Table I. Comparison of the ν(CN) Spectra of the $M(CN)_6$ Group

sample	no.	ν(CN)(IR), cm^{-1}			ν(CN)(Raman), cm^{-1}		
$[(n\text{-}Bu)_4N]_4[Ru^{II}(CN)_6]$	**1a**	2040 m, sh	2060 s	2070 w, sh	2043 s	2083 m	
$[Et_4N]_4[Fe^{II}(CN)_6]$	**1d**^{b}	2030 s	2050 vs	2080 m	2035 s	2072 m	
$[(n\text{-}Bu)_4N]_3[Ru^{III}(CN)_6]$	**2a**^{a}		2090 m		2098 m	2111 m	
$[(n\text{-}Bu)_4N]_3[Fe^{III}(CN)_6]$	**2b**		2095 vs		2108 m, sh	2112 s	
$[(Me_3Sn)_3Fe^{III}(CN)_6]$	**3b**		2145/2159 vs^c		2154 w	2167 w^d	
$[(n\text{-}Bu)_4N]_{0.5}(Me_3Sn)_3[Ru^{II}{}_{0.5}Ru^{III}{}_{0.5}(CN)_6]$	**3a′**^{a}	2070 m, br	2140 m		not observable^d		
$[(Et_4N)(Me_3Sn)_3Ru^{II}(CN)_6]_\infty{}^e$			2060 s	2080 m, sh	2080 m, sh	2091 s	2135 m

^{a} IR spectrum of Nujol mull. ^{b} ν(CN) bands identical with those of **1b**. ^{c} Doublet under high resolution. ^{d} Very poor Raman scattering. ^{e} Cf. ref 10.

From the relative intensities of the ν(CN) bands of **2a** and of the resulting $[Ru^{II}(CN)_6]^{4-}$ anion (cf. Table I), the relative efficiency of slightly different reductants may be estimated, e.g. NaI, NH_4I, KI > $[Me_4N]I$ > KBr, $[Et_4N]I$, Cp_2Fe > $[(n\text{-}Pr)_4N]I$ > $[(n\text{-}Bu)_4N]I$.

Interestingly, **2b** oxidizes under the strictly repeated standard conditions only the iodides of Na^+–Me_4N^+, while e.g. the novel coordination polymer $[(Me_3Sn)_3Fe^{III}(CN)_6]_\infty \hat{=} [Fe^{III}(\mu\text{-}CN\text{–}Me_3Sn\text{–}NC)_3]_\infty$ (**3b**)[9] is about as efficient as the Ru(III) system **2a**. This feature agrees with the view that the nitrogen-bonded Me_3Sn^+ units could be considered as fixed counterions of a particularly large AN.

In contrast to the facile formation of **3b**,[9] attempts to also prepare the Ru homologue **3a** of **3b**, which is expected to be an even stronger oxidant than **2a** and **3b**, did not afford any precipitate when solutions of **2a** and Me_3SnCl were combined in H_2O, EtOH, THF, MeCN, and DMF, respectively. So far, only in CH_2Cl_2 could an initially orange-yellow, insoluble product **3a′** be obtained, which turns light brown even after strict manipulation under N_2 and exclusion of light. The vibrational spectra of **3a′** in the ν(CN) range display equally intense bands typical of both $[Ru^{III}(CN)_6]$ *and* $[Ru^{II}(CN)_6]$ units, probably with bridging CN ligands (cf. Table I). The IR spectrum is diagnostic not only of Me_3Sn groups but also of minor amounts of $[(n\text{-}Bu)_4N]^+$ ions, while short grinding of **3a′**, e.g. with KI, affords again elemental iodine. The elemental analysis is consistent with the formulation $[(n\text{-}Bu)_4N]_x(Me_3Sn)_3[Ru^{II}{}_xRu^{III}{}_{1-x}(CN)_6]$ with $x \approx 0.5$. A similar cation intercalate (with Fe instead of Ru and $x \approx 0.2$) was obtained by exhaustive grinding of **3b** with $[(n\text{-}Bu)_4N]I$.[10]

Recently, Osteryoung et al.[5] have noted that the salt **2b** dissolves in an acidic 1-methyl-3-ethylimidazolium chloride/aluminum chloride melt probably under partial reduction of $[Fe^{III}(CN)_6]^{3-}$ to $[Fe^{II}(CN)_6]^{4-}$ by Cl^- anions. The authors consider the formation of CN-bridged adducts of $[Fe^{III}(CN)_6]^{3-}$ and $AlCl_3$ responsible for a notable increase of the ferrocyanide/ferricyanide redox potential that would even allow the oxidation of Cl^-. These findings strongly resemble our own observation that **3b** behaves as a notably stronger oxidant than **2b** (vide supra) and suggest that the formation of pure **3a** might be likewise impeded by the oxidation of Cl^- ions owing to the formation of adducts of $[Ru^{III}(CN)_6]^{3-}$ and Me_3SnCl species.[11]

In view of the particularly interesting properties of pure **3a** as a strongly oxidizing zeolite-like material, our efforts to develop suitable conditions for its successful preparation are being continued.

