

Electrochemical Synthesis and Structural Characterization of Bis(triphenylphosphine)copper(I) Fluoroacetates*

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Bis(triphenylphosphine)copper(I) fluoroacetate complexes have been prepared by the electrochemical oxidation of copper metal in acetonitrile solutions of triphenylphosphine and mono-, di- and tri-fluoroacetic acid respectively. Recrystallization from toluene yields unsolvated mononuclear complexes $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCH}_3)_n\text{F}_n]$, $n = 1-3$, which have been characterized by single-crystal X-ray crystallographic determinations. Crystals of the three complexes are isomorphous with the acetate complex ($n = 0$), crystallizing in the monoclinic space group $P2_1/a$ with cell dimensions $a \approx 18.0$, $b \approx 11.0$ and $c \approx 19.3$ Å and $\beta \approx 120^\circ$. Residuals for the complexes with $n = 1, 2$ and 3 were $R = 0.077$, 0.045 and 0.048 for 3677, 2789 and 3527 'observed' [$I > 3\sigma(I)$] reflections respectively. The bond distances Cu-P are 2.232(3), 2.222(3); 2.234(2), 2.219(2); and 2.235(2), 2.228(2) Å with the corresponding P-Cu-P angles increasing from 135.0(1) to 135.8(1) to 136.7(1)°, this latter value being the largest recorded for $[\text{Cu}(\text{PPh}_3)_2]^+$. The asymmetry of the co-ordination of the carboxylate group increases along the series with Cu-O distances of 2.144(6) and 2.363(7); 2.118(4), 2.465(6); and 2.113(4), 2.545(5) Å for $n = 1, 2$ and 3 respectively. Crystallization of the difluoro- and trifluoro-acetate complexes from ethanol results in isomorphous orthorhombic $Pb2_1a$ crystals ($a \approx 22.2$, $b \approx 18.5$, $c \approx 9.0$ Å) with monodentate carboxylate and co-ordinated ethanol; the monofluoroacetate is unsolvated. For $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCHF}_2)(\text{EtOH})]$ R was 0.052 for 2090 'observed' reflections with Cu-P 2.248(3), 2.236(3) Å and P-Cu-P 120.5(1)°; Cu-O(carboxylate) is 2.074(8) Å and Cu-O(ethanol) is 2.169(8) Å. For $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCF}_3)(\text{EtOH})]$ R was 0.043 for 2350 'observed' reflections, Cu-P being 2.248(2), 2.240(2) Å and P-Cu-P 120.8(1)°; Cu-O(carboxylate) is 2.104(6) Å and Cu-O(ethanol) is 2.160(6) Å.

The bis(triphenylphosphine)copper(I) cation is a soft acceptor ion which can accommodate a wide range of co-ordinating anions to form inner-sphere complexes of the type $[\text{Cu}(\text{PPh}_3)_2\text{X}]$. In all these complexes the donor properties of the anion and the steric interactions between the anion and the phenyl substituents on the phosphine each play a significant role in determining the geometry of the CuP_2 core and the co-ordination mode of the anion.¹⁻⁴ In this context the structural chemistry of complexes of the relatively hard carboxylate anions with this cation is of interest as wide variation in the substituent group is readily achieved and provides the potential to change the donor properties of the anion from a strong to a weak base while keeping the steric profile essentially constant; in addition, the steric profile of the anion may be varied. Published structural data on the formate and acetate complexes show that the small formate anion co-ordinates to the copper as a symmetrical bidentate ligand with Cu-O and Cu-P distances of 2.226(3) and 2.247(1) Å and a P-Cu-P angle of 128.3(4)°,⁵ whereas acetate co-ordinates unsymmetrically with Cu-O 2.162(5), 2.257(7), Cu-P 2.240(3), 2.233(2) Å and the P-Cu-P angle increasing to 133.4°.⁶

