the variable-temperature techniques commonly employed. The full range of pressures would lead to more complexes converting from high spin to low spin than have been observed by the temperature range ~4–500 K. The goal in the study of these spin-state phase transitions is to understand the mechanism of the phase transitions. What is the nature of the cooperativity? In a general sense the goal is to discover the universality class or classes[19] that characterize the phase transitions in these complexes. To determine the universality class it is necessary to determine two things: the dimensionality of the lattice and the dimensionality of the order parameter. In the first case it is important to determine from the packing diagram of the complex or by other means whether the intermolecular interactions dictate a one-, two-, or three-dimensional lattice of spin-crossover complexes. Are there stacks or layers of complexes? The dimensionality of the order parameter refers to the nature of the pairwise interactions of complexes. Are these interactions of a Heisenberg, Ising, or XY type? Pressure should be a useful variable in this endeavor.

Finally, it must be noted that increasing the pressure does not have the same effect on a spin-crossover complex as decreasing the temperature. As the temperature is decreased, intermolecular interactions probably change little. Decreasing the temperature changes Boltzmann populations and reduces the thermal energy available to drive nucleation and growth processes. On the other hand, increasing the pressure could dramatically increase intermolecular interactions and also affect intramolecular energetics.

Acknowledgment. This work was supported in part by National Institutes of Health Grant HL13652 and in part by the Materials Science Division, Department of Energy, under Contract DE-AC02-76ER01198.

Registry No. $Fe(dppen)_2Cl_2$, 58031-48-4; $Fe(dppen)_2Br_2$, 58031-47-3.

---

(19) Careri, G. *Order and Disorder in Matter*; Benjamin/Cummings Publishing Co.: Reading, MA, 1984.

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907-3699

Dirhenium Complexes Containing Pairs of Bridging Acetate and Bis(diphenylphosphino)amine Ligands. Cis and Trans Isomers of the Type $[Re_2(O_2CCH_3)_2X_2(Ph_2PNHPPh_2)_2]^{n+}$ (X = Cl, Br; n = 0, 1)

Daniel R. Derringer, Phillip E. Fanwick, Justin Moran, and Richard A. Walton*

Received September 29, 1988

The reactions of dirhenium(III) carboxylates of the type $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (**1**, X = Cl, Br) with bis(diphenylphosphino)amine (dppa) in hot ethanol afford reduced, mixed-halide–phosphine complexes with two, one, or zero bridging acetate ligands. Yellow $Re_2(O_2CCH_3)X_4(dppa)_2$ (**2**) is produced in reactions of very short duration (ca. 3 min), while longer reaction times (ca. 15 min) favor yellow *trans*-$[Re_2(O_2CCH_3)_2X_2(dppa)_2]X$ (**3**). After several days, under these same reaction conditions, *cis*-$Re_2(O_2CCH_3)_2X_2(dppa)_2$ (**4**) is produced. While **2** can undergo reductive decarboxylation to give $Re_2X_4(dppa)_2$ (**5**), the latter species does not appear to be an important precursor to **4**, as it is in an analogous system involving reactions of **1** with bis(diphenylphosphino)methane (dppm) (see: *J. Am. Chem. Soc.* **1988**, *110*, 5024). The most important reaction pathway to **4** is via the sequence **1** → **2** → **3** → **4**. The complex **4** (X = Cl) reacts with the one-electron oxidant $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ to produce paramagnetic *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$ (**6**). The redox properties of **2**–**6** have been studied by the cyclic voltammetric technique. The pair of complexes **4** and **6** (X = Cl) were characterized structurally by X-ray crystallography. Crystal data for **4** at 19 °C: monoclinic space group $P2_1/c$, a = 14.267 (2) Å, b = 15.831 (4) Å, c = 23.824 (3) Å, β = 100.163 (9)°, V = 5296 (3) $Å^3$, Z = 4. The structure was refined to R = 0.034 and R_w = 0.049 for 5026 data with $F^2 > 3.0\sigma(F^2)$. Crystal data for **6** at −100 °C: monoclinic space group $C2/c$, a = 34.539 (5) Å, b = 14.015 (4) Å, c = 26.018 (5) Å, β = 103.83 (2)°, V = 12229 (9) $Å^3$, Z = 8. This structure was refined to R = 0.047 and R_w = 0.065 for 6311 data with $F^2 > 3.0\sigma(F^2)$.

Introduction

Metal–metal-bonded dimetal complexes that contain two bridging bidentate phosphine ligands of the type $R_2PCH_2PR_2$ are well-known.[1-3] However, systems in which these complexes exist in cis and trans isomeric forms are very rare. We recently encountered a set of such examples in the case of the cis and trans isomers of $[Re_2(O_2CR)_2X_2(dppm)_2]^{n+}$ (R = CH_3, C_2H_5, C_6H_5; X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$; n = 0, 1),[4,5] and in seeking to expand this chemistry, we have extended our studies to include several related systems that contain the bis(diphenylphosphino)amine ligand (abbreviated dppa). In the course of this work we have structurally characterized the redox pair *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ and *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$ and describe herein the full details of this study.

Experimental Section

Starting Materials. The compounds $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (X = Cl, Br),[6] were prepared by using established literature procedures. Bis(diphenylphosphino)amine (abbreviated dppa) was prepared by the procedure of Nöth et al.[7] All solvents were obtained from commercial sources and were used as received.

Reaction Procedures. Syntheses were performed in an atmosphere of drying nitrogen, and solvents were deoxygenated prior to use. Some reactions were carried out in the presence of a pine boiling stick to promote crystal formation.

A. Synthesis of $Re_2(O_2CCH_3)X_4(dppa)_2$ (2). (i) X = Cl. A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.100 g, 0.150 mmol) and dppa (0.350 g,

---

(1) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.
(2) Cotton, F. A. *Polyhedron* **1987**, *6*, 667.
(3) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.
(4) Cutler, A. R.; Derringer, D. R.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1988**, *110*, 5024.
(5) An interesting example of isomerization has also been encountered in the case of the diplatinum(II) complex $Pt_2(C{\equiv}CMe)_4(depm)_2$ (depm = $Et_2PCH_2PEt_2$), but in this instance there is no metal–metal bond present. See: McLennan, A. J.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 485.
(6) Chakravarty, A. R.; Cotton, F. A.; Cutler, A. R.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3619 and references cited therein.
(7) Nöth, H.; Meinel, L. *Z. Anorg. Allg. Chem.* **1967**, *349*, 225.