Experimental Section

The following instruments were used to characterize the products: Perkin-Elmer Model 577 (infrared spectroscopy), Ramanov U-1000 of Jobin Yvon (Raman spectroscopy), Cary Model 17 I (UV/vis spectroscopy), and a Johnson Matthey susceptometer after D. F. Evans (magnetic susceptibility). Only the preparation and spectroscopy of **1d** and **3a′** as well as all grinding experiments were carried out under a N_2 atmosphere.

A. Preparation of $[(n\text{-}C_4H_9)_4N]_4[Ru^{II}(CN)_6]$ (1a) and Related Salts. $K_4[Ru(CN)_6]$[12] was converted into $H_4Ru(CN)_6$[13] by reaction with aqueous HCl and Et_2O, and the latter into $[R_4N]_4[Ru(CN)_6]$ by titration with $[R_4N]OH$ (R = C_2H_5 or $n\text{-}C_4H_9$), solvent removal, and drying.[4]

B. Preparation of $[(n\text{-}C_4H_9)_4N]_3[Ru^{III}(CN)_6$ (2a). A solution of 0.25 g (0.20 mmol) of $[(n\text{-}C_4H_9)_4N]_4[Ru(CN)_6]$ in 10 cm^3 of anhydrous DMF was stirred at room temperature in a flask protected against moisture by a $CaCl_2$ tube. After 3 h, 50 cm^3 of absolute Et_2O was added, and the resulting suspension was kept overnight in the refrigerator. Finally, after filtration, a brilliant yellow solid was isolated, washed with Et_2O, and dried under vacuum for a few hours: 0.18 g (90%). Anal. Calcd for $C_{54}H_{108}N_9Ru$: C, 65.88; H, 11.06; N, 12.80. Found: C, 65.42; H, 10.88; N, 12.61. UV/vis absorptions (MeCN), cm^{-1}: 35 700, 33 700, 30 400, 28 100, 21 500 (ϵ_0, cm^2 mol^{-1}: 1090, 2340, 2410, 1720, 830).

C. Solid-State Redox Reactions with 2a, "Standard" Procedure. A 0.02-g sample (0.02 mmol) of **2a** was mixed with 0.06 mmol of the respective reductant. After intense grinding of this mixture under an atmosphere of N_2 for 5 min, washing with several portions of toluene to remove all iodine, and final drying, the spectra of the KBr pellets were recorded.

D. Reaction of 2a with $(CH_3)_3SnCl$. Under an N_2 atmosphere and in the absence of light, solutions of 0.040 g (0.041 mmol) of $[(n\text{-}C_4H_9)_4N]_3[Ru(CN)_6]$ and 0.025 g (0.125 mmol) of $(CH_3)_3SnCl$ in 10 cm^3 CH_2Cl_2 were combined under stirring. The orange-yellow precipitate formed after several seconds was separated out by filtration, washed with a small amount of CH_2Cl_2, and dried in vacuo (room temperature): 0.043 g. Selected bands (cm^{-1}): Me_3Sn^+, 550 m (IR), 518 s (Ra); $[(n\text{-}Bu)_4N]^+$, 1490 m, 1380 w, 1155 m (IR). Anal. Calcd for $(Me_3Sn)_3Ru(CN)_6 \hat{=} C_{15}H_{27}N_6RuSn_3$: C, 26.63; H, 4.02; N, 12.42; Sn, 52.63. Calcd for $[(n\text{-}Bu)_4N]_{0.5}(Me_3Sn)_3[Ru^{II}{}_{0.5}Ru^{III}{}_{0.5}(CN)_6] \hat{=} C_{23}H_{45}N_{6.5}RuSn_3$: C, 31.76; H, 5.21; N, 10.47; Sn, 40.94. Found: C, 34.53; H, 5.83; N, 10.02; Sn, 40.32.

