with the experimental evidence that no η^2-C,O carbonyl sulfide–transition-metal complexes have been isolated so far.

In the analyzed series the π back-donation increases in the order $SCCH_2 < COS < SCNH < CS_2$, while the interaction energy rises in the order $COS < CS_2 \ll SCNH < SCCH_2$. As already noted for the OCX compounds, the trend of the interaction energy cannot be directly related to that of the π back-donation, although this is the main bonding interaction, but it is necessary to take into account also the delocalization of the electron density toward the heterogroup, which increases in the order $SCCH_2 < SCNH \simeq COS \ll CS_2$ (see Table IV). The bond between the iron and the CS_2 molecule is weaker than what one might expect by considering just the π back-donation since there is a high delocalization of the electron density on the S atom (59%), while in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCCH_2)$ we have a strong bond since almost all the electron density is localized in the Fe–CS moiety (only 3% of the electron density is localized in the CH_2 group).

Again we can notice that the high nucleophilic character of the uncoordinated sulfur atom in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$ is confirmed by the experimental evidence that it undergoes alkylation with a variety of electrophiles,[22] while the CH_2 group in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCCH_2)$ should not be attacked by alkylating agents, such as CH_3I.

It is interesting to note also that in all the analyzed systems the carbon atom induces a trans influence stronger than that due to the oxygen (or sulfur) atom, as is suggested by the overlap populations reported in Table III. Indeed, the overlap population of the Fe–C bond trans to the carbon atom is 0.05–0.09 e, while that of the Fe–C bond trans to the oxygen (or sulfur) atom is 0.12–0.17 e. From Table III we can see also that the C–S bond in the SCX series is weaker than the C–O bond in the OCX series: indeed, the C–S overlap population varies between –0.01 e in the compound with CS_2 and 0.14 e in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCNH)$, while the C–O overlap population assumes values between 0.32 and 0.37 e. This is more evidence that the SCX ligand gives rise to a stronger coordination bond than the analogous OCX molecule.

Conclusions

The study at the "ab initio" Hartree–Fock level of the systems $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCX)$ and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCX)$ (with X = O, S, NH, CH_2) has shown that the main bonding interaction between the fragment $Fe(CO)_2(PH_3)_2$ and the unsaturated molecule is the π back-donation from the transition metal to the π-acceptor ligand and the strength of this coordination bond increases on going from OCX to SCX. Moreover, the π back-donation is the driving force of the ligand deformation, which allows a better overlap between the π^* ligand and the d_π iron orbitals and, therefore, leads to an increased interaction energy.

Our results confirm that the low reactivity of carbon dioxide, compared to that of CS_2, toward transition-metal fragments is mainly due to the weaker π acidity exhibited by this molecule. The preference of the carbonyl sulfide for the η^2-C,S coordination can be explained in the same context: this coördination bonding mode is preferred, with respect to the η^2-C,O mode, because of the increased π back-donation, in agreement with the experimental evidence that no η^2-C,O carbonyl sulfide–transition-metal complexes have been isolated so far.

In the two analyzed series of compounds of $Fe(CO)_2(PH_3)_2$ with OCX and SCX, the delocalization of electron density on the heterogroup increases on going from X = CH_2 to X = S, suggesting that the uncoordinated sulfur atom in the compounds with COS and CS_2 has a high nucleophilic character, while the CH_2 group in the compounds with ketene and thioketene should not undergo alkylation very easily.

Acknowledgment. Thanks are expressed to the IBM European Center for Scientific and Engineering Computing (ECSEC, Rome) for provision of computing facilities and visiting grants. Support by the Italian National Research Council (CNR), the Ministry of Public Education (MPI), and the U.S. Navy (Grant N00014-86-K-0380) is gratefully acknowledged.

Registry No. $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$, 110174-28-2; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$, 110174-29-3; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCNH)$, 110174-30-6; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCCH_2)$, 110174-31-7; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$, 110174-32-8; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CSO)$, 110174-34-0; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCNH)$, 110174-33-9; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCCH_2)$, 110174-35-1; Fe, 7439-89-6.

