}HN_2C_2Me_2)(\mu\text{-dppm})_2(NCMe)]PF_6$ (Figure S3) (44 pages); tables of observed and calculated structure factors (82 pages). Ordering information is given on any current masthead page.

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Protonation of the 1,1-Dithiolene Ligands in the $[Cu_8(L)_6]^{4-}$ Cubanes (L = $[S_2C{=}C(COOR)_2]^{2-}$) and Synthesis of the $[Cu_8(L)_{6-n}(H\text{-}L)_n]^{-(4-n)}$ Clusters. Synthesis and Structural Characterization of the $[Cu_{10}(H\text{-}L)_6(L)_2]$ Decanuclear Cluster

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Addition of 1, 2, or 3 equiv of acid to CH_3CN solutions of the $K_4Cu_8(R_2DED)_6$ cubane cluster complexes (R_2DED = $[S_2C{=}C(COOR)_2]^{2-}$; R = Et (I), *t*-Bu (II)) by using standarized $HClO_4/CH_3CN$ solutions results in the formation of the protonated complexes $[Cu_8(L)_{6-n}(H\text{-}L)_n]^{-(4-n)}$ (L = Et_2DED, n = 1, 2, 3; L = *t*-Bu_2DED, n = 1, 2) that were isolated as crystalline tetraarylphosphonium or tetraalkylammonium salts. The protonated clusters can be titrated with standard base to give back the "parent" cubanes in quantitative yields. The cubane structure of the $[Cu_8(L)_5(H\text{-}L)]^{3-}$ (L = *t*-Bu_2DED) cluster has been established unequivocally by ^{13}C NMR spectroscopy. Upon addition of 4 equiv of acid to $K_4Cu_8(t\text{-}Bu_2DED)_6$, a red Cu(I) cluster of stoichiometry $[Cu_{10}(H\text{-}L)_6(L)_2]$ (L = *t*-Bu_2DED) forms and can be isolated in crystalline form (III). Neutral complex III crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell. The cell dimensions are a = 14.435 (3) Å, b = 16.979 (3) Å, c = 14.843 (3) Å, α = 98.16 (4)°, β = 108.90 (2)°, γ = 85.42 (4)°. Intensity data were collected with a four-circle computer-controlled diffractometer using the θ–2θ scan technique. Refinement by full-matrix least-squares techniques of 374 parameters on 4284 data gave a final R value of 0.067. The copper framework in III consists of two Cu_4 subunits. Of the four ligands surrounding each of the Cu_4 subunits, three are protonated at the ethylenic carbon adjacent to the CS_2 unit ("methine" carbon) and can be considered dithio acid monoanions $(H\text{-}t\text{-}Bu_2DED)^-$. The fourth ligand is a 1,1-ethylenedithiolate dianion, $(t\text{-}Bu_2DED)^{2-}$. The latter connects the Cu_4 fragment to the bridging copper atom by coordination via oxygen and sulfur atoms. A third coordination site on the bridging copper is occupied by a dithio acid sulfur on the adjacent Cu_4 fragment. The coordination geometry about each of the copper atoms in the structure is distorted trigonal and nearly planar. Ranges of selected structural parameters are as follows: Cu–S, 2.230 (3)–2.322 (3) Å; Cu–Cu, 2.656 (2)–3.056 (2) Å; Cu–O, 1.898 (8) Å; S–Cu–S, 106.0 (1)–131.8 (1)°; Cu–S–C, 98.5 (4)–110.0 (4)°.

Introduction

The polynuclear aggregates obtained in reactions of Cu(I) with sulfur-containing ligands display a wide variety in composition and structure. Among these clusters are included many structurally characterized species that contain core units of the stoichiometries Cu_4S_6,[1-7] Cu_4S_8,[8,9] Cu_5S_6,[10] Cu_5S_7,[11] Cu_8S_{12},[12-14] $Cu_8S_{12}Cl$,[15,16] and Cu_3S_6.[17]