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Further Studies on Dirhenium Complexes That Contain the Bridging Ligand 2-(Diphenylphosphino)pyridine. Isolation and Characterization of *cis*-$[Re_2(O_2CR)_2X_2(Ph_2Ppy)_2]^{n+}$ (R = CH_3, C_2H_5; X = Cl, Br; *n* = 0, 1)

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During the course of our studies on the reactions of the dirhenium(III) carboxylate complexes $Re_2(O_2CR)_2X_4L_2$ (R = CH_3, C_2H_5; X = Cl, Br; L = H_2O, py, 4-Mepy) with the phosphines PPh_3 and Ph_2Ppy, we isolated and characterized several complexes of the type $Re_2(\mu\text{-}O_2CR)X_4(PPh_3)_2$ and $Re_2(\mu\text{-}O_2CR)X_4(Ph_2Ppy)_2$ that are derivatives of the paramagnetic $Re_2{}^{5+}$ core.[1] In one

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specific system, namely, that involving the reaction between $Re_2(O_2CC_2H_5)_2Cl_4(4\text{-}Mepy)_2$ and Ph_2Ppy in acetone, we also isolated another product (described as "blue-black crystals") whose identity at the time elluded us.[1] We have now succeeded in identifying this product as the dirhenium(II) complex *cis*-$Re_2(\mu\text{-}O_2CC_2H_5)_2Cl_2(\mu\text{-}Ph_2Ppy)_2$, and in the present report we describe the details of its properties as well as the synthesis and characterization of some other Ph_2Ppy complexes of this type. These complexes not only make for an interesting comparison with other dirhenium complexes that contain two, three, or four bridging Ph_2Ppy ligands[2] but show a close relationship to complexes of the type *cis*- or *trans*-$Re_2(\mu\text{-}O_2CR)_2X_2(\mu\text{-}LL)_2$ [R = CH_3, C_2H_5, C_6H_5, 4-C_5H_4N; X = Cl, Br; LL = dppm ($Ph_2PCH_2PPh_2$), dpam ($Ph_2AsCH_2AsPh_2$), dppa ($Ph_2PNHPPh_2$)][3-5] that have been of recent interest.

Experimental Section

Starting Materials. The compounds $Re_2(O_2CC_2H_5)_2X_4(4\text{-}Mepy)_2$ (X = Cl, Br)[6] and $Re_2Cl_4(Ph_2Ppy)_2(PEt_3)$[2] were prepared according to known literature procedures. The bromide complex $Re_2Br_4(Ph_2Ppy)_2(PEt_3)$ was prepared by the following procedure. An acetone solution (15 mL) of $Re_2Br_6(PEt_3)_2$ (0.30 g, 0.31 mmol) and Ph_2Ppy (0.50 g, 1.90 mmol) was refluxed for 1 h in the presence of a pine boiling stick. The dark crystals that formed were washed with diethyl ether and vacuum dried; yield 0.089 g (23%). The identity of this compound was based upon a comparison of its electrochemical and spectroscopic properties with those reported for its chloride analogue $Re_2Cl_4(Ph_2Ppy)_2(PEt_3)$.[2]

The ligand 2-(diphenylphosphino)pyridine (abbreviated Ph_2Ppy) was prepared by the use of a procedure similar to that described by Maisonnet et al.[7] All solvents were obtained from commercial sources and were used as received.

Reaction Procedures. Syntheses were performed with the use of an atmosphere of dry nitrogen, and solvents were deoxygenated prior to use.

A. Syntheses of *cis*-$Re_2(O_2CR)_2Cl_2(Ph_2Ppy)_2$. (i) R = CH_2CH_3. (a) From $Re_2(O_2CC_2H_5)_2Cl_4(4\text{-}Mepy)_2$. A mixture of $Re_2(O_2CC_2H_5)_2Cl_4(4\text{-}Mepy)_2$ (0.10 g, 0.12 mmol) and Ph_2Ppy (0.06 g, 0.22 mmol) was refluxed in acetone (12 mL) for 3 days. The solution was filtered while hot to remove a crop of small dark purple crystals. These were washed with diethyl ether and vacuum dried; yield 0.02 g (15%). Anal. Calcd for $C_{40}H_{38}Cl_2N_2O_4P_2Re_2$: C, 43.05; H, 3.43; Cl, 6.35. Found: C, 42.22; H, 3.64; Cl, 6.21.

The initial reaction filtrate was allowed to partially evaporate in air for 1 day to yield a crop of maroon crystals previously characterized as $Re_2(O_2CC_2H_5)Cl_4(Ph_2Ppy)_2\cdot{}^1/_2(CH_3)_2CO$.[1]

(b) From $Re_2Cl_4(Ph_2Ppy)_2(PEt_3)$. A mixture of $Re_2Cl_4(Ph_2Ppy)_2(PEt_3)$ (0.100 g, 0.089 mmol) and $NaO_2CC_2H_5$ (0.178 g, 1.85 mmol) was refluxed in methanol (15 mL) for 1 day. A dark purple product was filtered off, washed with acetone and diethyl ether, and vacuum dried; yield 0.052 g (52%).

(ii) R = CH_3. This complex was prepared from $Re_2Cl_4(Ph_2Ppy)_2(PEt_3)$ and LiO_2CCH_3 by the use of a procedure similar to that described for its propionate analogue; yield 25%. Anal. Calcd for $C_{38}H_{34}Cl_2N_2O_4P_2Re_2$: C, 41.95; H, 3.15. Found: C, 42.07; H, 3.17.