0.908 mmol) was combined with ethanol (20 mL) and refluxed for 3 min. The reaction mixture was cooled, and the yellow title complex was filtered off, washed with toluene and ethanol, and then dried under vacuum; yield 0.088 g (44%). Anal. Calcd for $C_{50}H_{45}Cl_4O_2N_2P_4Re_2$: C, 44.69; H, 3.35. Found: C, 44.51; H, 3.90. Additionally, a small quantity (0.010 g, 5%) of *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]Cl$ was obtained from the filtrate (see section B(i)(a)).

This reaction was also carried out with the use of a lower $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$:dppa stoichiometric ratio (ca. 1:2). A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.08 g, 0.12 mmol) and dppa (0.10 g, 0.26 mmol) was refluxed in 15 mL of ethanol for 30 min. The reaction mixture was cooled and filtered. The yellow crystalline solid was washed with fresh ethanol and aspirated to dryness; yield 0.05 g (30%).

(ii) X = Br. The reaction was carried out in a fashion analogous to that described in section A(i)(a) above with the use of a $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$:dppa stoichiometric ratio of 1:6; yield 17%. Anal. Calcd for $C_{50}H_{45}Br_4N_2O_2P_4Re_2$: C, 39.46; H, 2.98. Found: C, 39.08; H, 3.49

B. Synthesis of *trans*-$[Re_2(O_2CCH_3)_2X_2(dppa)_2]X$ (3). (i) X = Cl. (a) From $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$. A suspension of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.100 g, 0.150 mmol) and dppa (0.350 g, 0.908 mmol) in ethanol (20 mL) was refluxed for 15 min. During this time a yellow precipitate ($Re_2(O_2CCH_3)Cl_4(dppa)_2$) formed and subsequently disappeared. The reaction mixture was cooled and filtered, and the volume of the filtrate was reduced. Addition of a small volume (ca. 1 mL) of acetone to this filtrate afforded the yellow title complex; yield 0.090 g (44%). When the reaction was stopped after 10 min, both insoluble $Re_2(O_2CCH_3)Cl_4(dppa)_2$ (0.032 g, 16%) and *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]Cl$ (0.045 g, 22%) were isolated.

The complex *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]Cl$ was converted into its PF_6^- salt as follows. Stoichiometric quantities of *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]Cl$ (0.040 g, 0.029 mmol) and KPF_6 (0.0054 g, 0.029 mmol) were combined with ethanol (5 mL), and the mixture was stirred at reflux for 10 min. The yellow product was filtered off and dried. It was then recrystallized from acetone/diethyl ether; yield 0.013 g (30%). Anal. Calcd for $C_{52}H_{56}Cl_2F_6N_2O_8P_5Re_2$ (i.e., $[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6{\cdot}4H_2O$): C, 40.32; H, 3.64. Found: C, 39.50; H, 3.70. This complex had absorptions at 3425 (m–s, br) and 1638 (m–w, br) cm^{-1} in its IR spectrum (Nujol mull) assignable to ν(O–H) and δ(O–H), respectively, while the ν(P–F) mode of the PF_6^- anion appeared as a doublet at 838 (m–s) cm^{-1}.

(b) From $Re_2(O_2CCH_3)Cl_4(dppa)_2$. A solution of NaO_2CCH_3 (0.005 g, 0.061 mmol) in ethanol (20 mL) was saturated with $N_2(g)$ and then transferred to a round-bottom flask that contained a mixture of $Re_2(O_2CCH_3)Cl_4(dppa)_2$ (0.070 g, 0.052 mmol) and dppa (0.040 g, 0.104 mmol). This mixture then was refluxed for 15 min. The resultant yellow-orange solution was evaporated to dryness. A small volume of acetone was added to the residue to afford the insoluble yellow complex; yield 0.040 g (56%).

(ii) X = Br. From $Re_2(O_2CCH_3)_2Br_4(H_2O)_2$. The complex *trans*-$[Re_2(O_2CCH_3)_2Br_2(dppa)_2]Br$ was isolated in low yield by a procedure analogous to that described in section B(i)(a); yield 11%. Anal. Calcd for $C_{52}H_{48}Br_3N_2O_4P_4Re_2$: C, 41.61; H, 3.22. Found: C, 40.98; H, 3.54.

C. Synthesis of *cis*-$Re_2(O_2CCH_3)_2X_2(dppa)_2$ (4). (i) X = Cl. A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (1.000g, 1.496 mmol) and dppa (2.15 g, 5.58 mmol) in ethanol (40 mL) was stirred at reflux for 6 days. The reaction mixture was allowed to cool. The orange-brown product that separated was filtered off and washed with toluene, ethanol, and diethyl ether and then dried under vacuum; yield, 0.880 g (44%). Anal. Calcd for $C_{52}H_{48}Cl_2N_2O_4P_4Re_2$: C, 46.88; H, 3.63. Found: C, 48.07; H, 4.42. The high C and H analyses reflect the presence of a small amount of lattice ethanol. This was confirmed by ^1H NMR spectroscopy.

The same product was formed with the use of a $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$:dppa stoichiometric ratio of ca. 1:6.

(ii) X = Br. The complex *cis*-$Re_2(O_2CCH_3)_2Br_2(dppa)_2$ was prepared by a procedure similar to the one described in section C(i); yield 17%. Anal. Calcd for $C_{52}H_{48}Br_2N_2O_2P_4Re_2$: C, 43.95; H, 3.40. Found: C, 44.26; H, 3.80.

D. Conversion of *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]Cl$ to *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$. The salt *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]Cl$ (0.050 g, 0.037 mmol), LiO_2CCH_3 (0.010 g, 0.15 mmol), and dppa (0.035 g, 0.091 mmol) were combined with ethanol (15 mL), and the mixture was refluxed for 3.5 h. The mixture was cooled, and a small quantity (ca. 5 mg) of unreacted *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]Cl$ was filtered off. The orange-brown filtrate was taken to dryness, and the brown residue (0.085 g) was characterized by cyclic voltammetry. The cis isomer was identified as the major component.

When *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]Cl$ was dissolved in ethanol and the solution heated for periods up to 7 days in the absence of added LiO_2CCH_3 and dppa, then *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ did not appear to be formed in any significant quantity as monitored by cyclic voltammetry.

