28-5; Zn[HB(3-*i*-Pr-4-Br-pz)$_3$]N$_3$, 119010-29-6; Mo[HB(3-*i*-Pr-4-Br-pz)$_3$](NO)(CO)$_2$, 119010-31-0; Mo[HB(3-*i*-Pr-4-Br-pz)$_3$](η^3-CH$_2$C(CH$_3$)CH$_2$)(CO)$_2$, 119010-30-9; 3(5)-isopropylpyrazole, 49633-25-2; isopropyl methyl ketone, 563-80-4; ethyl formate, 109-94-4; hydrazine chloride, 2644-70-4; 3(5)-isopropyl-4-bromopyrazole, 60061-60-1; potassium tetrahydroborate, 13762-51-1.

Supplementary Material Available: Listings of thermal parameters (Tables S1, S5, S9, and S13), hydrogen atom positions (Tables S2, S6, S10, and S14), and all bond distances and angles (Tables S4, S8, S12, and S16) (13 pages); listings of observed and calculated structure factors (Tables S3, S7, S11, and S15) (10 pages). Ordering information is given on any current masthead page.

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Reactions of the Polyhydrides $Re_2H_8(PPh_3)_4$ and $ReH_7(PPh_3)_2$ with Acetic Acid/Acetic Anhydride. Isolation and Characterization of the Rhenium(I) Carbonyl Complexes $Re(O_2CCH_3)(CO)_{1+x}(PPh_3)_{3-x}$ ($x = 0, 1$) and the Homoleptic Dirhenium(III) Carboxylate Complex $Re_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)_2$

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The dirhenium octahydride $Re_2H_8(PPh_3)_4$ reacts with acetic acid/acetic anhydride mixtures in dichlorobenzene to give the homoleptic acetate complex $Re_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)_2$ as the major product together with small quantities of the carbonyl complex $Re(O_2CCH_3)(CO)_2(PPh_3)_2$. The related reaction with propionic acid/propionic anhydride gives only $Re(O_2CC_2H_5)(CO)_2(PPh_3)_2$ in very low yield. Treatment of $ReH_7(PPh_3)_2$ with these same acid/anhydride mixtures in THF, in the presence of PPh$_3$, affords yellow $Re(O_2CR)(CO)(PPh_3)_3$ (R = CH$_3$, C$_2$H$_5$) in high yield. Solutions of these complexes in 0.1 M *n*-Bu$_4$NPF$_6$/CH$_2$Cl$_2$ show a reversible couple in their cyclic voltammograms associated with a one-electron oxidation to their 17-electron cations. Chemical oxidation of $Re(O_2CR)(CO)(PPh_3)_3$ to the paramagnetic, orange salts $[Re(O_2CR)(CO)(PPh_3)_3]PF_6$ has been accomplished by using $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in acetone. The acetate complex $[Re(O_2CCH_3)(CO)(PPh_3)_3]PF_6 \cdot THF$ has been characterized structurally by X-ray crystallography. Crystal data at 20 °C: space group *Pnma*, $a = 15.785$ (4) Å, $b = 22.577$ (3) Å, $c = 23.824$ (3) Å, $V = 5656$ (5) Å^3, and $Z = 4$. The structure was refined to $R = 0.033$ and $R_w = 0.040$ for 2600 data with $F^2 > 3.0\sigma(F^2)$.

Introduction

The reversible protonation reactions (using HBF$_4$·Et$_2$O) of rhenium polyhydride complexes of the types $Re_2H_8(PR_3)_4$, $Re(\eta^2\text{-}H_2)H_5(PR_3)_2$, and $ReH_5(PR_3)_3$ have recently been examined[1-3] and extended to include the analogous auration reactions with $[Au(PR_3)]^+$.[2,4] These protonation reactions are important from the point of view of activating these relatively stable molecules and for an understanding of the interconversion between isomeric dihydrido and η^2-dihydrogen ligands.[5] Since rhenium polyhydrides rank second to none among the transition elements in the variety of species that can be stabilized,[6] we are currently examining their reactivities toward a selection of other acids. In the present report we describe the products that are obtained from the reactions of $ReH_7(PPh_3)_3$ and $Re_2H_8(PPh_3)_4$ with acetic acid/acetic anhydride mixtures and the related propionic acid/propionic anhydride mixtures.

Experimental Section

Starting Materials. The polyhydride complexes $Re_2H_8(PPh_3)_4$, $ReH_7(PPh_3)_2$, and $ReH_5(PPh_3)_3$ were prepared by standard literature methods.[7] Other reagents and solvents were obtained from commercial sources. Solvents were deoxygenated prior to use. All reactions were carried out under an atmosphere of nitrogen at a pressure provided by bubbling the outlet nitrogen through a column of mercury approximately 8 cm in depth or with the use of a mineral oil bubbler.