To extend this structural chemistry we have prepared the series of fluoro-substituted acetate complexes $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCH}_3)_n\text{F}_n]$ for $n = 1-3$ by electrochemical oxidation of copper metal in acetonitrile solutions of triphenylphosphine and mono-, di- and tri-fluoroacetic acid respectively, expecting any changes in co-ordination and the geometry of the P_2CuO_2 co-ordination sphere to be primarily the result of changes in the base strength of the anions which varies considerably, the pK_a

values ranging from 4.78 for acetic acid, 2.60 for fluoroacetic acid, 1.34 for difluoroacetic acid to 0.50 for trifluoroacetic acid;⁷ considerable similarity in steric interactions is strongly suggested by the single crystal X-ray crystallographic structure determinations which showed all three complexes to be isomorphous with the parent acetate complex. The asymmetry in carboxylate co-ordination observed for the acetate was found to increase systematically with decreasing base strength of the anion, possibly assisting to rationalize the observation that recrystallization of the di- and tri-fluoroacetate complexes from ethanol, but not the monofluoroacetate complex, resulted in displacement of the one oxygen from the co-ordination sphere by ethanol.

Experimental

Electrochemical Synthesis.—The electrochemical procedures used were similar to those described in the literature.⁸ A copper anode and a platinum-wire cathode were placed in HPLC grade acetonitrile (30 cm³) containing triphenylphosphine (1.0 g) and a 30% aqueous solution (2.0 cm³) of the appropriate acid under argon. A potential of 5.0 V was applied across the electrodes of the unstirred solution for 2–7 h, depending on the rate of copper dissolution for each acid, to give a 2:1 or slightly greater molar ratio of triphenylphosphine to copper as determined by the mass of copper dissolved from the anode. On completion of the electrolysis the solvent was evaporated to yield a viscous oil. Trituration of these oils with ethanol yielded white crystalline products which were recrystallized from warm ethanol and shown by X-ray single-crystal structural determinations to be $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCH}_2\text{F})]$, $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCHF}_2)(\text{EtOH})]$ and $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCF}_3)(\text{EtOH})]$ respectively. Further recrystallization of these complexes from

* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

toluene yielded well formed crystals of the unsolvated complexes $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCH}_3)_n\text{F}_n]$, that of the monofluoro species having identical cell dimensions to the product from ethanol: $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCH}_2\text{F})]$, m.p. 182–184 °C, ν_{asym} 1595 cm^{-1} (Found: C, 68.4; H, 4.9. $\text{C}_{38}\text{H}_{32}\text{CuFO}_2\text{P}_2$ requires C, 68.60; H, 4.85%; $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCHF}_2)]$, m.p. 184–186 °C, ν_{asym} 1636 cm^{-1} (Found: C, 65.9; H, 4.7. $\text{C}_{38}\text{H}_{31}\text{CuF}_2\text{O}_2\text{P}_2$ requires C, 66.8; H, 4.6%; $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCF}_3)]$, m.p. 177–179 °C (lit.,⁹ 179 °C), ν_{asym} 1660 cm^{-1} (Found: C 65.5; H, 4.4. $\text{C}_{38}\text{H}_{30}\text{CuF}_3\text{O}_2\text{P}_2$ requires C, 65.5; H, 4.3%).

Structure Determinations.—Unique data sets were measured at ca. 295 K within the limit $2\theta_{\text{max}}$ 50° on specimens mounted in capillaries using an Enraf-Nonius CAD-4 four-circle diffractometer (2θ - θ scan mode; monochromatic Mo- $K\alpha$ radiation, λ 0.71073 Å). N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinements after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x , y , z , U_{iso})_H were included, constrained at estimated values. Conventional residuals at convergence, R , R' on $|F|$ are quoted for the preferred enantiomer where appropriate, statistical reflection weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$ being used. Neutral-atom complex scattering factors were used;¹⁰ computation used the XTAL 3.2 program system¹¹ implemented by S. R. Hall. Pertinent results are presented in Figs. 1 and 2 and Tables 1–7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Crystal/refinement data. $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCH}_2\text{F})]$ **1**, $\text{C}_{38}\text{H}_{32}\text{CuFO}_2\text{P}_2$, M 664.9, monoclinic, space group $P2_1/a$ (C_{2h}^5 , no. 14), a 18.06(2), b 11.096(4), c 19.26(1) Å, β 121.72(6)°, U 3284 Å³, D_c ($Z = 4$) 1.34 g cm⁻³, $F(000)$ 1376, μ_{Mo} 8.3 cm⁻¹. Specimen: 0.30 × 0.50 × 0.40 mm, $A^*_{\text{min,max}}$ 1.23, 1.43. N 5751, N_o 3677. R 0.077, R' 0.085.