Notes

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Reactions of the Dirhenium(III) Carboxylate Complexes $Re_2(O_2CR)_2X_4L_2$ (R = Me, Et; X = Cl, Br; L = H_2O, py, 4-Mepy) with the Monodentate Phosphines PPh_3 and Ph_2Ppy. Complexes of the Paramagnetic Re_2^{5+} Core That Contain a Single Carboxylate Bridge

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While the dirhenium(III) complexes $Re_2(O_2CR)_2X_4$ (X = Cl, Br) and their 1:2 adducts $Re_2(O_2CR)_2X_4L_2$ (L = H_2O, py, 4-Mepy, DMF, Me_2SO, Ph_3PO) have been known for several years and their syntheses, structures, and spectroscopic properties are quite well documented,[1-3] an examination of their chemiccal reactivity has been largely neglected. Recently, we studied the reactions of several complexes of the type $Re_2(O_2CR)_2X_4L_2$ (X = Cl, Br; R = Me, Et; L = H_2O, py, DMF, Me_2SO) with monodentate tertiary phosphines in alcohol solvents.[4,5] Whereas $Re_2(O_2CCH_3)_2Cl_4L_2$ (L = H_2O, py) react with PMe_3, PMe_2Ph, and $PMePh_2$ to give the dirhenium(II) complexes $Re_2Cl_4(PR_3)_4$, the novel dirhenium(IV,II) alkoxide complexes $(R'O)_2X_2ReReX_2(PPh_3)_2$ were produced in the reactions between $Re_2(O_2CR)_2X_4L_2$ (X = Cl, Br; R = Me, Et; L = H_2O, DMF, Me_2SO) and PPh_3 in refluxing alcohol solvents R′OH (R′ = Me, Et, *n*-Pr, *i*-Pr).[4,5] During the course of these investigations we noted that the reactions between $Re_2(O_2CCH_3)_2Cl_4L_2$ (L = py, 4-Mepy) and PPh_3 in refluxing ethanol did not yield $(EtO)_2Cl_2ReReCl_2(PPh_3)_2$. Since we did not understand why these reactions should be different, we have now examined them in further detail and discovered that they yield a derivative of the paramagnetic dirhenium(II,III) core viz. $Re_2(O_2CCH_3)Cl_4(PPh_3)_2$. The chemistry of this and related systems is described in the present report.

Experimental Section

Starting Materials. The compounds $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br) were synthesized as described in the literature.[6,7] These were converted

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into the corresponding bis(acetato) complexes $Re_2(O_2CCH_3)_2X_4L_2$ (X = Cl, Br; L = H_2O, py, 4-Mepy) or into the propionate derivative $Re_2(O_2CC_2H_5)_2Cl_4(4\text{-Mepy})_2$ by using the published procedure.[5] All common solvents were used as received from commercial sources. The triphenylphosphine (PPh_3) ligand was recrystallized twice from hot ethanol prior to use. The compound 2-(diphenylphosphino)pyridine (Ph_2Ppy) was synthesized from Ph_2PCl and 2-bromopyridine[8] and recrystallized from hot methanol prior to use.

Reaction Procedures. All syntheses were performed in an atmosphere of dry nitrogen under the pressure provided by passing the outlet nitrogen through a column of mercury aproximately 8 cm in height. All solvents were deoxygenated prior to use.

A. Reactions with PPh_3. (a) Synthesis of $Re_2(O_2CCH_3)Cl_4(PPh_3)_2$. (i) In Ethanol. A mixture of $Re_2(O_2CCH_3)_2Cl_4(py)_2$ (0.13 g, 0.16 mmol) and PPh_3 (0.28 g, 1.07 mmol) was refluxed in 20 mL of ethanol for 30 h. The reaction mixture was then cooled to room temperature, and the resulting dark red crystals were filtered off, washed with fresh ethanol, and dried in vacuo; yield 0.05 g, 35%. Anal. Calcd for $C_{38}H_{33}Cl_4O_2P_2Re_2$: C, 41.57; H, 3.03. Found: C, 41.50; H, 3.47. Workup of the reaction filtrate did not yield any other identifiable products (as monitored by cyclic voltammetry).

A similar yield of the same product was obtained by the reaction of $Re_2(O_2CCH_3)_2Cl_4(4\text{-Mepy})_2$ and PPh_3 in this same solvent.