B. Synthesis of *cis*-$Re_2(O_2CC_2H_5)_2Br_2(Ph_2Ppy)_2$. (i) From $Re_2(O_2CC_2H_5)_2Br_4(4\text{-}Mepy)_2$. A mixture of $Re_2(O_2CC_2H_5)_2Br_4(4\text{-}Mepy)_2$ (0.400 g, 0.390 mmol) and Ph_2Ppy (0.220 g, 0.807 mmol) was refluxed in acetone (20 mL) for 3 days to afford a dark purple crystalline material. The crystals were washed with hot acetone (2 × 15 mL) and dichloromethane (5 mL) to dissolve a maroon component, and the insoluble dark purple microcrystalline product that remained was vacuum dried; yield 0.160 g (34%). Anal. Calcd for $C_{40}H_{38}Br_2N_2O_4P_2Re_2$: C, 39.87; H, 3.18; Br, 13.26. Found: C, 38.93; H, 3.65; Br, 13.02.

The solvent from the maroon extract was slowly evaporated to yield a maroon powder; yield 0.052 g (10%). Anal. Calcd for $C_{37}H_{33}Br_4N_2O_2P_2Re_2$: C, 34.41; H, 2.58. Found: C, 33.75; H, 2.78. The identity of this product as $Re_2(O_2CC_2H_5)Br_4(Ph_2Ppy)_2$ was further established by a comparison of its spectroscopic and electrochemical properties to those of its chloride analogue.[1] Specifically, its electronic absorption spectrum (recorded in CH_2Cl_2) displayed absorption maxima (in nm) at 531 (ϵ = 1600) and 396 (ϵ = 3800), while the cyclic voltammogram of a solution of this complex in 0.1 M TBAH/CH_2Cl_2 showed processes at $E_{1/2}(ox) = +0.58$ V and $E_{1/2}(red) = -0.36$ V vs Ag/AgCl.

Table I. Crystallographic Data for *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]PF_6$

chem formula	$Re_2Cl_2P_3F_6O_4N_2C_{38}H_{34}$	space group	$P2_1/n$ (No. 14)
a, Å	15.076 (3)	T, °C	20
b, Å	15.925 (3)	λ(Mo Kα), Å	0.71073
c, Å	20.425 (4)	ρ_{calcd}, g cm^{-3}	1.766
β, deg	108.97 (2)	μ(Mo Kα), cm^{-1}	55.66
V, Å^3	4637 (3)	transm coeff	1.000–0.722
Z	4	R^a	0.061
fw	1232.92	$R_w{}^b$	0.079

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

(ii) From $Re_2Br_4(Ph_2Ppy)_2(PEt_3)$. A quantity of $Re_2Br_4(Ph_2Ppy)_2(PEt_3)$ (0.100 g, 0.079 mmol) and $NaO_2CC_2H_5$ (0.178 g, 1.85 mmol) was refluxed in methanol (15 mL) for 1 day. A small quantity of a dark purple product was filtered off, washed with acetone and diethyl ether, and vacuum dried; yield 0.016 g (17%).

C. Synthesis of *cis*-$[Re_2(O_2CR)_2Cl_2(Ph_2Ppy)_2]PF_6$. (i) R = CH_2CH_3. A mixture of $Re_2(O_2CC_2H_5)_2Cl_2(Ph_2Ppy)_2$ (0.100 g, 0.083 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.0330 g, 0.100 mmol) was stirred for 15 min in dichloromethane (15 mL). The maroon reaction mixture was filtered, and the filtrate was allowed to evaporate to about half of its original volume. Diethyl ether was added to the resulting solution to initiate precipitation of a maroon product. The solution was then cooled to 0 °C for 2 h and filtered. The product was washed with diethyl ether (3 × 15 mL) and dried under vacuum; yield 0.086 g (82%). Anal. Calcd for $C_{40}H_{38}Cl_2F_6N_2O_4P_3Re_2$: C, 38.10; H, 3.04. Found: C, 37.26; H, 3.34.

(ii) R = CH_3. This complex was prepared by following the use of a procedure similar to that described for its propionate analogue; yield 87%. Anal. Calcd for $C_{38}H_{34}Cl_2F_6N_2O_4P_3Re_2$: C, 37.02; H, 2.78. Found: C, 36.79; H, 3.24.

Preparation of Single Crystals for Structure Determination. Suitable crystals of *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]PF_6$ were obtained as maroon plates when diethyl ether was allowed to diffuse into a 1,2-dichloroethane solution of this complex over a period of 1 week.