Table I. Crystallographic Data for *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ (**4**) and *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6{\cdot}(CH_3)_2CO{\cdot}{}^1/_2(C_2H_5)_2O$ (**6**)

	4	**6**
chemical formula	$Re_2Cl_2P_4O_4N_2C_{52}H_{48}$	$Re_2Cl_2P_5F_6O_{5.5}N_2C_{57}H_{59}$
a, Å	14.267 (2)	34.539 (5)
b, Å	15.831 (4)	14.015 (4)
c, Å	23.824 (3)	26.018 (5)
β, deg	100.163 (9)	103.83 (2)
V, $Å^3$	5296 (3)	12229 (9)
Z	4	8
fw	1332.18	1572.28
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
T, °C	19	−100
λ, Å	Mo Kα (0.71073)	Mo Kα (0.71073)
ρ_{calcd}, g cm^{-3}	1.671	1.708
μ(Mo Kα), cm^{-1}	48.93	43.12
transmissn coeff	1.000–0.725	1.000–0.635
R^a	0.034	0.047
$R_w{}^b$	0.049	0.065

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

E. $Re_2X_4(dppa)_2$ (5). (i) X = Cl. A quantity of yellow $Re_2(O_2CCH_3)Cl_4(dppa)_2$ (0.100 g, 0.074 mmol) was suspended in ethanol (20 mL) and the mixture refluxed in the presence of a pine boiling stick for 50 h. The dark purple (almost black) crystalline product formed on the stick. The stick was removed from the reaction medium and the crystals harvested. The crystals were dried under vacuum; yield 0.050 g (52%). Anal. Calcd for $C_{48}H_{42}Cl_4N_2P_4Re_2$: C, 44.87; H, 3.30. Found: C, 45.34; H, 4.22.

When this reaction was carried out for $5^1/_2$ days, $Re_2Cl_4(dppa)_2$ was again obtained in good yield (60%). The filtrate from this reaction was shown by cyclic voltammetry to contain *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]Cl$, together with some of the cis isomer.

(ii) X = Br. The complex $Re_2(O_2CCH_3)Br_4(dppa)_2$ (0.030 g, 0.020 mmol) was suspended in ethanol (10 mL) and refluxed in the presence of a pine boiling stick for about 22 h. The reaction mixture was allowed to cool. The dark purple product was filtered off and dried under vacuum; yield 0.005 g (17%). A major component of the ethanol filtrate was *trans*-$[Re_2(O_2CCH_3)_2Br_2(dppa)_2]Br$. The solvent was evaporated, and the identity of this latter product in the residue was confirmed by cyclic voltammetric measurements on a solution in 0.1 M TBAH–CH_2Cl_2.

F. *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$ (6). The oxidant $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.055 g, 0.17 mmol) and *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ (0.200 g, 0.150 mmol) were combined with dichloromethane (20 mL) and stirred at room temperature for 30 min. The resultant solution was filtered into ca. 100 mL of diethyl ether to precipitate the green product. A crystalline sample of this complex was obtained upon its recrystallization from acetone/diethyl ether at ca. 5 °C; yield 0.150 g (68%). Anal. Calcd for $C_{52}H_{48}Cl_2F_6N_2O_4P_5Re_2$: C, 42.28; H, 3.28; Cl, 4.80. Found: C, 41.00; H, 3.27; Cl, 5.13. These elemental microanalyses are in accord with the presence of a small amount of lattice dichloromethane. Anal. Cald for *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6{\cdot}{}^1/_4CH_2Cl_2$: C, 41.88; H, 3.26; Cl, 5.92.

Preparation of Single Crystals for Structure Determination. Orange-brown, cubelike crystals of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$, (**4**, X = Cl) that were suitable for X-ray crystallographic studies were obtained directly from the appropriate reaction mixture (see section C(i)). Suitable crystals of *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$, (**6**), were obtained as green plates when an acetone solution of the compound was mixed with diethyl ether (in air), and then cooled to ca. 5 °C in a refrigerator.

X-ray Crystallography. The structures of **4** and **6** were determined by application of general procedures that are described more fully elsewhere.[8] The basic crystallographic parameters are listed in Table I. In the case of **6**, the data were collected at low temperature (−100 °C) to prevent degradation of the crystals due to lattice solvent loss (vide infra). The cell constants are based on 25 reflections with $20.4 < \theta < 22.1°$ for **4** and $22.0 < \theta < 22.5°$ for **6**. Three standard reflections were measured after every 5000 s of beam time during data collection. There were no systemmatic variations in intensity for either of the crystals.

Calculations were performed on a MicroVAX computer using the Enraf-Nonius structure determination package. For **4** and **6** the atoms

---

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

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for Non Phenyl Ring Atoms, Non Lattice Solvent Molecule Atoms and Non Hexafluorophosphate Anion Atoms of **4** and **6** and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*[a]
(i) *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ (**4**)				
Re(1)	0.32547 (3)	0.04176 (3)	0.22484 (2)	2.402 (9)
Re(2)	0.20142 (3)	−0.03120 (3)	0.25268 (2)	2.411 (9)
Cl(1)	0.4568 (2)	0.1456 (2)	0.2099 (1)	4.29 (7)
Cl(2)	0.0527 (2)	−0.0840 (2)	0.2859 (1)	4.06 (7)
P(11)	0.4427 (2)	−0.0597 (2)	0.2652 (1)	2.64 (6)
P(12)	0.3091 (2)	−0.0065 (2)	0.1295 (1)	2.81 (6)
P(21)	0.2795 (2)	−0.1637 (2)	0.2764 (1)	2.73 (6)
P(22)	0.1294 (2)	−0.0686 (2)	0.1578 (1)	2.60 (6)
O(11)	0.2323 (5)	0.1443 (4)	0.1984 (3)	3.4 (2)
O(12)	0.3406 (5)	0.1067 (5)	0.3054 (3)	3.3 (2)
O(21)	0.1227 (5)	0.0854 (4)	0.2422 (3)	3.2 (2)
O(22)	0.2407 (5)	0.0177 (5)	0.3366 (3)	3.5 (2)
N(1)	0.3940 (6)	−0.1578 (5)	0.2656 (4)	3.0 (2)
N(2)	0.2103 (6)	−0.0705 (6)	0.1147 (4)	2.9 (2)
C(11)	0.1525 (8)	0.1460 (7)	0.2155 (5)	3.2 (2)
C(12)	0.0905 (9)	0.2228 (7)	0.2003 (6)	4.4 (3)
C(21)	0.2977 (8)	0.0802 (7)	0.3436 (5)	3.4 (3)
C(22)	0.3160 (9)	0.1226 (8)	0.4013 (5)	4.5 (3)
(ii) *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6\cdot(CH_3)_2CO\cdot{}^1/_2(C_2H_5)_2O$ (**6**)				
Re(1)	0.32597 (1)	0.10391 (3)	0.25663 (2)	1.238 (8)
Re(2)	0.37718 (1)	0.01822 (3)	0.23878 (2)	1.231 (8)
Cl(1)	0.26378 (7)	0.1914 (2)	0.2700 (1)	2.06 (5)
Cl(2)	0.43578 (7)	−0.0551 (2)	0.2140 (1)	2.41 (6)
P(11)	0.27787 (7)	−0.0277 (2)	0.2340 (1)	1.44 (5)
P(12)	0.34394 (8)	0.0933 (2)	0.3534 (1)	1.57 (5)
P(21)	0.34875 (7)	−0.1416 (2)	0.2347 (1)	1.44 (5)
P(22)	0.41681 (7)	0.0135 (2)	0.3304 (1)	1.59 (5)
O(11)	0.3098 (2)	0.1447 (5)	0.1775 (3)	1.6 (1)
O(12)	0.3593 (2)	0.2277 (5)	0.2610 (3)	2.1 (2)
O(21)	0.3537 (2)	0.0449 (5)	0.1580 (3)	1.8 (2)
O(22)	0.4060 (2)	0.1478 (5)	0.2333 (3)	1.6 (1)
N(1)	0.3015 (2)	−0.1344 (6)	0.2430 (4)	1.6 (2)
N(2)	0.3873 (2)	0.0361 (7)	0.3731 (3)	1.7 (2)
C(111)	0.3265 (3)	0.1067 (8)	0.1448 (5)	2.2 (2)
C(112)	0.3145 (3)	0.134 (1)	0.0874 (5)	3.0 (3)
C(211)	0.3919 (3)	0.2244 (8)	0.2467 (4)	1.8 (2)
C(212)	0.4159 (3)	0.3160 (9)	0.2471 (6)	2.9 (3)