(ii) In Acetone. A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.12 g, 0.18 mmol) and PPh_3 (0.14 g, 0.53 mmol) was refluxed in 15 mL of acetone for 48 h. The reaction mixture was cooled and filtered, and the dark red crystals were washed with fresh acetone and then dried in vacuo; yield 0.07 g, 35%. The spectral and electrochemical properties of this product matched those of the material prepared in ethanol. No other identifiable products were isolated from a workup of the reaction filtrate.

(b) Synthesis of $Re_2(O_2CCH_3)Br_4(PPh_3)_2$. A mixture of $Re_2(O_2CCH_3)_2Br_4(H_2O)_2$ (0.20 g, 0.24 mmol) and PPh_3 (0.22 g, 0.84 mmol) was refluxed in 15 mL of acetone for 24 h. The usual workup procedure gave the complex as dark red crystals; yield 0.10 g, 33%. Anal. Calcd for $C_{38}H_{33}Br_4O_2P_2Re_2$: C, 35.78; H, 2.61. Found: C, 35.50; H, 2.44.

A similar reaction between $Re_2(O_2CCH_3)_2Br_4(4\text{-Mepy})_2$ and PPh_3 in refluxing ethanol produced a mixture of $Re_2(O_2CCH_3)Br_4(PPh_3)_2$ and the mixed-valent ethoxide complex of stoichiometry $Re_2(OEt)_2Br_4(PPh_3)_2$.[4,5] These were not easily separated, so this procedure was not used further.

B. Reactions with Ph_2Ppy. (a) $Re_2(O_2CCH_3)Cl_4(Ph_2Ppy)_2\cdot 2(CH_3)_2CO$. A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.09 g, 0.13 mmol) and Ph_2Ppy (0.16 g, 0.61 mmol) was refluxed in 15 mL of acetone for 12 h. The resulting red reaction mixture was cooled and filtered and the dark red crystalline solid washed with fresh acetone and dried; yield 0.08 g, 51%. Anal. Calcd for $C_{42}H_{43}Cl_4N_2O_4P_2Re_2$: C, 41.49; H, 3.56; Cl, 11.66. Found: C, 41.50; H, 3.64; Cl, 11.45. The presence of lattice acetone was confirmed by IR spectroscopy of a Nujol mull (ν(CO) at 1702 (s) cm^{-1}).

The same complex (but without solvent of crystallization) could be isolated in similar yield when THF was used as the reaction solvent.

(b) $Re_2Cl_4(Ph_2Ppy)_3$. When the dark red acetone filtrate from the preceding reaction was exposed to air for 24 h, partial evaporation occurred along with concomitant growth of small bronze red crystals on the walls of the reaction flask. These crystals were filtered off, washed sparingly with fresh acetone, and dried; yield 0.01 g, 6%. The identity of this product was based on a comparison of its spectroscopic and electrochemical properties with those of an authentic sample.[8]

The same compound was also isolated as a minor product from the THF reaction filtrate.

(c) $Re_2(O_2CCH_3)Br_4(Ph_2Ppy)_2\cdot{}^1/_2(CH_3)_2CO$. A sample of $Re_2(O_2CCH_3)_2Br_4(H_2O)_2$ (0.11 g, 0.13 mmol) along with Ph_2Ppy (0.16 g, 0.61 mmol) was dissolved in 15 mL of acetone and the mixture refluxed for 12 h. The small crop of dark red crystals was filtered off after the reaction mixture had been allowed to cool to room temperature. The solid was washed with acetone, dried, and recrystallized from CH_2Cl_2/acetone; yield 0.01 g, 6%. Anal. Calcd for $C_{37.5}H_{34}Br_4N_2O_{2.5}P_2Re_2$: C, 34.47; H, 2.62. Found: C, 34.47; H, 2.85. The small amount of lattice acetone was confirmed by IR spectroscopy of a Nujol mull (ν(CO) at 1709 (m–w) cm^{-1}).

(d) $Re_2Br_4(Ph_2Ppy)_3$. The filtrate from the preceding reaction (c) was allowed to evaporate partially. The crop of bronze red crystals was filtered off, washed sparingly with acetone, and dried: yield 0.02 g. Identification of this product is based upon the close similarity of its electrochemical properties to those of an authentic sample of its chloride analogue $Re_2Cl_4(Ph_2Ppy)_3$.[8] A 0.1 M TBAH/CH_2Cl_2 solution of this complex displays redox processes at $E_{1/2}$ = +1.18 V and $E_{1/2}$ = +0.50 V vs Ag/AgCl, both of which correspond to oxidations. However, samples of this complex were contaminated by significant quantities of $Re_2(O_2CCH_3)Br_4(Ph_2Ppy)_2$.