A. Reactions of $Re_2H_8(PPh_3)_4$ with $RCO_2H/(RCO)_2O$ (R = CH$_3$, C$_2$H$_5$). (i) $Re_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)_2$. A mixture of glacial acetic acid and acetic anhydride (10:1 by volume) (3.0 mL) was added to a solution of $Re_2H_8(PPh_3)_4$ (0.570 g, 0.400 mmol) in 100 mL of 1,2-dichlorobenzene. The mixture was refluxed for 4 h. The cooled reaction mixture was filtered under nitrogen, and the resulting light brown precipitate was washed with diethyl ether (20 mL); yield 0.153 g (53%). Anal. Calcd for $C_{12}H_{18}O_{12}Re_2$: C, 19.83; H, 2.50. Found: C, 19.19; H, 2.58. It is insoluble in THF, diethyl ether, acetone, dichloromethane, and ethanol and only slightly soluble in methanol, which turns it green. Its IR spectrum (Nujol mull) shows the following characteristic bands (cm^{-1}): 1554 (s, br), ≃1450 (vs, br), ≃1040 (sh), 1028 (m), 682 (s), 644 (w), 624 (w), 607 (w), 465 (m), 365 (ms), 340 (ms), ≃230 (ms).

This product is readily converted into $Re_2(O_2CCH_3)_4Cl_2$ upon reaction with hydrogen chloride. A slurry of $Re_2(O_2CCH_3)_6$ (0.065 g, 0.090 mmol) in ethanol (5 mL) was stirred under N$_2$(g) at 0 °C (ice bath), while HCl gas was bubbled through the solution for 3 min. During this time the suspension turned from brown to orange, while the solution acquired a green coloration. The orange solid was filtered off and dried; yield 0.050 g (82%). The identity of this product was established on the basis of its IR and electronic absorption spectral properties.[8,9]

(ii) $Re(O_2CCH_3)(CO)_2(PPh_3)_2$ (1). Diethyl ether (50 mL) was added to the dark green filtrate from part A(i), and the resulting solution was slowly evaporated under a gentle stream of nitrogen until the volume was approximately 5 mL. The solution was then refrigerated for about 2 weeks. A small crop of yellow crystals was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.020 g (3%). Anal. Calcd for $C_{40}H_{33}O_4P_2Re$: C, 58.18; H, 4.03. Found: C, 58.20; H, 4.32.

(iii) $Re(O_2CC_2H_5)(CO)_2(PPh_3)_2$ (2). A procedure similar to that described in part A(i) was used. A mixture of propionic acid and propionic anhydride (10:1 by volume) was reacted with $Re_2H_8(PPh_3)_4$ in 1,2-dichlorobenzene. The reaction was stopped after a 6-h reflux but did not afford any insoluble $Re_2(\mu\text{-}O_2CC_2H_5)_4(O_2CC_2H_5)_2$. The solution was treated as described in part A(ii). A few yellow crystals were filtered off, washed with diethyl ether, and dried under vacuum; yield ca. 2%.

B. Reactions of $ReH_7(PPh_3)_2$ with $RCO_2H/(RCO)_2O$ (R = CH$_3$, C$_2$H$_5$). (i) $Re(O_2CCH_3)(CO)(PPh_3)_3$ (3). A mixture of glacial acetic

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Table I. Crystallographic Data for $[Re(O_2CCH_3)(CO)(PPh_3)_3]PF_6{\cdot}THF$ (**5**)

formula	$ReP_4F_6O_4C_{61}H_{56}$	T, °C	20 ± 1
a, Å	15.785 (4)	radiation (λ, Å)	Mo Kα (0.71073)
b, Å	22.577 (3)		
c, Å	15.872 (7)	ρ_{calc}, g cm^{-3}	1.500
V, Å^3	5656 (5)	μ(Mo Kα), cm^{-1}	23.52
Z	4	transmission coeff	1.000–0.760
fw	1277.21	R	0.033
space group	*Pnma* (No. 62)	R_w	0.040

acid and acetic anhydride (10:1 by volume) (0.5 mL) was added to a slurry of $ReH_7(PPh_3)_2$ (0.20 g, 0.028 mmol) and triphenylphosphine (0.15 g, 0.056 mmol) in 5 mL of THF. The mixture was refluxed for 25 min. Methanol (100 mL) was added to the cooled reaction mixture, and the resulting yellow solution was stirred for 10 min. The yellow precipitate was filtered off, washed with methanol, and dried under vacuum; yield 0.22 g (75%). Anal. Calcd for $C_{57}H_{48}O_3P_3Re$: C, 64.57; H, 4.57. Found: C, 64.34; H, 5.04.