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

were located and refined from initial Patterson maps. In both instances an empirical absorption correction was applied,[9] the linear absorption coefficients being 48.93 (for **4**) and 43.12 cm^{-1} (for **6**). No correction for extinction was applied. The least squares program minimized the function $\sum w(|F_o| - |F_c|)^2$, where w is a weighting factor defined as $w = 1/\sigma^2(F_o)$. Hydrogens were not included in the least-squares refinement. For complex **4** all atoms were refined anisotropically. All atoms for complex **6**, except lattice acetone and diethyl ether, were refined anisotropically. Corrections for anamolous scattering were applied to all atoms refined anisotropically.[10]

While there was no lattice solvent present in crystals of **4**, we found acetone and diethyl ether in crystals of **6**. There was one molecule of acetone and half of a molecule of diethyl ether present per formula unit. The acetone was present at a general position while the diethyl ether was present on a special position that exhibited 2-fold symmetry.

Table III. Important Bond Distances (Å) for **4** and **6**[a]

(i) *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ (**4**)			
Re(1)–Re(2)	2.3067 (5)	P(11)–N(1)	1.702 (8)
Re(1)–Cl(1)	2.565 (3)	P(12)–N(2)	1.721 (8)
Re(1)–P(11)	2.395 (3)	P(21)–N(1)	1.702 (8)
Re(1)–P(12)	2.369 (3)	P(22)–N(2)	1.675 (8)
Re(1)–O(11)	2.123 (6)	O(11)–C(11)	1.27 (1)
Re(1)–O(12)	2.154 (6)	O(12)–C(21)	1.25 (1)
Re(2)–Cl(2)	2.534 (3)	O(21)–C(11)	1.27 (1)
Re(2)–P(21)	2.394 (3)	O(22)–C(21)	1.27 (1)
Re(2)–P(22)	2.387 (3)	C(11)–C(12)	1.51 (1)
Re(2)–O(21)	2.153 (6)	C(21)–C(22)	1.51 (1)
Re(2)–O(22)	2.125 (6)		
(ii) *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6\cdot(CH_3)_2CO\cdot{}^1/_2(C_2H_5)_2O$ (**6**)			
Re(1)–Re(2)	2.2757 (5)	P(11)–N(1)	1.692 (8)
Re(1)–Cl(1)	2.568 (2)	P(12)–N(2)	1.667 (7)
Re(1)–P(11)	2.458 (2)	P(21)–N(1)	1.699 (7)
Re(1)–P(12)	2.450 (2)	P(22)–N(2)	1.709 (8)
Re(1)–O(11)	2.080 (6)	O(11)–C(111)	1.26 (1)
Re(1)–O(12)	2.070 (6)	O(12)–C(211)	1.27 (1)
Re(2)–Cl(2)	2.489 (2)	O(21)–C(111)	1.26 (1)
Re(2)–P(21)	2.438 (2)	O(22)–C(211)	1.26 (1)
Re(2)–P(22)	2.449 (2)	C(111)–C(112)	1.50 (2)
Re(2)–O(21)	2.099 (6)	C(211)–C(212)	1.53 (1)
Re(2)–O(22)	2.092 (6)		

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

Table IV. Important Bond Angles (deg) for **4** and **6**[a]