Table I. Crystallographic Data and Data Collection Parameters for $Re_2(O_2CCH_3)Cl_4(PPh_3)_2\cdot H_2O$[a]

formula	$Re_2Cl_4P_2O_3C_{38}H_{35}$
fw	1115.86
space gp	$P\bar{1}$
a, Å	9.905 (2)
b, Å	11.228 (2)
c, Å	19.591 (2)
α, deg	96.01 (1)
β, deg	96.55 (1)
γ, deg	111.86 (2)
V, Å^3	1983 (1)
Z	2
d_{calcd}, g cm^{-3}	1.868
cryst dimens, mm	0.29 × 0.11 × 0.04
temp, °C	22.0
radiation (wavelength, Å)	Mo K_α (0.71073)
monochromator	graphite
linear abs coeff, cm^{-1}	65.68
abs cor applied	empirical[b]
diffractometer	Enraf-Nonius CAD4
scan method	θ–2θ
h, k, l limits	−10 to +10, −12 to +12, 0 to +21
2θ range, deg	4.00–45.00
scan width, deg	0.85 + 0.35 tan θ
takeoff angle, deg	4.80
programs used	Enraf-Nonius SDP
F_{000}	1070.0
p factor used in weighting	0.070
no. of data collcd	5185
no. of data with $I > 3.0\sigma(I)$	3964
no. of variables	442
largest shift/esd in final cycle	0.25
R[c]	0.048
R_w[d]	0.066
goodness of fit[e]	1.617

[a] Numbers in parentheses following certain data are estimated standard deviations occurring in the least significant digit. [b] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. [e] Goodness of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

(e) $Re_2(O_2CC_2H_5)Cl_4(Ph_2Ppy)_2\cdot{}^1/_2(CH_3)_2CO$. A mixture of $Re_2(O_2CC_2H_5)_2Cl_4(4\text{-Mepy})_2$ (0.20 g, 0.23 mmol) and Ph_2Ppy (0.11 g, 0.43 mmol) was refluxed in 20 mL of acetone for 2 days. The solution was filtered while hot to remove a crop of tiny blue-black crystals (0.04 g) and the filtrate was partially evaporated in air to afford bronze red crystals. These were filtered off, washed sparingly with acetone and dried; yield 0.07 g, 27%. Anal. Calcd for $C_{38.5}H_{36}Cl_4N_2O_{2.5}P_2Re_2$: C, 40.46; H, 3.18. Found: C, 40.22; H, 3.66. The presence of lattice acetone was confirmed by IR spectroscopy of a Njuol mull (ν(CO) at 1703 (m) cm^{-1}).

X-ray Structure Determination on $Re_2(O_2CCH_3)Cl_4(PPh_3)_2$. Crystals of this complex were grown under a nitrogen atmosphere. A sample of the complex was dissolved in deoxygenated CH_2Cl_2 contained in a test tube. The test tube was then lowered in an upright position into an Erlenmeyer flask that contained deoxygenated diethyl ether. The flask was capped and left to stand undisturbed. After several days, small needlelike crystals had formed on the sides of the test tube and were isolated by decanting the supernatant.

Crystal data and information relating to data collection and structure refinement are listed in Table I. Details of the crystal data collection and reduction methods we used are available elsewhere.[9] An empirical absorption correction was applied,[10] but no correction was made for extinction. All atoms were refined anisotropically, and corrections for anomalous scattering were applied.[11] Hydrogen was not included in the

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(11) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution, see: Cromer, D. T.; Waber, J. T. *Ibid.*, Table 2.2B.