(ii) $Re(O_2CC_2H_5)(CO)(PPh_3)_3$ (4). A procedure similar to that described in part B(i) was used. The yellow product was recrystallized from CH_2Cl_2/methanol; yield 78%. Anal. Calcd for $C_{58}H_{50}O_3P_3Re$: C, 64.85; H, 4.70. Found: C, 64.02; H, 4.84.

C. Oxidation of $Re(O_2CR)(CO)(PPh_3)_3$ with $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$. (i) $[Re(O_2CCH_3)(CO)(PPh_3)_3]PF_6$ (5). A solution of $Re(O_2CCH_3)(CO)(PPh_3)_3$ (0.04 g, 0.038 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.013 g, 0.039 mmol) in 5 mL of acetone was stirred for 30 min. Diethyl ether (50 mL) was added to the orange solution to precipitate the bright orange product; yield 0.044 g (96%).

(ii) $[Re(O_2CC_2H_5)(CO)(PPh_3)_3]PF_6$ (6). A procedure similar to that described in part C(i) was used. The bright organge product was washed with diethyl ether and dried under vacuum; yield 88%. Anal. Calcd for $C_{58}H_{52}F_6O_4P_4Re$ (i.e. the monohydrate): C, 56.30; H, 4.24. Found: C, 56.06; H, 4.43.

Preparation of Single Crystals for Structure Determination. Crystals of the dicarbonyl complex $Re(O_2CCH_3)(CO)_2(PPh_3)_2$ (**1**) were obtained upon recrystallization from CH_2Cl_2/diethyl ether, while crystals of $[Re(O_2CCH_3)(CO)(PPh_3)_3]PF_6{\cdot}THF$ (**5**) were grown by slow diffusion of deoxygenated heptane into a dilute solution of the complex in THF.

X-ray Crystallography. The structures of $Re(O_2CCH_3)(CO)_2(PPh_3)_2$ (**1**) and $[Re(O_2CCH_3)(CO)(PPh_3)_3]PF_6$ (**5**) were determined by application of general procedures that are described more fully elsewhere.[10] However, following our completion of the structure determination of **1**, we discovered that this structure had been reported previously.[11] Accordingly, our structural data for **1** are available only as supplementary material. The basic crystallographic parameters for **5** are listed in Table I. The cell constants are based on 25 reflections with $16.5 < \theta < 18.9°$. Three standard reflections were measured after every 5000 s of beam time during data collection. It was necessary to allow for a decay correction in the case of this complex; we used the decay correction program CHORT (part of the Enraf-Nonius SDP package) to correct for this.

Calculations were performed on a MicroVAX computer using the Enraf-Nonius structure determination package. The atoms were located and refined from an initial Patterson map. An empirical absorption correction was applied,[12] the linear absorption coefficient being 23.52 cm^{-1}. No correction for extinction was applied. The least-squares program minimized the function $w(|F_o| - |F_c|)^2$, where w is a weighting factor defined as $w = 1/\sigma^2(F_o)$. Positions for hydrogen atoms were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. For the methyl group, one hydrogen was located in a difference Fourier map, its position was idealized, and the remaining positions were calculated. We assumed that the value of B(H), i.e. the isotropic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While the hydrogens were used in the calculation of F_o, they were not included in the least-squares refinement. All non-hydrogen atoms were refined anisotropically, with the exception of the lattice THF molecule present in the structure of $[Re(O_2CCH_3)(CO)(PPh_3)_3]PF_6$. Corrections for anomalous scattering were applied to all atoms refined anisotropically.[13]

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Phenyl Atoms of the Cation in **5** and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Re	0.06253 (2)	$^1/_4$	0.04383 (2)	2.376 (7)
P(1)	0.1520 (2)	$^1/_4$	0.1690 (2)	2.70 (6)
P(2)	0.0331 (1)	0.35641 (9)	0.0197 (1)	3.01 (4)
O(1)	−0.1051 (4)	$^1/_4$	0.1366 (5)	4.3 (2)
O(10)	0.0363 (4)	$^1/_4$	−0.0911 (4)	3.2 (2)
O(11)	0.1672 (4)	$^1/_4$	−0.0472 (4)	3.5 (2)
C(1)	−0.0384 (6)	$^1/_4$	0.1034 (6)	3.1 (2)
C(12)	0.1175 (6)	$^1/_4$	−0.1082 (6)	3.2 (2)
C(13)	0.1450 (8)	$^1/_4$	−0.1996 (7)	5.4 (3)