(i) *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ (**4**)			
Re(1)–Re(2)–Cl(2)	169.20 (7)	Re(2)–Re(1)–Cl(1)	167.81 (7)
Re(1)–Re(2)–P(21)	99.08 (6)	Re(2)–Re(1)–P(11)	93.79 (6)
Re(1)–Re(2)–P(22)	94.34 (6)	Re(2)–Re(1)–P(12)	99.41 (7)
Re(1)–Re(2)–O(21)	87.0 (2)	Re(2)–Re(1)–O(11)	89.8 (2)
Re(1)–Re(2)–O(22)	90.0 (2)	Re(2)–Re(1)–O(12)	86.8 (2)
Cl(2)–Re(2)–P(21)	91.02 (9)	Cl(1)–Re(1)–P(11)	90.56 (9)
Cl(2)–Re(2)–P(22)	88.29 (9)	Cl(1)–Re(1)–P(12)	91.4 (1)
Cl(2)–Re(2)–O(21)	82.6 (2)	Cl(1)–Re(1)–O(11)	84.4 (2)
Cl(2)–Re(2)–O(22)	85.5 (2)	Cl(1)–Re(1)–O(12)	81.8 (2)
P(21)–Re(2)–P(22)	96.35 (9)	P(11)–Re(1)–P(12)	96.45 (9)
P(21)–Re(2)–O(21)	171.8 (2)	P(11)–Re(1)–O(11)	171.4 (2)
P(21)–Re(2)–O(22)	93.6 (2)	P(11)–Re(1)–O(12)	90.6 (2)
P(22)–Re(2)–O(21)	88.5 (2)	P(12)–Re(1)–O(11)	90.6 (2)
P(22)–Re(2)–O(22)	168.4 (2)	P(12)–Re(1)–O(12)	170.3 (2)
O(21)–Re(2)–O(22)	80.9 (3)	O(11)–Re(1)–O(12)	81.8 (3)
(ii) *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6\cdot(CH_3)_2CO\cdot{}^1/_2(C_2H_5)_2O$ (**6**)			
Re(1)–Re(2)–Cl(2)	172.22 (6)	Re(2)–Re(1)–Cl(1)	174.61 (6)
Re(1)–Re(2)–P(21)	99.73 (5)	Re(2)–Re(1)–P(11)	93.94 (6)
Re(1)–Re(2)–P(22)	95.56 (6)	Re(2)–Re(1)–P(12)	99.17 (6)
Re(1)–Re(2)–O(21)	88.7 (2)	Re(2)–Re(1)–O(11)	88.9 (2)
Re(1)–Re(2)–O(22)	87.8 (2)	Re(2)–Re(1)–O(12)	90.3 (2)
Cl(2)–Re(2)–P(21)	87.33 (8)	Cl(1)–Re(1)–P(11)	81.47 (8)
Cl(2)–Re(2)–P(22)	86.60 (8)	Cl(1)–Re(1)–P(12)	84.54 (8)
Cl(2)–Re(2)–O(21)	87.6 (2)	Cl(1)–Re(1)–O(11)	88.1 (2)
Cl(2)–Re(2)–O(22)	84.9 (2)	Cl(1)–Re(1)–O(12)	93.7 (2)
P(21)–Re(2)–P(22)	98.21 (8)	P(11)–Re(1)–P(12)	101.02 (8)
P(21)–Re(2)–O(21)	93.7 (2)	P(11)–Re(1)–O(11)	87.9 (2)
P(21)–Re(2)–O(22)	171.1 (2)	P(11)–Re(1)–O(12)	167.7 (2)
P(22)–Re(2)–O(21)	166.5 (2)	P(12)–Re(1)–O(11)	167.5 (2)
P(22)–Re(2)–O(22)	85.7 (2)	P(12)–Re(1)–O(12)	89.7 (2)
O(21)–Re(2)–O(22)	81.6 (2)	O(11)–Re(1)–O(12)	80.7 (3)

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

Further details concerning the data sets, the structure solutions, and the structure refinements may be obtained from P.E.F. Table II lists the positional parameters and their errors for the non phenyl group atoms, the nonsolvent molecule atoms, and the non hexafluorophosphate anion atoms of **4** and **6**, while Tables III and IV list important intramolecular bond distances and angles. Tables giving full details of crystal data and data collection parameters (Tables S1 and S2), positional parameters for the phenyl carbon atoms of **4** and **6** and the lattice solvent molecule atoms and the atoms of PF_6^- of **4** (Tables S3 and S4), thermal parameters (Tables S5 and S6), and complete bond distances (Tables S7 and S8) and bond angles (Tables S9 and S10) are available as supplementary material, as well as figures (Figure S1 and S2) that show the full atomic numbering schemes for **4** and **6**.

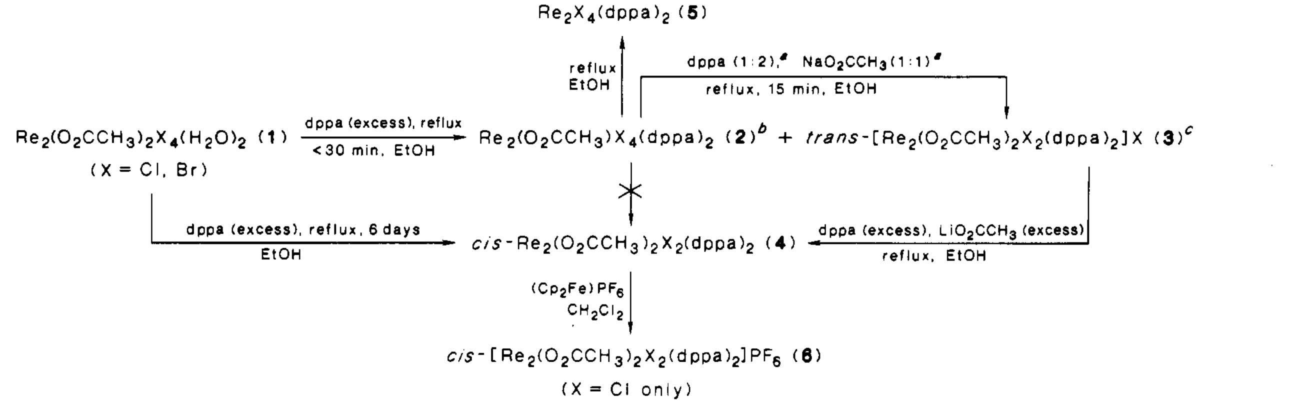
Physical Measurements. IBM Instruments IR/32 and Perkin-Elmer 1800 FTIR spectrometers were used to record infrared spectra of compounds as Nujol mulls supported on KBr plates in the region 4800–400 cm^{-1}. Electronic absorption spectra were recorded on IBM Instruments 9420 UV-visible, Cary 17D, and Hewlett Packard HP 8451A spectrophotometers. Electrochemical measurements were carried out by the use

---

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

(10) 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.

Scheme I



[a] Numbers in parentheses refer to the stoichiometric ratios of reagents (i.e., dirhenium complex:dppa and dirhenium complex:NaO_2CCH_3). [b] The formation of complex **2** is favored by reaction times of a few minutes. [c] The formation of complex **3** is favored by reaction times of 15–30 min.

of a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A Pt-bead working electrode and a Pt-wire auxiliary electrode were utilized. $E_{1/2}$ 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 the ferrocenium/ferrocene couple is at $E_{1/2}$ = +0.47 V vs. Ag/AgCl. Conductivity measurements were performed on solutions of the samples at a concentration of ca. 1.0×10^{-3} M. Measurements were made with an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. Phosphorus resonances were referenced externally to 85% H_3PO_4. X-Band ESR spectra of dichloromethane solutions were recorded at ca. −160 °C with the use of a Varian E-109 spectrometer.