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for Non-Phenyl-Ring Atoms and Non-Hydrogen Atoms and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Re(1)	0.28277 (5)	0.27361 (4)	0.28505 (3)	2.66 (1)
Re(2)	0.14489 (5)	0.22347 (4)	0.18068 (3)	2.47 (1)
Cl(11)	0.5305 (4)	0.4123 (3)	0.2995 (2)	4.02 (9)
Cl(12)	0.2342 (4)	0.4424 (3)	0.3433 (2)	3.75 (8)
Cl(21)	−0.0899 (3)	0.0545 (3)	0.1580 (2)	3.93 (8)
Cl(22)	0.0306 (3)	0.3714 (3)	0.1805 (2)	3.45 (8)
P(11)	0.1213 (4)	0.1273 (3)	0.3497 (2)	3.05 (8)
P(21)	0.3226 (3)	0.3571 (3)	0.1182 (2)	2.74 (8)
O(1)	0.3605 (9)	0.1306 (8)	0.2588 (4)	3.1 (2)
O(2)	0.2164 (9)	0.0759 (8)	0.1550 (5)	3.0 (2)
O(1H)	0.129 (1)	0.602 (1)	0.5191 (8)	10.5 (5)
C(1)	0.310 (1)	0.061 (1)	0.1990 (8)	3.6 (3)
C(2)	0.367 (2)	−0.047 (1)	0.1795 (9)	5.1 (4)

[a] Anisotropically refined atoms are given in the form of isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Data for the carbon atoms of the phenyl rings are available as supplementary material.

Table III. Important Bond Distances (Å) and Angles (deg) for $Re_2(O_2CCH_3)Cl_4(PPh_3)_2{\cdot}H_2O$[a]

(a) Distances

Re(1)–Re(2)	2.2165 (7)	Re(2)–Cl(22)	2.333 (4)
Re(1)–Cl(11)	2.330 (3)	Re(2)–P(21)	2.399 (3)
Re(1)–Cl(12)	2.340 (4)	Re(2)–O(2)	2.07 (1)
Re(1)–P(11)	2.409 (3)	O(1)–C(1)	1.27 (2)
Re(1)–O(1)	2.07 (1)	O(2)–C(1)	1.26 (2)
Re(2)–Cl(21)	2.347 (3)	C(1)–C(2)	1.55 (2)

(b) Angles

Re(2)–Re(1)–Cl(11)	119.4 (1)	Re(1)–Re(2)–O(2)	90.0 (2)
Re(2)–Re(1)–Cl(12)	104.98 (9)	Cl(21)–Re(2)–Cl(22)	88.5 (1)
Re(2)–Re(1)–P(11)	101.95 (8)	Cl(21)–Re(2)–P(21)	139.2 (1)
Re(2)–Re(1)–O(1)	90.3 (2)	Cl(21)–Re(2)–O(2)	84.0 (2)
Cl(11)–Re(1)–Cl(12)	89.0 (1)	Cl(22)–Re(2)–P(21)	88.9 (1)
Cl(11)–Re(1)–P(11)	137.8 (1)	Cl(22)–Re(2)–O(2)	165.2 (2)
Cl(11)–Re(1)–O(1)	83.9 (2)	P(21)–Re(2)–O(2)	88.5 (2)
Cl(12)–Re(1)–P(11)	88.4 (1)	Re(1)–O(1)–C(1)	117.9 (9)
Cl(12)–Re(1)–O(1)	164.7 (2)	Re(2)–O(2)–C(1)	118.4 (8)
P(11)–Re(1)–O(1)	87.8 (3)	O(1)–C(1)–O(2)	123 (1)
Re(1)–Re(2)–Cl(21)	120.7 (1)	O(1)–C(1)–C(2)	118 (1)
Re(1)–Re(2)–Cl(22)	104.77 (8)	O(2)–C(1)–C(2)	119 (1)
Re(1)–Re(2)–P(21)	99.24 (8)		

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

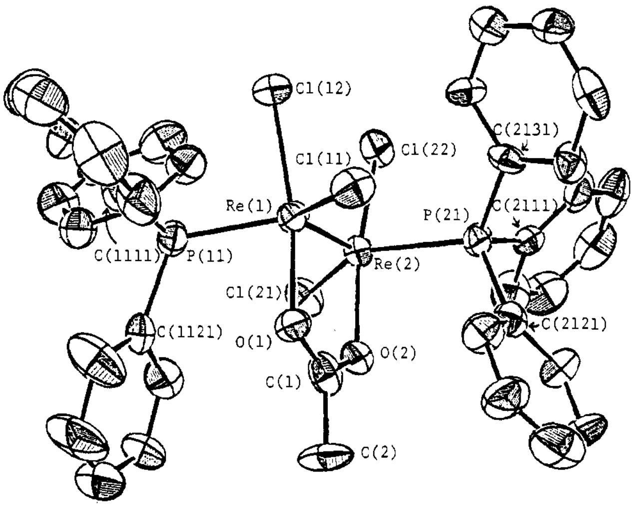

Figure 1. ORTEP view of $Re_2(O_2CCH_3)Cl_4(PPh_3)_2$. Thermal ellipsoids are drawn at the 50% probability level. The carbon atom C(1131) of one of the phenyl rings bound to P(11) is obscured in this view.

least-squares refinement. Information relating to the structure determination is available as supplementary material.