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

Table III. Important Bond Distances (Å) for **5**[a]

Re–P(1)	2.437 (3)	P(2)–C(211)	1.823 (7)
Re–P(2)	2.477 (2)	P(2)–C(221)	1.828 (8)
Re–O(10)	2.181 (7)	P(2)–C(231)	1.815 (7)
Re–O(11)	2.194 (7)	O(1)–C(1)	1.18 (1)
Re–C(1)	1.85 (1)	O(10)–C(12)	1.31 (1)
P(1)–C(111)	1.82 (1)	O(11)–C(12)	1.25 (1)
P(1)–C(121)	1.850 (8)	C(12)–C(13)	1.51 (1)

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

Table IV. Important Bond Angles (deg) for **5**[a]

P(1)–Re–P(2)	103.59 (4)	C(111)–P(1)–C(121)	102.5 (3)
P(1)–Re–P(2)	103.59 (4)	C(111)–P(1)–C(121)	102.5 (3)
P(1)–Re–O(10)	155.6 (2)	C(121)–P(1)–C(121)	103.1 (5)
P(1)–Re–O(11)	95.8 (2)	Re–P(2)–C(221)	115.6 (3)
P(1)–Re–C(1)	94.7 (3)	Re–P(2)–C(221)	111.5 (3)
P(2)–Re–P(2)	151.83 (9)	Re–P(2)–C(231)	114.5 (3)
P(2)–Re–O(10)	79.18 (5)	C(211)–P(2)–C(221)	103.7 (4)
P(2)–Re–O(11)	92.26 (6)	C(211)–P(2)–C(231)	105.3 (4)
P(2)–Re–C(1)	85.28 (8)	C(221)–P(2)–C(231)	105.1 (3)
O(10)–Re–O(11)	59.8 (2)	Re–O(10)–C(12)	91.0 (6)
O(10)–Re–C(1)	109.7 (4)	Re–O(11)–C(12)	92.2 (6)
O(11)–Re–C(1)	169.5 (4)	Re–C(1)–O(1)	175.8 (9)
Re–P(1)–C(111)	126.5 (3)	O(10)–C(12)–O(11)	117.0 (9)
Re–P(1)–C(121)	109.9 (2)	O(10)–C(12)–C(13)	119 (1)
Re–P(1)–C(121)	109.9 (2)	O(11)–C(12)–C(13)	124 (1)

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

We found the presence of lattice THF in the crystals of $[Re(O_2CCH_3)(CO)(PPh_3)_3]PF_6$. The multiplicity of THF, which was allowed to vary, converged to 0.98. Accordingly, the complex was assumed to contain one molecule of THF per formula unit. In this structure the rhenium cation lies on a special position with a mirror plane that contains the carbonyl ligand, the unique phosphine, and the carbon and oxygen atoms of the acetate ligand. The molecule of THF lies on a special position that exhibits 2-fold symmetry, while the PF_6^- has crystallographically imposed $\bar{1}$ symmetry.

Further details concerning the data set, the structure solution, and the structure refinement may be obtained from P.E.F. Table II lists the positional parameters and their errors for the non-phenyl atoms, the non-solvent molecule atoms, and the non-hexafluorophosphate atoms of **5**, while Tables III and IV list important intramolecular bond distances and angles for this structure. Tables giving full details of the crystal data and data collection parameters for **1** and **5** (Tables S1 and S2), the non-hydrogen positional parameters of **1** (Table S3), the positional parameters for the phenyl carbon atoms, the lattice solvent molecule atoms, and the atoms of the PF_6^- anion of $[Re(O_2CCH_3)(CO)(PPh_3)_3]PF_6{\cdot}THF$ (Table S4), the positional parameters for the hydrogen atoms of **1** and **5** (Tables S5 and S6), the thermal parameters of **1** and **5** (Tables S7 and S8), and complete bond distances (Tables S9 and S10) and bond angles (Tables 11 and 12) are available as supplementary material, as well as a figure (Figure S1) showing the full atomic numbering scheme for **1**.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer Model 1800 IR Fourier

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transform (4000–450 cm^{-1}) spectrometer. Electronic absorption spectra were recorded on an IBM Instruments 9420 (900–300 nm) UV-visible spectrophotometer. Electrochemical measurements were carried out by the use 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. $E_{1/2}$ 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. ^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuterated solvent. ^{31}P{^{1}H} NMR spectra were obtained on a Varian XL-200 spectrometer. An internal deuterium lock and an external reference, 85% H_3PO_4, were used. Conductivity measurements were performed on acetone solutions of the samples at a concentration of ca 1.0 × 10^{-3} M. Measurements were made on an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. X-Band ESR spectra of CH_2Cl_2 glasses were recorded at ca −160 °C with a Varian E-109 spectrometer.