X-ray Crystallography. The structure of *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]PF_6$ was determined by the application of standard procedures. The basic crystallographic procedures are listed in Table I. The cell constants are based on 25 reflections with $15.0 < \theta < 20.0°$. Three standard reflections were measured after every 5000 s of beam time during data collection; there was no systematic variation in intensity. Calculations were performed on a MicroVAX computer using the Enraf-Nonius structure determination package.

The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. Lorentz and polarization corrections were applied to the data. An empirical absorption correction was used,[8] the linear absorption coefficient being 55.66 cm^{-1}. No corrections for extinction were applied. The structure was refined in full-matrix least-squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. The positions for the hydrogen atoms were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. For the methyl groups of the acetate ligands, one hydrogen was located in a difference Fourier map, its position idealized, and the remaining positions were calculated. We assumed that the value of B(H), i.e. the isotopic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, they were not included in the least-squares refinement. The non-hydrogen atoms of the dirhenium cation were refined anisotropically; corrections for anomalous scattering were applied to all atoms so refined.[9] The fluorine atoms of the PF_6^- anion were characterized

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Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for Non-Phenyl Atoms of the *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]^+$ Cation and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
Re(1)	0.10369 (6)	0.16810 (6)	0.16994 (5)	2.44 (2)
Re(2)	−0.02222 (6)	0.15773 (6)	0.07289 (5)	2.44 (2)
Cl(11)	0.2218 (5)	0.1496 (4)	0.2880 (3)	4.0 (2)
Cl(21)	−0.1301 (5)	0.1393 (4)	−0.0504 (3)	3.9 (2)
P(1)	0.0076 (5)	0.2231 (4)	0.2334 (3)	3.0 (2)
P(2)	0.0055 (4)	0.2967 (4)	0.0375 (3)	2.6 (1)
O(21)	0.077 (1)	0.0421 (9)	0.1868 (8)	2.6 (4)
O(22)	−0.051 (1)	0.0353 (9)	0.0950 (9)	3.6 (4)
O(31)	0.196 (1)	0.123 (1)	0.1212 (8)	2.9 (4)
O(32)	0.072 (1)	0.109 (1)	0.0263 (8)	3.1 (4)
N(112)	−0.134 (1)	0.196 (1)	0.111 (1)	3.3 (5)
N(212)	0.152 (1)	0.290 (1)	0.156 (1)	3.1 (5)
C(23)	0.013 (2)	0.002 (2)	0.149 (1)	4.0 (7)
C(24)	−0.001 (2)	−0.089 (2)	0.163 (2)	5.4 (8)
C(33)	0.160 (2)	0.102 (1)	0.059 (1)	3.2 (6)
C(34)	0.220 (2)	0.074 (2)	0.020 (1)	3.8 (7)

[a] Anisotropically refined atom *B* values are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Data for the phenyl and pyridyl ring carbon atoms and the atoms of the PF_6^- anion are available as supplementary material.

Table III. Important Bond Distances (Å) and Bond Angles (deg) for the *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]^+$ Cation[a]

	Distances		
Re(1)–Re(2)	2.261 (1)	Re(2)–Cl(21)	2.532 (5)
Re(1)–Cl(11)	2.506 (5)	Re(2)–P(2)	2.406 (5)
Re(1)–P(1)	2.401 (6)	Re(2)–O(22)	2.08 (1)
Re(1)–O(21)	2.10 (1)	Re(2)–O(32)	2.11 (1)
Re(1)–O(31)	2.08 (1)	Re(2)–N(112)	2.16 (2)
Re(1)–N212)	2.13 (1)		
	Angles		
Re(2)–Re(1)–Cl(11)	165.1 (1)	Re(1)–Re(2)–Cl(21)	164.8 (1)
Re(2)–Re(1)–P(1)	91.0 (1)	Re(1)–Re(2)–P(2)	91.0 (1)
Re(2)–Re(1)–O(21)	85.5 (3)	Re(1)–Re(2)–O(22)	93.1 (4)
Re(2)–Re(1)–O(31)	93.2 (3)	Re(1)–Re(2)–O(32)	85.7 (3)
Re(2)–Re(1)–N212)	100.1 (4)	Re(1)–Re(2)–N112)	101.2 (4)
Cl(11)–Re(1)–P(1)	83.6 (2)	Cl(21)–Re(2)–P(2)	85.7 (2)
Cl(11)–Re(1)–O(21)	81.0 (3)	Cl(21)–Re(2)–O(22)	89.7 (4)
Cl(11)–Re(1)–O(31)	92.5 (4)	Cl(21)–Re(2)–O(32)	79.5 (4)
Cl(11)–Re(1)–N(212)	94.0 (4)	Cl(21)–Re(2)–N(112)	93.8 (4)
P(1)–Re(1)–O(21)	94.5 (4)	P(2)–Re(2)–O(22)	175.3 (4)
P(1)–Re(1)–O(31)	175.8 (4)	P(2)–Re(2)–O(32)	89.8 (4)
P(1)–Re(1)–N(212)	91.7 (5)	P(2)–Re(2)–N(112)	97.7 (4)
O(21)–Re(1)–O(31)	86.5 (5)	O(22)–Re(2)–O(32)	88.2 (5)
O(21)–Re(1)–N(212)	171.6 (5)	O(22)–Re(2)–N(112)	86.8 (6)
O(31)–Re(1)–N(212)	87.0 (6)	O(32)–Re(2)–N(112)	171.7 (5)