On the basis of this structure analysis, the crystals were concluded to be those of a monohydrate. Interestingly, there had been no clear indication of water of crystallization in the IR spectrum of the bulk sample of the freshly synthesized complex. However, the IR spectrum of the batch of crystals grown from CH_2Cl_2/diethyl ether showed a broad feature at ca. 3400 cm^{-1}. This is in accord with the presence of water and implies that the water of crystallization became incorporated during the recrystallization procedure.

Further details concerning the data set, the structure solution, and the structure refinement may be obtained from P.E.F. Table II lists the atomic positional parameters and their errors for non-phenyl-ring atoms and non-hydrogen atoms, while Table III lists important intramolecular bond distances and angles. Tables listing atomic positional parameters and their errors for phenyl ring carbon atoms (Table S1), thermal parameters (Table S2), and complete bond distances and bond angles (Tables S3 and S4, respectively) are available as supplementary material, as well as a figure (Figure S1) showing the full atomic numbering scheme.

Physical Measurements. Spectroscopic and electrochemical measurements were recorded as described previously.[5]

Analytical Procedures. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results and Discussion

The reactions of several complexes of the type $Re_2(O_2CR)_2X_4L_2$ (X = Cl, Br; R = Me, Et; L = H_2O, DMF, Me_2SO) with PPh_3 in refluxing alcohol solvents R′OH (R′ = Me, Et, *n*-Pr, *i*-Pr) give the mixed-valent $Re^{IV}Re^{II}$ complexes $(R'O)_2X_2ReReX_2(PPh_3)_2$.[4,5] We now find that the related reactions of the pyridine and 4-methylpyridine adducts $Re_2(O_2CCH_3)_2Cl_4L_2$ (L = py, 4-Mepy) with PPh_3 in refluxing ethanol give the acetate-bridged complex $Re_2(\mu\text{-}O_2CCH_3)Cl_4(PPh_3)_2$, the identity of which has been confirmed by X-ray crystallography (vide infra). The analogous reaction between $Re_2(O_2CCH_3)_2Br_4(4\text{-Mepy})_2$ and PPh_3 gives $Re_2(O_2CCH_3)Br_4(PPh_3)_2$, but this product is contaminated by some of the ethoxide complex $(EtO)_2Br_2ReReBr_2(PPh_3)_2$.[4,5] An alternative procedure that worked equally well employs the reaction of the hydrate $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (X = Cl, Br) with PPh_3 in refluxing acetone. This latter procedure was readily adaptable to the synthesis of the analogous complexes that contain the Ph_2Ppy ligand, viz., $Re_2(O_2CCH_3)X_4(Ph_2Ppy)_2$ (X = Cl, Br), isolable as their acetone solvates. As byproducts of these particular reactions we isolated low yields of the known dirhenium(II) complex $Re_2X_4(Ph_2Ppy)_3$.[8] The propionate derivative $Re_2(O_2CC_2H_5)Cl_4(Ph_2Ppy)_2$ was isolated when a mixture of Re_2-

Table IV. Electrochemical and Electronic Absorption Spectral Data for $Re_2(O_2CR)X_4L_2$ (R = Me, Et; X = Cl, Br; L = PPh_3, Ph_2Ppy)

complex	electronic abs spectrum, nm[a]	voltammetric half-wave potentials, V[b]: oxidn	redn
$Re_2(O_2CCH_3)Cl_4(PPh_3)_2$	1200 (1700), 710 (230), 506 (400), 438 (400)	+0.56[c]	−0.62
$Re_2(O_2CCH_3)Br_4(PPh_3)_2$	1230 (2100), 745 (300), 520 (425), 408 (1600)	+0.58	−0.58
$Re_2(O_2CCH_3)Cl_4(Ph_2Ppy)_2$	1330 (1100), 730 (300), 540 (1950), ~400 sh	+0.47	−0.56
$Re_2(O_2CCH_3)Br_4(Ph_2Ppy)_2$	1360 (1100), 755 (220), 534 (1950), 400 (4700)	+0.58	−0.40
$Re_2(O_2CC_2H_5)Cl_4(Ph_2Ppy)_2$	1330 (1050), 732 (250), 540 (2100), 400 sh	+0.49	−0.49