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

Results and Discussion

In an earlier paper[4] we reported the use of dirhenium(III) carboxylates of the types $Re_2(O_2CR)_4X_2$ and $Re_2(O_2CR)_2X_4(H_2O)_2$ (X = Cl, Br), together with $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br), as the key synthetic starting materials in the preparation of the cis and trans isomers of $Re_2(O_2CR)_2X_2(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$). Since the reactions involving $Re_2(O_2CR)_2X_4(H_2O)_2$ proved to be the more complicated and interesting ones, we have chosen to focus on the reactions of these particular starting materials (X = Cl, Br) with bis(diphenylphosphino)amine (dppa) in the present work.

The reactions between $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (**1**, X = Cl, Br) and dppa in hot ethanol afford reduced, mixed halophosphine complexes with two, one, or zero bridging acetate ligands (see Scheme I). The reactions proceed first to give the paramagnetic Re_2^{5+} complexes $Re_2(\mu\text{-}O_2CCH_3)X_4(\mu\text{-dppa})_2$ (**2**). The formation and isolation of **2** is favored by reactions of short duration (<30 min) and lower stoichiometric proportions of dppa (**1**:dppa $\simeq$ 1:2). That **2** is a precursor to **3** has been shown by the reaction of pure **2** with a mixture of sodium acetate (1 equiv) and dppa (2 equiv) in ethanol for 15 min whereupon **3** can be isolated in ca. 60% yield. This chemistry differs from that previously reported for the reaction of $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ with the analogous $Ph_2PCH_2PPh_2$ (dppm) ligand, in that $Re_2(O_2CCH_3)X_4(dppm)_2$ was the predominant product in these instances even with reaction times considerably in excess of 30 min (2 h or so); it should be noted that in these reactions a low stoichiometric ratio of **1** to dppm was used (ca. 1:2). While we cannot rule out the formation of small amounts of *trans*-$[Re_2(O_2CCH_3)_2X_2(dppm)_2]X$, this is at most a very minor product unlike the case of the corresponding dppa salt **3**.

When the reactions that convert **1** to **2** and then **3** are allowed to proceed for prolonged periods (without the isolation of **2** and **3**) the major identified product is *cis*-$Re_2(O_2CCH_3)_2X_2(dppa)_2$ (**4**). The formation of **4** has been shown to occur through the sequence of conversions **1** → **2** → **3** → **4**, since when *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]Cl$ is first isolated from the reaction mixture and then rereacted with a mixture of dppa and NaO_2CCH_3 in ethanol, **4** is the primary product. Under conditions very similar to these, we have shown that **2** converts directly to **3** (see Scheme I); we have no evidence to support the direct conversion of **2** to **4** without the intermediacy of **3**. Note that the thermolysis of **2** in ethanol gives $Re_2X_4(dppa)_2$ (**5**). Since **5** does not react with LiO_2CCH_3 in ethanol to give **4** in any significant amounts,[11] we can rule out a **2** → **5** → **4** sequence as playing any significant role in the conversion of **1** to **4** in ethanol.

Table V. Electrochemical Data for Dirhenium Complexes of Bis(diphenylphosphino)amine

complex	voltammetric half-wave potentials,[a] V		
	$E_{1/2}(ox)^b$	$E_{1/2}(red)^b$	$E_{p,c}$
$Re_2(O_2CCH_3)Cl_4(dppa)_2$	+0.49 (110)	-0.53^c	
$Re_2(O_2CCH_3)Br_4(dppa)_2$	+0.57 (120)	-0.39^c	
trans-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]Cl^d$	+0.97 (110)	−0.22 (100)	
trans-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$	+1.01 (110)	−0.15 (120)	
trans-$[Re_2(O_2CCH_3)_2Br_2(dppa)_2]Br^e$	+0.99 (120)	−0.19 (120)	
cis-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$	+1.39 (120)	+0.35 (120)[f]	−1.58
cis-$Re_2(O_2CCH_3)_2Br_2(dppa)_2$	+1.40 (120)	+0.39 (120)[f]	−1.52
cis-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$	+1.40 (100)	+0.37 (100)	−1.60
$Re_2Cl_4(dppa)_2{}^g$	+0.93 (140)	+0.44 (140)[f]	
$Re_2Br_4(dppa)_2$	+1.05 (150)	+0.41 (110)[f]	

[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}. Under our experimental conditions, $E_{1/2}$ for the Cp_2Fe^+/Cp_2Fe couple was +0.47 V vs Ag/AgCl. [b] Numbers in parentheses are ΔE_p values (i.e., $E_{p,a} - E_{p,c}$). [c] $E_{p,c}$ value. [d] Accurate determination of $E_{p,a}$ for outer sphere Cl^- (at ca. +1.0 V) precluded by overlap with the $E_{1/2}(ox)$ couple associated with the dirhenium core. [e] $E_{p,a}$ = +0.7 V for outer sphere Br^-. [f] $E_{1/2}(ox)$ value. [g] Good agreement with data reported in ref 12.

(a) Spectroscopic and Electrochemical Characterizations. The identities of the complexes **2**–**5** are based upon the close similarity of their spectroscopic and electrochemical properties to those of their dppm analogues.[4,12] Only the complex $Re_2Cl_4(dppa)_2$ has been reported previously, having been prepared by the reaction of $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ with dppa in benzene.[12]

Cyclic voltammetric (CV) data on solutions in 0.1 M TBAH–CH_2Cl_2 are listed in Table V (all potentials are vs Ag/AgCl). For *cis*-$Re_2(O_2CCH_3)_2X_2(dppa)_2$ (**4**) and *trans*-$[Re_2(O_2CCH_3)_2X_2(dppa)_2]X$ (**3**), these measurements show the existence of two reversible one-electron oxidations in the case of **4** (at ca. +1.4 and

---

(11) The complex $Re_2Cl_4(dppa)_2$ was heated with an excess of LiO_2CCH_3 in ethanol for periods of 18 h and 2 days. The dark reaction mixtures were evaporated to dryness, and cyclic voltammograms were recorded on the CH_2Cl_2 soluble portions. There was no evidence for the presence of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ in other than (at most) very small amounts.

(12) Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882.

Table VI. Comparison of Key Structural Data for *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2P\text{-}A\text{-}PPh_2)_2]^{0/+}$ (A = CH_2 or NH)

complex	χ,[a] deg	Re–Re dist, Å	av bond dist, Å		
			Re–P	Re–O	Re–Cl
cis-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$[b]	11.5 (3)	2.3151 (7)	2.396 (3)	2.127 (8)	2.546 (4)
cis-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ (**4**)	12.8 (2)	2.3067 (5)	2.386 (3)	2.139 (6)	2.550 (3)
cis-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$ (**6**)	10.3 (2)	2.2757 (5)	2.449 (2)	2.085 (6)	2.528 (2)

complex	av bond angle, deg				
	Re–Re–P	Re–Re–O	Re–Re–Cl	P–Re–P	O–Re–O
cis-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$[b]	97.75 (9)	88.3 (3)	167.36 (9)	95.0 (1)	80.2 (3)
cis-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ (**4**)	96.66 (6)	88.4 (2)	168.50 (7)	96.40 (9)	81.4 (3)
cis-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$ (**6**)	97.10 (6)	88.9 (2)	173.42 (6)	99.62 (8)	81.2 (3)

[a] Average torsional angle. [b] Data taken from ref 4.