Our studies on aggregates with the Cu_4S_6[2] and Cu_8S_{12}[12-14] frameworks have been directed particularly in analyzing the possible factors that dictate the formation of structurally different cores with the same Cu/S ratio. In previous reports,[2,14] we have suggested that with nonchelating ligands such as the RS^- thiolates a Cu:S ratio of 2:3 favors the formation of the Cu_4S_6 "adamantane" type of core. The long S–S distances inherent in the adamantane structure (~4.0 Å with "normal" Cu–S bond lengths of ca. 2.3 Å) preclude the ability of normal bidentate chelates with small intraligand S–S distances (S–S "bite" distances ~3.0 Å) to span the edges of the S_6 octahedron in the Cu_4S_6 core. As a consequence various dinegative 1,1-dithiolate chelates with "bites" close to 3.0 Å invariably form the $[Cu_8L_6]^{4-}$ "cubane" clusters with the Cu_8S_{12} core and idealized T_h symmetry. In the latter the trigonal-planar coordination of the CuS_3 structural and the Cu–S and Cu–Cu nearest neighbor distances are similar to those in the Cu_4S_6 cores.

The stabilities of the $[Cu_4L_3]^{2-}$ and $[Cu_8L_6]^{4-}$ clusters become comparable when the sulfur chelating ligands are characterized by relatively long S–S intraligand distances. Such is the case for the sulfur "rich" derivative of the 1,1-dicarbo-*tert*-butoxyethylene-2,2-dithiolate ligand, $[R_2DED]^{2-}$.

We have shown[18] that the transformation of $[Cu_4L_3]^{2-}$ to $[Cu_8L_6]^{4-}$ (L = $[S\text{-}t\text{-}Bu_2DED]^{2-}$) is affected by the nature of the counterion and relatively weak interionic interactions.

The coordinated $[t\text{-}Bu_2DED]^{2-}$ ligand also can undergo protonation at the "methine" carbon and is transformed to the dithio acid, $[H\text{-}t\text{-}Bu_2DED]^-$, ligand. The latter reaction can be used to explore the structural changes that the $[Cu_8L_6]^{4-}$ cluster (L = *t*-Bu_2DED) undergoes as the ligands are protonated sequentially. In a previous, short communication, we reported[19] on the acid–base

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(1) Griffith, E. H.; Hunt, G. W.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1972**, 432.
(2) Coucouvanis, D.; Murphy, C. N.; Kanodia, S. K. *Inorg. Chem.* **1980**, *19*, 2993.
(3) Dance, I. G.; Calabrese, J. C. *Inorg. Chim. Acta* **1976**, *19*, L41.
(4) Siiman, O.; Huber, C. P.; Post, M. L. *Inorg. Chim. Acta* **1977**, *25*, L11.
(5) Betz, P.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 311.
(6) Muller, A.; Romer, M.; Krickemeyer, E.; Bogge, H. *Naturwissenschaften* **1984**, *71*, 43.
(7) Henkel, G.; Krebs, B.; Betz, P.; Fietz, H.; Saatkamp, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1326.
(8) Hesse, R. *Ark. Kemi* **1963**, *20*, 481.
(9) Lawton, S. L.; Rohrbaugh, W. J.; Kokotaillo, G. T. *Inorg. Chem.* **1972**, *11*, 612.
(10) Dance, I. G. *J. Chem. Soc., Chem. Commun.* **1976**, 103.
(11) Dance, I. G. *J. Chem. Soc., Chem. Commun.* **1976**, 68.
(12) McCandlish, L. E.; Bissel, E. C.; Coucouvanis, D.; Fackler, J. P.; Jr.; Knox, K. *J. Am. Chem. Soc.* **1968**, *90*, 7357.
(13) Hollander, F. J.; Coucouvanis, D. *J. Am. Chem. Soc.* **1974**, *96*, 5646.
(14) Hollander, F. J.; Coucouvanis, D. *J. Am. Chem. Soc.* **1977**, *99*, 6268.
(15) Birker, P. J. M. W. L.; Freeman, H. C. *J. Chem. Soc., Chem. Commun.* **1976**, 312.
(16) Schugar, H. J.; Ou, C.; Thick, J. A.; Potenza, J. A.; Lalancette, P. A.; Furey, W. *J. Am. Chem. Soc.* **1976**, *98*, 3047.
(17) Henkel, G.; Betz, P.; Krebs, B. *J. Chem. Soc., Chem. Commun.* **1984**, 314.
(18) Kanodia, S.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 469.
(19) Coucouvanis, D.; Swenson, D.; Baenziger, N. C.; Pedelty, R.; Caffery, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 8097.

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