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

Results and Discussion

(a) Reactions of $Re_2H_8(PPh_3)_4$. The reaction of this complex with acetic acid/acetic anhydride mixtures in hot 1,2-dichlorobenzene affords a tan insoluble complex of stoichiometry $Re_2(O_2CCH_3)_6$ as the major product (53% yield). This compound has little solubility in common solvents, and it turns a dark green color when exposed to the air. Its formulation as the homoleptic acetate complex $Re_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)_2$ is primarily based upon its ready conversion in high yield to the well-characterized orange chloride analogue $Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$.[14] The IR spectrum of the homoleptic acetate complex (see Experimental Section) is strikingly similar to that of the structurally characterized homoleptic diruthenium(II,III) acetate $Ru_2(\mu\text{-}O_2CCH_3)_4\cdot(CH_3CO_2)_2H\cdot0.7H_2O$.[15-18] Its solid-state diffuse-reflectance electronic absorption spectrum shows bands at 700 and 470 (sh) nm, the former being assigned to the $\delta \rightarrow \delta^*$ transition, which is so characteristic of quadruply bonded $(Re\overset{4}{-}Re)^{6+}$ species.[14]

The yellow carbonyl complex $Re(O_2CCH_3)(CO)_2(PPh_3)_2$ (**1**) was isolated as a minor product in the workup of the filtrate that remained following the isolation of $Re_2(O_2CCH_3)_6$. The analogous propionate complex $Re(O_2CC_2H_5)(CO)_2(PPh_3)_2$ (**2**) was also obtained in very low yield from the reaction between $Re_2H_8(PPh_3)_4$ and $C_2H_5CO_2H/(C_2H_5CO)_2O$. Interestingly, this latter reaction did not afford insoluble $Re_2(O_2CC_2H_5)_6$ under our reaction conditions.[19,20] In both these reactions, the source of the CO is presumably the carboxylic acid and/or anhydride. The IR spectra (Nujol mulls) show characteristic ν(CO) bands at 1926 (s) and 1850 (vs) cm^{-1} for **1** and 1928 (s) and 1853 (vs) cm^{-1} for **2**. The spectrum of **1** in CS_2 solution is similar to this with ν(CO) at 1931 (s) and 1854 (vs) cm^{-1}. The ^{1}H NMR spectrum of **1** (in CD_2Cl_2) displays resonances at δ +7.43 (C_6H_5) and δ +0.44 (CH_3) in the correct intensity ratio (observed 10.4:1, calculated 10:1). These spectral properties of **1** and **2** are in good agreement with literature data for these two complexes.[11,21] The cyclic voltammogram of a solution of **1** in 0.1 M TBAH/CH_2Cl_2 (Figure 1) shows an irreversible oxidation at $E_{p,a}$ = +1.15 V vs Ag/AgCl as its most characteristic feature with a coupled reduction wave at $E_{p,c}$ = +0.97 V vs Ag/AgCl ($i_{p,c}/i_{p,a} \ll 1$).

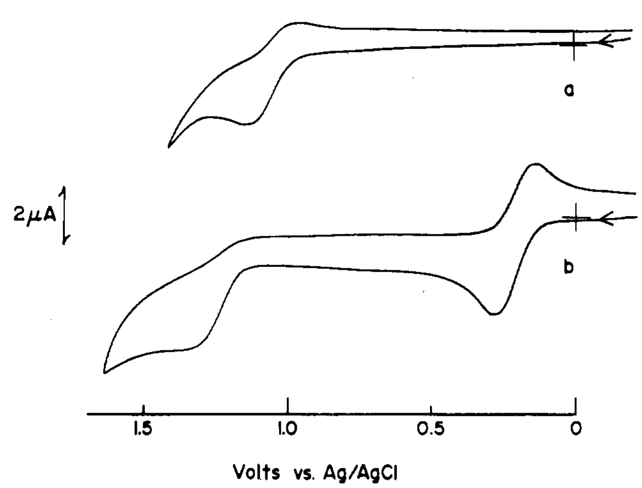

Figure 1. Single-scan cyclic voltammograms of (a) $Re(O_2CCH_3)(CO)_2(PPh_3)_2$ and (b) $Re(O_2CCH_3)(CO)(PPh_3)_3$, recorded at v = 200 mV s^{-1} in 0.1 M TBAH/CH_2Cl_2 with the use of a Pt-bead electrode.