+0.4 V) and a one-electron oxidation (at ca. +1.0 V) and a one-electron reduction (at ca. −0.2 V) in the case of **3**. The redox behavior of **3** therefore resembles the CV properties of solutions of $Re_2X_4(dppa)_2$ (**5**) in 0.1 M TBAH–CH_2Cl_2 in that the reversible processes $Re_2^{5+} + e^- \rightleftarrows Re_2^{4+}$ and $Re_2^{6+} + e^- \rightleftarrows Re_2^{5+}$ are very accessible. For **3** (X = Cl), controlled-potential electrolysis at −0.35 V (n = 1.0) converted this yellow cation to orange *trans*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$. Reoxidation at −0.15 V regenerates **3** essentially quantitatively. Efforts were not made to characterize further the neutral trans isomer of $Re_2(O_2CCH_3)_2Cl_2(dppa)_2$. However, the chemical oxidation of the neutral cis isomer **4** was carried out by using $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in dichloromethane and gave the paramagnetic salt *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$ (**6**). Crystals of both **4** (X = Cl) and **6** were grown and their structures determined by X-ray crystallography (vide infra). The CV of **6** is the same as that of **4** (X = Cl), except that the process at +0.4 V now corresponds to a reduction of the bulk complex. For the monoacetate complexes **2**, the CV data are similar to those reported for $Re_2(O_2CCH_3)X_4(dppm)_2$,[4] with a reversible couple at ca. +0.5 V (this corresponds to an oxidation of the bulk complex, i.e., $Re_2^{5+} \rightarrow Re_2^{6+}$) and an irreversible reduction at $E_{p,c}$ ca. −0.45 V ($Re_2^{5+} \rightarrow Re_2^{4+}$).

The IR spectra of all the dppa complexes (recorded as Nujol mulls) show characteristic ν(N–H) modes for the coordinated dppa ligands (e.g. 3415 (m) cm^{-1} for **2** (X = Cl), 3145 (m–w) cm^{-1} for **3** (X = Cl), 3446 (w, br), 3330 (w), and 3252 (w, br) cm^{-1} for **4** (X = Cl), and 3405 (m–w) cm^{-1} for **5** (X = Cl)). We do not have a simple explanation for the wide range of spectral frequencies and complexities other than the occurrence of varying degrees of hydrogen-bonding interactions in the solid state and/or some variation in hybridization at the nitrogen atoms due to $N(p_\pi)\text{-}P(d_\pi)$ bonding. The electronic absorption spectra of these complexes (recorded in CH_2Cl_2) show a close resemblance to the corresponding spectra of the dppm derivatives.[4] Especially diagnostic is the $\delta \rightarrow \delta^*$ transition of the paramagnetic Re_2^{5+} complexes (types **2**, **3**, and **6**) that occurs with a λ_{max} value between 900 and 1300 nm ($\epsilon \simeq (1\text{-}2) \times 10^3$). Representative spectral data are available in Table S11.

Complexes **2**, **3**, **4**, and **6** are moderately soluble in several polar solvents. Conductivity measurements show that **2** and **4** are nonelectrolytes, while solutions of **3** (X = Cl, Br) and **6** in acetone and acetonitrile have conductances that accord with these complexes being 1:1 electrolytes (Λ_m values in the range 114–140 Ω^{-1} $cm^2 mol^{-1}$ for $C_m \simeq 1 \times 10^{-3}$ M).[13]

The ^1H NMR spectra of *cis*-$Re_2(O_2CCH_3)_2X_2(dppa)_2$ (X = Cl, Br) are very similar and confirm the diamagnetic nature of the Re_2^{4+} core. Spectra in CD_2Cl_2 (X = Cl) or $CDCl_3$ (X = Br) show the same complex pattern for the phenyl protons (δ +7.8 to δ +6.8), together with a singlet for the acetate protons (δ +1.98 for X = Cl and X = Br) and a broad N–*H* resonance (with the appearance of a poorly resolved triplet) at δ +4.84 for X = Cl and δ +5.02 for X = Br. The $^{31}P\{^1H\}$ NMR spectrum of the chloride derivative (in CD_2Cl_2) displays a singlet at δ +39.7. While the paramagnetic salts **2**, **3**, and **6** do not exhibit well-defined NMR spectra, they gave complex X-band ESR spectra (recorded in CH_2Cl_2 at −160 °C) that are in all instances strikingly similar to those of their dppm analogues.[4] Each signal spans the range 1.5–5.5 kG and is centered at $g \simeq 2.18$ (±0.02). Although resolvable coupling of approximately 400 G is present on the higher field region of these signals (probably due to Re hyperfine), the overall splitting is too complex to be fully interpreted without recourse to computer simulation. Suffice it to say that these patterns are characteristic of the Re_2^{5+} core with a $\sigma^2\pi^4\delta^2\delta^{*1}$ configuration.

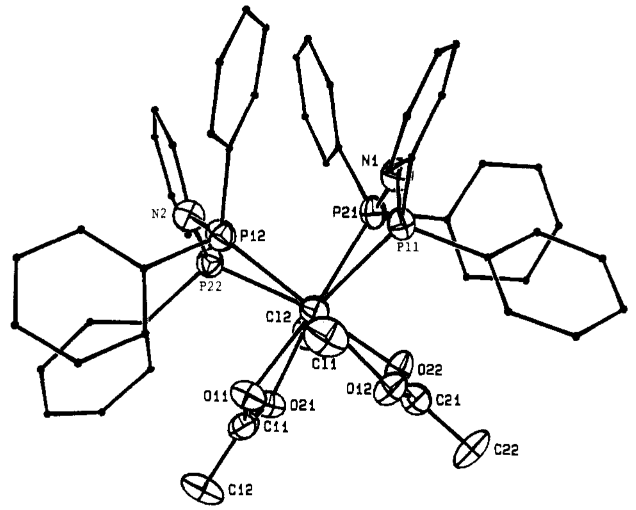


Figure 1. ORTEP representation of the structure of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ (**4**) as viewed down the Re–Re axis. One rhenium atom, Re(1), obscures the other. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings, which are drawn as circles of arbitrary radius.