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

by large thermal motions and a wide disparity in the P–F bond lengths. While there was some improvement in these parameters when the atoms of PF_6^- were refined isotropically, the refinement of the anion was not very satisfactory.[10] Nonetheless, this problem did not affect in any significant way our conclusions concerning the key structural features of the much more important dirhenium cation. The largest peak in the final difference Fourier map (2.58 e/Å^3) did not appear to be of any chemical significance.

Positional parameters and their errors for the non-phenyl atoms of the dirhenium cation of *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]PF_6$ are listed in Table II. Important intramolecular bond distances and angles are given in Table III. Tables giving full details of the crystal data and data collection parameters (Table S1), the positional parameters for the non-hydrogen atoms (Table S2), the positional parameters for the hydrogen atoms (Table S3), the thermal parameters (Table S4), and complete bond distances (Table S5) and bond angles (Table S6) are available as supplementary material.

Physical Measurements. Electrochemical and spectroscopic characterizations were carried out with the use of instrumentation and techniques described previously.[4]

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

Results and Discussion

The reactions between the dirhenium(III) complexes $Re_2(O_2CC_2H_5)_2X_4(4\text{-Mepy})_2$ (X = Cl, Br) and Ph_2Ppy in refluxing acetone for periods of 1 day or less have been shown to favor the formation of the paramagnetic complexes $Re_2(O_2CC_2H_5)X_4(Ph_2Ppy)_2$.[1] We have found in the present study that longer reaction times (ca. 3 days) result in further reduction and the isolation of *cis*-$Re_2(O_2CC_2H_5)_2X_2(Ph_2Ppy)_2$. Even though less than 2 equiv of Ph_2Ppy was used in the reaction with $Re_2(O_2CC_2H_5)Cl_4(4\text{-Mepy})_2$, the yield of *cis*-$Re_2(O_2CC_2H_5)_2Cl_2(Ph_2Ppy)_2$ was still significant (ca. 15%). This indicates that a disproportionation mechanism (via $Re_2(O_2CC_2H_5)Cl_4(Ph_2Ppy)_2$) could be operative rather than the formation of *cis*-$Re_2(O_2CC_2H_5)_2Cl_2(Ph_2Ppy)_2$ being a consequence of the direct phosphine-induced reduction of $Re_2(O_2CC_2H_5)Cl_4(Ph_2Py)_2$. However, as an alternative, and more desirable synthetic strategy, we found that the prereduced dirhenium(II) complexes $Re_2X_4(Ph_2Ppy)_2(PEt_3)$[2] react with $NaO_2CC_2H_5$ in refluxing methanol for 1 day to give these same complexes. The acetate complex $Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2$ has been prepared by a similar procedure. The ^1H NMR spectrum of the latter complex (recorded in CD_2Cl_2) shows a resonance at δ +2.25 due to CH_3 of the acetate ligands that has the correct integration relative to the phenyl resonances.

These three complexes exhibit almost identical electronic absorption spectra, and they also display very similar cyclic voltammetric properties (Table IV). The electronic absorption spectra differ quite markedly from those of the analogous complexes that contain the dppm and dppa ligands.[3,4] Of special note are the much larger intensities of the bands in the visible region of the spectra of $Re_2(O_2CR)_2X_2(Ph_2Ppy)_2$ (see Table IV) compared to the related spectra of *cis*-$Re_2(O_2CR)_2X_2(LL)_2$ (LL = dppm, dppa); for example, bands at 815 and 465 nm in the spectrum of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ have ϵ values of only 170 and 270 $M^{-1}\,cm^{-1}$, respectively.[2] We attribute these high-intensity features in the visible region of the spectra of the purple complexes $Re_2(O_2CR)_2X_2(Ph_2Ppy)_2$ to $Re_2^{4+} \rightarrow py(\pi^*)$ transitions associated with the coordinated pyridyl fragment of the Ph_2Ppy ligands. We note that the dirhenium(II) complexes $Re_2Cl_4(Ph_2Ppy)_2(PR_3)$ (R = Et, *n*-Bu), which contain Ph_2Ppy ligands that bridge the two metal centers through their P and N donor atoms,[2] also contain intense bands ($\epsilon \simeq 5000$) in their electronic absorption spectra between 600 and 400 nm.