The structure of the acetate complex **1** was established by X-ray crystallography. It has a cis arrangement of carbonyl ligands and PPh_3 ligands that are trans to one another. Compound **1** is essentially isostructural with its manganese(I) analogue, which has been structurally characterized.[22] Soon after our completion of the structure determination of **1**, we discovered that its structure had been published previously.[11] Accordingly, details of our structure analysis are available only as supplementary material.

(b) Reactions of $ReH_7(PPh_3)_2$. The reaction of this heptahydride complex with acetic acid/acetic anhydride in refluxing THF in the presence of 2 equiv of PPh_3 for ca. 30 min gives the monocarbonyl complex $Re(O_2CCH_3)(CO)(PPh_3)_3$ (**3**) in yields of ca. 80%. The reaction proceeds similarly at room temperature but requires a much longer reaction time. The related reaction with $C_2H_5CO_2H/(C_2H_5CO)_2O$ gives $Re(O_2CC_2H_5)(CO)(PPh_3)_3$ (**4**). In the absence of added phosphine a mixture of $Re(O_2CCH_3)(CO)_2(PPh_3)_2$ and $Re(O_2CCH_3)(CO)(PPh_3)_3$ (identified by IR spectroscopy) is formed in the acetic acid/anhydride reaction. Treatment of this mixture with an excess of PPh_3 in refluxing THF for 1 h did not convert **1** into **3**. This no doubt reflects the kinetically inert nature of the 18-electron complex **1**. Apparently, the key to the formation of **3** is the availability of free PPh_3 ligand during the elimination of H_2, which occurs when $ReH_7(PPh_3)_3$ is protonated by acetic acid. In this same context, we find that $ReH_5(PPh_3)_3$ does not react with acetic acid/acetic anhydride under the same conditions as those under which $ReH_7(PPh_3)_3$ is converted into **3**. This is in accord with the much more inert nature of $ReH_5(PPh_3)_3$ compared to $ReH_7(PPh_3)_2$.[6]

Both complexes form solutions in acetone that are essentially nonconducting with $\Lambda_m \simeq 10\ \Omega^{-1}\ cm^2\ mol^{-1}$ for $c_m \simeq 1 \times 10^{-3}$ M. IR spectral measurements (Nujol mulls) on **3** and **4** show the presence of a strong ν(CO) band at 1818 cm^{-1}. However, in the case of the acetate complex **3**, this band position does vary slightly depending upon the solvent used for recrystallization. These variations are attributed to solid-state effects, since, irrespective of the sample source, the positions of ν(CO) in solution spectra are dependent only upon the spectral solvent, viz. 1822 cm^{-1} in THF and 1808 cm^{-1} in CH_2Cl_2. The ^{1}H NMR spectra (measured in CD_2Cl_2) are very simple and integrate in accord

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

(15) This complex was first formulated as $Ru_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)_2\cdot0.7H_2O$ by Drew et al.[16] but more recently reformulated as a diruthenium(II,III) complex by Cotton et al.[17] We thank Professor F. A. Cotton for providing us with details of his study prior to the publication of these results.

(16) Drew, M. G. B.; Higgins, P.; McCann, G. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1385.

(17) Cotton, F. A.; Matusz, M.; Zhong, B. *Inorg. Chem.* **1988**, *27*, 4368.

(18) We prepared a sample of this compound by the reported procedure[16] and agree with the assignment of the $\nu(CO_2)$ modes of the bridging and "monodentate" acetate ligands. We found good agreement between the two spectra in the region 1600–500 cm^{-1} with regard to both the relative intensities of the bands and the frequencies, which were within ±5 cm^{-1} of one another.

(19) We have not yet identified the major rhenium-containing species that is formed in this reaction. Work is under way to examine this reaction in more detail.

(20) Preliminary experiments indicate that the reaction of $Re_2(O_2CCH_3)_6$ with propionic acid/propionic ahydride mixtures does not provide a route to $Re_2(O_2CC_2H_5)_6$, although we are exploring this reaction, and others like it, in more detail. We thank Professor F. A. Cotton for suggesting this as a possible route to $Re_2(O_2CC_2H_5)_6$.

(21) La Monica, G.; Cenini, S.; Ponta, F.; Pizzotti, M. *J. Chem. Soc., Dalton Trans.* **1976**, 1777.