[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 using a Pt-bead electrode; data obtained at v = 200 mV/s. Under these conditions ΔE_p values (i.e. $E_{p,a} - E_{p,c}$) were in the range 85–120 mV and the ferrocenium/ferrocene couple has $E_{1/2}$ = +0.47 V vs Ag/AgCl. [c] $E_{p,a}$ value given since $i_{p,c} < i_{p,a}$.

$(O_2CC_2H_5)_2Cl_4(4\text{-Mepy})_2$ and Ph_2Ppy was refluxed in acetone, although our attempts to prepare the related PPh_3 derivative were not successful.

(a) Spectroscopic and Electrochemical Properties. The electronic absorption spectra of the five mono(carboxylato)-bridged complexes that possess the Re_2^{5+} core are very similar to one another (Table IV). The most noteworthy and diagnostic feature is the presence of an intense absorption between 1200 and 1400 nm that is assigned to the spin-allowed $\delta \rightarrow \delta^*$ transition, which is characteristic of complexes that contain the $\sigma^2\pi^4\delta^2\delta^{*1}$ electronic configuration.[1,12,13] Solutions of these complexes in CH_2Cl_2 have magnetic moments (as measured by the Evans method) that confirm the presence of one unpaired electron (e.g. for $Re_2(O_2CCH_3)Br_4(Ph_2Ppy)_2\cdot{}^1/_2(CH_3)_2CO$, $\mu_{eff} = 1.63\ \mu_B$). The paramagnetic nature of these species is further demonstrated by X-band ESR spectral measurements on $Re_2(O_2CCH_3)Cl_4(PPh_3)_2$ and $Re_2(O_2CCH_3)Cl_4(Ph_2Ppy)_2$ in CH_2Cl_2/toluene glasses at −160 °C. Both complexes show anisotropic, highly structured patterns that are centered at $g \simeq 2.16$ and 2.20, respectively, and that are located between ca. 1 and 5 kG. The spectrum of the PPh_3 complex is the best resolved, and the complexity presumably reflects hyperfine splittings arising from the rhenium ($I = {}^5/_2$) and phosphorus ($I = {}^1/_2$) nuclei. The most prominent lowest field lines in this spectrum show spacings of ca. 250 G; these are most likely assignable to the A^{Re} hyperfine splitting. The ESR spectra resemble in a general way those reported for other Re_2^{5+} species.[13-15]

The electrochemical properties of these complexes resemble one another very closely, and like other complexes that possess the Re_2^{5+} core,[1,13] they exhibit two one-electron processes, one corresponding formally to an oxidation and the other to a reduction. Consequently, the complexes $Re_2(O_2CR)X_4(PR_3)_2$ (R = Me, Et; X = Cl, Br; PR_3 = PPh_3, Ph_2Ppy) can exist in three distinct oxidation states, viz. $[Re_2(O_2CR)X_4(PR_3)_2]^{1+,0,1-}$. Voltammetric potentials as measured by cyclic voltammetry on 0.1 M TBAH/CH_2Cl_2 solutions are listed in Table IV.

(b) Crystal Structure of $Re_2(\mu\text{-}O_2CCH_3)Cl_4(PPh_3)_2$. A single-crystal X-ray structure analysis on a crystal of this complex grown from CH_2Cl_2/diethyl ether has confirmed the presence of a multiply bonded dimetal M_2L_8-type structure,[1,2] within which there is a single acetate bridging ligand. Important bond lengths and angles for this complex are listed in Table III, and an ORTEP representation of the structure is shown in Figure 1. While no crystallographic symmetry is imposed on the molecule, it possesses an essentially eclipsed rotational geometry and a surprisingly short Re–Re bond (2.216 (1) Å). This bond is significantly shorter than that found in $Re_2Cl_5(dppm)_2$ (2.263 (1) Å; dppm = $Ph_2PCH_2PPh_2$)[16] and in most quadruply bonded carboxylato-bridged dirhenium(III) complexes.[1] This shortening might be a consequence of a *single* carboxylate bridge, which can optimize the metal–metal interaction while allowing for minimization of the nonbonded repulsions between the chloride and phosphine ligands. The Re–Cl and Re–P distances and appropriate angular distortions in this molecule appear normal and reflect the essential similarity of the two metal centers in this mixed-valent species. This formulation contrasts with the valence formalism $Re^{IV}Re^{II}$ that is appropriate for the structurally characterized unsymmetrical alkoxide derivatives $(R'O)_2X_2ReReX_2(PPh_3)_2$.[4,5]