The two one-electron oxidations that are observed in the cyclic voltammograms of 0.1 M $TBAH/CH_2Cl_2$ solutions of these complexes are at potentials very similar to those for complexes of the type *cis*-$Re_2(\mu\text{-}O_2CR)_2X_2(\mu\text{-}LL)_2$ (LL = dppm, dpam, dppa),[3-5] implying that the Ph_2Ppy complexes should be formulated as *cis*-$Re_2(\mu\text{-}O_2CR)_2X_2(\mu\text{-}Ph_2Ppy)_2$. In accord with the behavior observed for the dppm, dpam, and dppa derivatives,[3-5] we find that the Ph_2Ppy complexes are very easily oxidized to $[Re_2(O_2CR)_2X_2(Ph_2Ppy)_2]^+$. This was demonstrated in the case of X = Cl and R = CH_3 or C_2H_5 by the use of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ as oxidant in dichloromethane. The electronic absorption spectra of these two oxidized species are very similar to one another (Table IV). The cyclic voltammograms of their solutions in 0.1 M $TBAH/CH_2Cl_2$ are the same as those of their neutral precursors except that the process at ca. +0.1 V now corresponds to a reduction of the bulk complex. Their solutions in CH_2Cl_2 have magnetic moments (as measured by the Evans method) that confirm the presence of one unpaired electron (μ_{eff} = 1.7 (±0.1) μ_B). The paramagnetic nature of these species is further demonstrated by X-band ESR spectral measurements. These complexes, in CH_2Cl_2/toluene glasses at −160 °C, show complex,

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(10) The spectroscopic properties of the sample from which the crystal was selected for the structure determination were fully in accord with the presence of the PF_6^- anion (ν(P–F) at 840 (s) cm^{-1} in the IR spectrum). Accordingly, in site of our failure to model the anion in an entirely satisfactory fashion during the course of the structure refinement, we are confident that our structural conclusions are correct.

Table IV. Electrochemical and Electronic Absorption Spectra Data for *cis*-$[Re_2(O_2CR)_2X_2(Ph_2Ppy)_2]^{n+}$ (n = 0, 1)

complex	elect abs spectrum, nm[a]	voltammetric half-wave potentials, V[a] $E_{1/2}$(ox(2))[c]	$E_{1/2}$(ox(1))[c]
cis-$Re_2(O_2CC_2H_5)_2Cl_2(Ph_2Ppy)_2$	720 sh, 618 (5500), 541 (4300), 384 (4500), 345 (4300), 248 sh	+1.18 (110)	+0.10 (110)
cis-$Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2$	720 sh, 617 (6100), 543 (5100), 385 (5100), 348 (5000), 245 sh	+1.20 (120)	+0.11 (110)
cis-$Re_2(O_2CC_2H_5)_2Br_2(Ph_2Ppy)_2$	735 sh, 617 (4400), 538 (3400), 380 (3600), 340 sh, 285 sh, 255 sh	+1.22 (130)	+0.14 (120)
cis-$[Re_2(O_2CC_2H_5)_2Cl_2(Ph_2Ppy)_2]PF_6$	510 (3400), 390 sh, 356 (5500), 300 sh, 260 sh	+1.18 (120)	+0.10 (120)[d]
cis-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]PF_6$	505 (3500), 395 sh, 357 (5900), 300 sh, 260 sh	+1.20 (120)	+0.13 (120)[d]

[a] Measured in CH_2Cl_2; ϵ_{max} values in parentheses. [b] 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. Under our experimental conditions $E_{1/2}$ for the ferrocenium/ferrocene couple was +0.47 V vs Ag/AgCl. [c] Numbers in parentheses are ΔE_p values (i.e., $E_{p,a} - E_{p,c}$). [d] $E_{1/2}$(red) values.

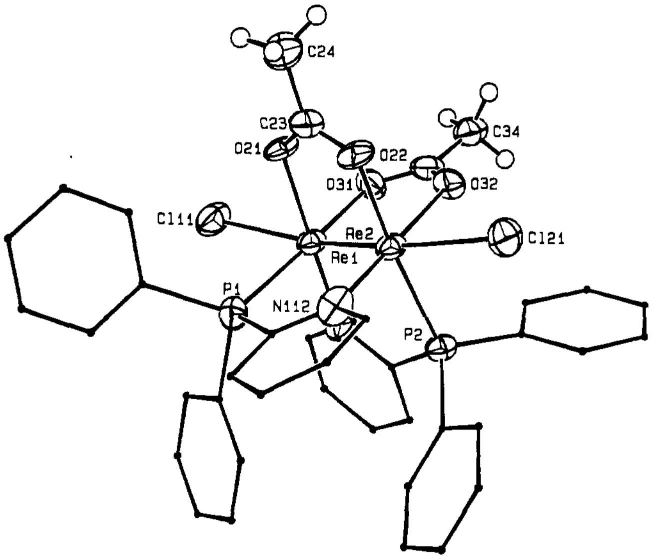

Figure 1. ORTEP view of the structure of the *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]^+$ cation. For clarity, the atomic numbering scheme is given for all atoms except the phenyl and pyridyl ring carbon atoms. the thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl and pyridyl rings, which are circles of arbitrary radius.