(22) Dean, W. K.; Simon, G. L.; Treichel, P. M.; Dahl, L. F. *J. Organomet. Chem.* **1973**, *50*, 193.

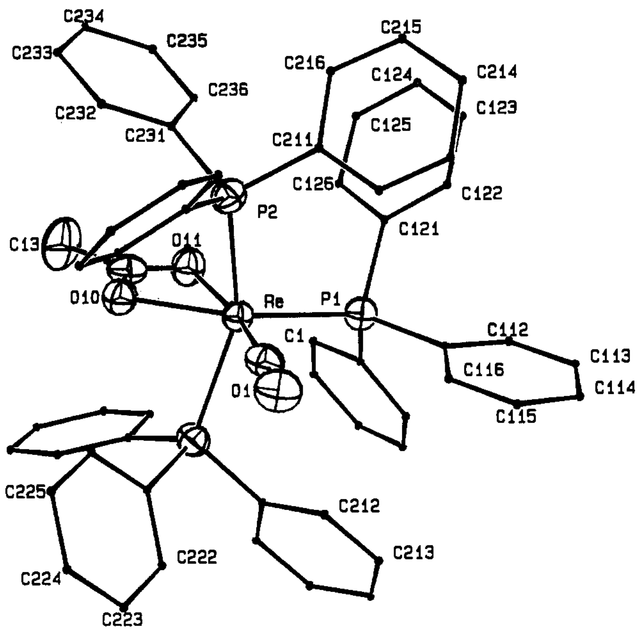

Figure 2. ORTEP representation of the $[Re(O_2CCH_3)(CO)(PPh_3)_3]^+$ cation in its PF_6^- salt **5**. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings, which are small circles of arbitrary radius.

with the proposed stoichiometries with a fairly complex set of phenyl proton resonances at $\delta \simeq +7.2$, a singlet at δ +0.78 (CH_3) for **3**, and a triplet at δ +0.44 (CH_3) and quartet at δ +1.14 (CH_2) for **4**. While the $^{31}P\{^1H\}$ NMR spectrum of **3** shows two closely spaced resonances at δ +24.5 and +24.1 (relative intensity ca. 2:1), only a single resonance is found in the spectrum of **4** at δ +24.0. The latter band is slightly asymmetric to its high-field side, no doubt reflecting the presence of two overlapping, almost coincident, peaks. The presence of two ^{31}P resonances is in accord with the structure of these complexes (vide infra).

The complexes of stoichiometry $Re(O_2CR)(CO)(PPh_3)_3$ have very similar electrochemical properties. Cyclic voltammetric (CV) measurements on solutions of these complexes in 0.1 M $TBAH/CH_2Cl_2$ show a reversible couple at $E_{1/2} \simeq +0.15$ V vs Ag/AgCl (+0.19 V for **3**, +0.14 V for **4**), which corresponds to a one-electron oxidation of the bulk complex, and an irreversible oxidation at $E_{p,a} = +1.25$ V (Figure 1). The acetate derivative **3** has been electrochemically oxidized to the orange monocation, which in turn has been electrochemically reduced back to the starting complex. This oxidation and subsequent reduction have been accomplished chemically by using the one-electron oxidant $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ and the one-electron reductant $(\eta^5\text{-}C_5H_5)_2Co$. The propionate complex **4** can be oxidized to $[Re(O_2CC_2H_5)(CO)(PPh_3)_3]PF_6$ in a similar fashion.

The one-electron-oxidized complexes $[Re(O_2CR)(CO)(PPh_3)_3]PF_6$ (**5**, R = CH_3; **6**, R = C_2H_5) are bright orange solids with electrochemical properties very similar to those of the neutral precursors **3** and **4** except that the process at $E_{1/2} \simeq +0.15$ V is now a reduction. The similarities between the cyclic voltammograms of the neutral and monocation species suggest that they have similar structures, i.e. that little structural rearrangement accompanies the electron transfer. The IR spectra of **5** and **6** (Nujol mulls) have a characteristic intense $\nu(CO)$ band at 1884 cm^{-1} (with a shoulder at 1872 cm^{-1}). The increase in $\nu(CO)$ for **5** and **6**, compared to **3** and **4**, is compatible with the decrease in $Re(d_\pi) \rightarrow CO(\pi^*)$ back-bonding, which is expected with the increase in positive charge at the metal centers in the oxidized species. Conductivity measurements on their solutions in acetone ($\simeq 1 \times 10^{-3}$ M) confirm them to be 1:1 electrolytes (Λ_m = 100–122 Ω^{-1} cm^2 mol^{-1}).