(b) X-ray Structural Results. The complete structural characterization of **4** (X = Cl) and **6** has been accomplished by X-ray crystallography. In the case of **6** the crystals proved to be those of the solvate *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6\cdot(CH_3)_2CO\cdot{}^1/_2(C_2H_5)_2O$. We have previously characterized structurally *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ and *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6$,[4] but never a redox pair of this general type. The important bond distances and angles are listed in Tables III and IV. ORTEP representations of these two structures as viewed down the Re–Re axes are shown in Figures 1 and 2.

The molecular structure of **4** is essentially identical with that of the previously reported *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$,[4] as can be seen from Table VI wherein we compare some of the key structural parameters for species of the type *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2P\text{-}A\text{-}PPh_2)_2]^{0/+}$ (A = CH_2, NH). Comparable average bond distances and angles of **4** and *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ are strikingly similar, if not identical, to within experimental error. In going from **4** to **6**, statistically significant differences do exist, the magnitude of which, however, is small. Changes in the average bond distances from **4** to **6** are as follows: the Re–Re distance decreases (ca. 0.031 Å), the Re–P distances increase (ca. 0.063 Å), the Re–O distances decrease (ca. 0.054 Å), and the Re–Cl distances decrease (ca. 0.022 Å). The

---

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

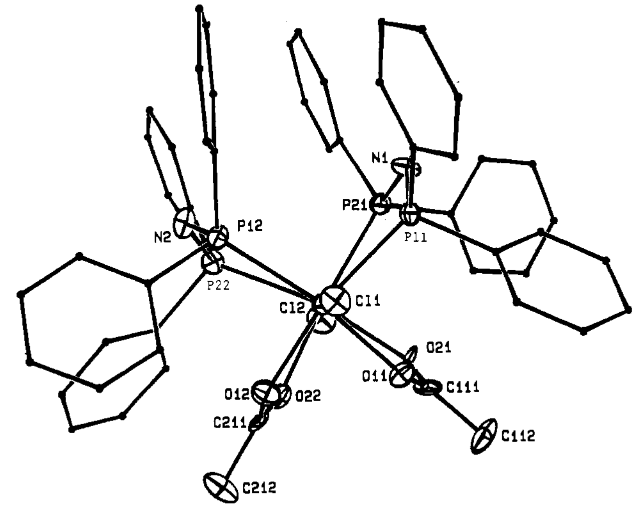


Figure 2. ORTEP representation of the structure of the *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]^+$ cation in its PF_6^- salt **6** as viewed down the Re–Re axis. One chlorine atom, Cl(1), partially obscures the rhenium atom Re(1), which in turn obscures Re(2). The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings, which are drawn as circles of arbitrary radius.

direction and magnitude of the changes in the Re–Re, Re–P, and Re–Cl distances are in accord with those reported for the species $[Re_2Cl_4(PMe_2Ph)_4]^{n+}$ (n = 0, 1).[14] These trends reflect the expected changes in (a) the Re–Re bond order, and (b) the effect of the core charge (Re_2^{4+} or Re_2^{5+}) on the Re–P and Re–Cl bonding. The increase in Re–P bond length between **4** and **6** presumably mirrors a decrease in Re–P π bonding. The average torsional angle (χ) changes very little in these complexes (Table VI), no doubt reflecting the constraints imposed by the bridging acetate ligands in particular.

(c) Concluding Remarks. The reaction of $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (**1**) with dppa in refluxing *ethanol* differs from analogous reactions with dppm[4] in a couple of important respects. First, the paramagnetic salts *trans*-$[Re_2(O_2CCH_3)_2X_2(dppa)_2]X$ (**3**) are key intermediates in the conversion of **1** to *cis*-$Re_2(O_2CCH_3)_2X_2(dppa)_2$ (**4**), whereas the dppm analogues of **3** were not isolated in the reactions between **1** and dppm in ethanol.[4] Second, **1** is converted into $Re_2X_4(dppm)_2$ via the intermediacy of $Re_2(O_2CCH_3)X_4(dppm)_2$ when reaction times of 15–18 h are used,[4,15] a reaction path that does not seem to be important in the dppa system (Scheme I). Apparently, $Re_2(O_2CCH_3)X_4(dppm)_2$ reductively decarboxylates more rapidly to give $Re_2X_4(dppm)_2$ than it reacts with acetate to produce *trans*-$[Re_2(O_2CCH_3)_2X_2(dppm)_2]X$, in contradistinction with the behavior of the dppa system. While $Re_2(O_2CCH_3)X_4(dppa)_2$ (**2**) can be thermolyzed in ethanol (in the absence of added acetate and dppa) to give $Re_2X_4(dppa)_2$ (**5**), we find that some *trans*-$[Re_2(O_2CCH_3)_2X_2(dppa)_2]X$ is also formed. This arises from the reaction of acetate ion (which is released in the conversion of **2** to **5**) with unreacted $Re_2(O_2CCH_3)X_4(dppa)_2$.

Acknowledgment. Support from the National Science Foundation, through Grant Nos. CHE85-06702 and CHE88-07444 to R.A.W. and Grant No. CHE86-15556 for the purchase of the MicroVAXII computer and diffractometer, is gratefully acknowledged. We also acknowledge the National Institutes of Health (Grant No. RR-01077) and the National Science Foundation (Grant No. 8714258) for funds for the purchase of the NMR spectrometers. We thank Ann R. Cutler for her assistance during the early stages of this study.

Supplementary Material Available: Tables giving full details of crystal data and data collection parameters (Tables S1 and S2), listings of positional parameters and their errors for the phenyl carbon atoms of **4** and **6** and the lattice solvent molecule atoms and the atoms of PF_6^- of **6** (Tables S3 and S4), listings of thermal parameters (Tables S5 and S6), complete listings of bond distances (Tables S7 and S8) and bond angles (Tables S9 and S10), and a listing of electronic absorption spectral data (Table S11) and figures showing the full atomic number schemes for **4** and the cation of **6** (Figures S1 and S2) (34 pages); tables of observed and calculated structure factors (79 pages). Ordering information is given on any current masthead page.

---

(14) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.

(15) We find that $Re_2Cl_4(dppm)_2$ readily converts to *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ when reacted with an excess of LiO_2CCH_3 using ethanol as solvent (Derringer, D. R. Unpublished results). As we have reported previously,[4] a similar reaction ensues when methanol is used in place of ethanol.