highly structured patterns that are centered at $g_\perp \simeq 2.82$ ($A_\perp \simeq 425$ G) and $g_\parallel \simeq 1.41$ ($A_\parallel \simeq 450$ G).

The conclusion that the complexes described in this report are correctly formulated as *cis*-$Re_2(\mu-O_2CR)_2X_2(\mu-Ph_2Ppy)_2$ has been confirmed by a crystal structure determination on the oxidized species *cis*-$[Re_2(\mu-O_2CCH_3)_2Cl_2(\mu-Ph_2Ppy)_2]PF_6$ (Figure 1). Important structural parameters are listed in Table III. Our attempts to grow suitable crystals of *cis*-$Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2$ were not successful. However, since the electrochemical properties of the oxidized complex and its neutral precursor are the same, except of course for the fact that the reversible couple at +0.10 V corresponds to a reduction in the case of the former complex and an oxidation for the latter (see Table IV), they must possess very similar structures. The structure of the *cis*-$[Re_2(\mu-O_2CCH_3)_2Cl_2(\mu-Ph_2Ppy)_2]^+$ cation is also very similar to that of the analogous dirhodium(II) complex *cis*-$Rh_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2$,[11] in which the individual sets of acetate and Ph_2Ppy ligands are cis to one another. Also, the two Ph_2Ppy ligands are arranged in a head-to-tail fashion. Of interest is a similar nonlinearity of the Cl–Re–Re–Cl and Cl–Rh–Rh–Cl units; the Re–Re–Cl and Rh–Rh–Cl angles are 165.0 (2) and 168.7 (1)°, respectively. The metal–metal distances in these two structures are of course quite different, with the Re–Re distance being 2.261 (1) Å and the Rh–Rh distance equal to 2.518 (1) Å; this in part reflects the different metal–metal bond orders, which are formally 3.5 and 1.0, respectively. An important consequence of this difference is the closer approach of the dirhenium structure to an ideal *eclipsed* conformation in order to maximize the δ component to the metal–metal bonding in the $\sigma^2\pi^4\delta^2\delta^{*1}$ configuration.[12] This is reflected by the torsional angles O(21)–Re(1)–Re(2)–O(22), O(31)–Re(1)–Re(2)–O(32), P(1)–Re(1)–Re(2)–N(112), and N(212)–Re(1)–Re(2)–P(2) being only 3.4 (6), 1.6 (6), 3.8 (6), and 0.7 (6)°, respectively. In contrast to this, the average torsional angle is much larger (15.5°) for the dirhodium complex.[11] This larger angle no doubt reflects the absence of any electronic barrier to rotation about the Rh–Rh single bond in the dirhodium complex.

The structure of *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]PF_6$ also resembles closely those of *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$[4] and the neutral complexes *cis*-$Re_2(O_2CCH_3)_2Cl_2(LL)_2$ (LL = dppm, dppa).[3,4] The Re–Re distance for *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dpa)_2]PF_6$ is 2.276 (1) Å, a value which is very close to that determined for its Ph_2Ppy analogue (2.261 (1) Å). It is also similar to the Re–Re distance of 2.270 (1) Å in the dirhenium(II) complex $Re_2Cl_4(Ph_2Ppy)_2)(PEt_3)$, a molecule that also contains cis bridging Ph_2Ppy ligands arranged head-to-tail.[2] The Re–P and Re–N distances in the structure of *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]^+$ are ca. 2.40 (1) and ca. 2.14 (2) Å, respectively. These values accord with those reported in the structure determination of $Re_2Cl_4(Ph_2Ppy)_2)(PEt_3)$.

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Supplementary Material Available: Tables giving full details of crystal data and data collection parameters (Table S1), positional parameters and their errors for the non-hydrogen atoms (Table S2) and for the hydrogen atoms (Table S3), thermal parameters (Table S4), bond distances (Table S5), and bond angles (Table S6) (16 pages); a table of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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Deprotonated Amide Nitrogen Coordinating to the Palladium(II) Ion. Crystal and Molecular Structure of Disodium Bis(*N*-tosylglycinato-*N*,*O*)palladate(II)

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Peptides and related ligands are able to bind several metal ions upon formation of one or more chelating rings involving up to three

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