This structural study demonstrates that these molecules are the first examples of *multiply bonded* dirhenium complexes that contain a single anionic ligand bridge. The complexes $Re_2(O_2CR)X_4L_2$ have a ligand arrangement which resembles that believed to be present in $Re_2Cl_4(PMe_3)_2(\mu\text{-dppm})$ and $Re_2Cl_4(PMe_3)_2(\mu\text{-dppa})$, where dppm = $Ph_2PCH_2PPh_2$ and dppa = $Ph_2PNHPPh_2$.[17]

Since the electrochemical and spectroscopic properties of $Re_2(O_2CCH_3)X_4(PPh_3)_2$ and their Ph_2Ppy analogues are so similar, it is likely that the latter complexes have a structure closely akin to that of $Re_2(O_2CCH_3)Cl_4(PPh_3)_2$. In this event they would contain monodentate phosphorus-bound Ph_2Ppy ligands, behavior that stands in marked contrast to the previously documented tendency of this ligand to bridge multiply bonded dirhenium units.[8] Alternatively, if the Ph_2Ppy ligands are bridging (through their N, P donor sets), then two chloride ligands would presumably be axially bound.

(c) Conclusions. While alcohol solvents favor the formation of $(R'O)_2X_2ReReX_2(PPh_3)_2$ in the reactions between PPh_3 and $Re_2(O_2CCH_3)_2X_4L_2$ when L = H_2O, DMF, or Me_2SO,[4,5] the paramagnetic acetate-bridged complexes $Re_2(O_2CCH_3)X_4(PPh_3)_2$ are formed when L = py or 4-Mepy. Although the ligands L dissociate during the course of these reactions and are not incorporated into the final products, they must in some way influence the loss of the acetate ligands from $Re_2(O_2CCH_3)_2X_4L_2$. If the loss of acetate proceeds via its protonation, then L must control this step. Alternatively, the reaction course may be controlled by the lability of L, the more labile ligands (H_2O, DMF, Me_2SO)[18] favoring the alkoxide product. However, these differences may be quite subtle, since with acetone as the solvent the diaquo adducts $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ react with PPh_3 to give $Re_2(O_2CR)X_4(PPh_3)_2$. We find no evidence that $(R'O)_2X_2ReReX_2(PPh_3)_2$ and $Re_2(O_2CR)X_4(PPh_3)_2$ can be converted into one another, either by the reaction of lithium acetate or acetic acid with the former or by the reaction of the latter with alcohol or with alcohol/PPh_3 mixtures.

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Supplementary Material Available: Experimental details relating to the crystal structure determination, listings of atomic positional parameters for the phenyl ring carbon atoms (Table S1), anisotropic thermal parameters (Table S2), complete bond distances (Table S3), and complete bond angles (Table S4), and a figure showing the full atomic numbering scheme (Figure S1) (11 pages); a table of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Iron-57 Mössbauer Spectra of $MnFeF_5\cdot 2H_2O$[†]

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The $M^{II}M^{III}F_5\cdot 2H_2O$ compounds, where M^{II} is a divalent and M^{III} is a trivalent transition-metal ion, have the structure of "zigzag" chains of vertex-sharing $M^{III}F_6$ co-octahedra cross-linked by bridging $M^{II}F_4(H_2O)_2$ octahedra.[1] Since a variety of paramagnetic M^{II} and M^{III} ions can be substituted in this structure, compounds with interesting magnetic properties have been prepared and have been investigated by magnetic susceptibilities[1-5,8] and, when M^{II} or M^{III} is Fe^{II} or Fe^{III}, by ^{57}Fe Mössbauer spectroscopy.[2,6,7] A recent low-temperature magnetic susceptibility

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