Complexes **5** and **6** are expected to be paramagnetic since they contain 17-electron cations. In accord with this, dichloromethane solutions of **5** and solutions of the electrochemically oxidized monocation in $TBAH/CH_2Cl_2$ display the same X-band ESR spectrum at −160 °C. The signal spans the range 2.1–3.6 kG and shows broad poorly resolved structure. It is centered at $g = 2.29$. Chemical reduction of **5** (with $(\eta^5\text{-}C_5H_5)_2Co$) and its electrochemical reduction regenerates the ESR-silent neutral complex **3**.

The structure of the cation in **5** is shown in Figure 2. The cation lies on a special position with a mirror plane that contains the carbonyl ligand, the carbon and oxygen atoms of the acetate ligand, and the phosphorus atom P(1) and one of the phenyl rings of the unique phosphine ligand. Important bond distances and bond angles are given in Tables III and IV. The geometry overall is that of a distorted octahedron. The distance Re–P(1) (2.437 (3) Å) involving the unique PPh_3 ligand is slightly shorter than the two Re–P(2) distances (2.477 (2) Å), which are trans to one another. Of the two Re–O(carboxylate) distances, the one trans to the Re–CO unit is slightly longer (2.194 (7) Å vs 2.181 (7) Å), although this difference is probably not statistically significant. Overall, the Re–ligand distances are very similar to those found in the structure of $Re(O_2CCH_3)(CO)_2(PPh_3)_2$,[11,23] although the out-of-plane Re–P distances in **5** are slightly longer than are the corresponding Re–P distances in **1**, while the Re–O distances are shorter in **5** than **1** (viz. average of 2.19 Å in **5** vs 2.22 Å in **1**[23]).

The largest angular distortions from an octahedral geometry are seen in the angles P(2)–Re–P(2) and O(10)–Re–O(11), which are 151.83 (9) and 59.8 (2)°, respectively. The former angle is much smaller than that in **1** (176.88 (4)°),[11,23] no doubt reflecting the steric effect of the third PPh_3 ligand in **5**.

(c) Concluding Remarks. The conversion of $Re_2H_8(PPh_3)_4$ to $Re_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)_2$ is noteworthy in that it provides an easy route to the first *homoleptic* carboxylate complex of group 7. The carbonyl complex $Re(O_2CCH_3)(CO)_2(PPh_3)_2$ is obtained as a minor byproduct in this reaction. However, much better synthetic routes to this compound already exist.[11,21] Of much more significance is the high-yield conversion of $ReH_7(PPh_3)_2$ to $Re(O_2CR)(CO)(PPh_3)_3$ (R = CH_3, C_2H_5) and the observation that the latter complexes are much more readily oxidized than $Re(O_2CCH_3)(CO)_2(PPh_3)_2$, a clear reflection of the effect of the net buildup of negative charge at the metal center that results upon replacing an electron-withdrawing CO ligand by the better σ-donor PPh_3 ligand. As measured by the CV technique, this oxidation shifts by ca. 0.9 V to more negative potentials, thereby permitting the easy chemical oxidation of $Re(O_2CR)(CO)(PPh_3)_3$ to the corresponding paramagnetic salt $[Re(O_2CR)(CO)(PPh_3)_3]PF_6$. Neither $Re(O_2CCH_3)(CO)(PPh_3)_3$ nor its much more reactive 17-electron monocation react with CO to displace the unique PPh_3 ligand and generate a $(PPh_3)_2$ complex. Indeed, on the basis of the structure determination of $[Re(O_2CCH_3)(CO)(PPh_3)_3]PF_6$, the unique in-plane PPh_3 ligand appears to be more strongly bound than the pair of trans PPh_3 ligands.

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Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters for **1** and **5** (Tables S1 and S2), the non-hydrogen positional parameters of **1** (Table S3), the positional parameters for the phenyl carbon atoms, the lattice solvent molecule atoms, and the atoms of the PF_6^- anion of **5** (Table S4), the positional parameters for the hydrogen atoms of **1** and **5** (Tables S5 and S6), the thermal parameters of **1** and **5** (Tables S7 and S8), and complete bond distances (Tables S9 and S10) and bond angles (Tables S11 and S12) for **1** and **5** and a figure (Figure S1) showing the full atomic numbering scheme for **1** (29 pages); tables of observed and calculated structure factors (43 pages). Ordering information is given on any current masthead page.

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(23) Data from our structure determination of $Re(O_2CCH_3)(CO)_2(PPh_3)_2$ are available as supplementary material or upon request from R.A.W.