$[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCHF}_2)]$ **2a**, $\text{C}_{38}\text{H}_{31}\text{CuF}_2\text{O}_2\text{P}_2$, M 682.9, monoclinic, space group $P2_1/a$, a 18.031(7), b 11.268(7), c 19.22(1) Å, β 122.03(5)°, U 3310 Å³, D_c ($Z = 4$) 1.37 g cm⁻³, $F(000)$ 1408, μ_{Mo} 8.0 cm⁻¹. Specimen: 0.04 × 0.17 × 0.28 mm, $A^*_{\text{min,max}}$ 1.03, 1.13. N 5031, N_o 2789. R 0.045, R' 0.042.

$[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCHF}_2)(\text{EtOH})]$ **2b**, $\text{C}_{40}\text{H}_{37}\text{CuF}_2\text{O}_3\text{P}_2$, M 728.9, orthorhombic, space group $Pb2_1a$ (C_{2v}^5 , no. 29, variant), a 22.164(9), b 18.472(8), c 8.97(1) Å, U 3673(5) Å³, D_c ($Z = 4$) 1.32 g cm⁻³, $F(000)$ 1512, μ_{Mo} 6.8 cm⁻¹. Specimen: 0.20 × 0.32 × 0.36 mm, $A^*_{\text{min,max}}$ 1.09, 1.15. N 3336, N_o 2090. R 0.052, R' 0.048 (preferred chirality).

$[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCF}_3)]$ **3a**, $\text{C}_{38}\text{H}_{30}\text{CuF}_3\text{O}_2\text{P}_2$, M 700.9, monoclinic, space group $P2_1/a$, a 18.123(9), b 11.357(5), c 19.34(1) Å, β 122.04(6)°, U 3374 Å³, D_c ($Z = 4$) 1.38 g cm⁻³, $F(000)$ 1440, μ_{Mo} 7.9 cm⁻¹. Specimen: 0.50 × 0.30 × 0.30 mm, $A^*_{\text{min,max}}$ 1.20, 1.37. N 5935, N_o 3527. R 0.048, R' 0.048.

$[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCF}_3)(\text{EtOH})]$ **3b**, $\text{C}_{40}\text{H}_{36}\text{CuF}_3\text{O}_3\text{P}_2$, M 746.9, orthorhombic, space group $Pb2_1a$, a 22.251(7), b 18.509(5), c 8.989(5) Å, U 3702 Å³, D_c ($Z = 4$) 1.34 g cm⁻³, $F(000)$ 1544, μ_{Mo} 6.8 cm⁻¹. Specimen: 0.20 × 0.30 × 0.40 mm, $A^*_{\text{min,max}}$ 1.09, 1.15. N 3362, N_o 2350. R 0.043, R' 0.043 (preferred chirality).

Abnormal features/variations in procedure. Although material available for complex **1** comprised well formed substantial unsolvated crystals from both ethanol and toluene, these diffracted poorly with wide peak widths and deterioration during the course of data collection; a number of attempts at achieving improved data beyond those recorded here were frustratingly disappointing. Thermal motion at the peripheral of the anionic ligand was high, but not resolvable into disordered components. In both the isomorphous complexes, **2b** and **3b**, the ethanol methyl groups were disordered over two sites, modelled, after independent population refinement, as atoms with equal occupancy. The hydroxyl hydrogen atoms could not be located. In **2a** and **2b** the two fluorine atoms appeared distributed equally

over the three available sites, and were modelled as such in the final refinement stages. The chirality of the asymmetric unit of the specimen of **2b** as determined by refinement was the opposite of that of the specimen of **3b** chosen.

Results and Discussion

Synthesis.—A variety of methods for the synthesis of tertiary phosphine copper(I) carboxylate complexes have been reported. The most direct is the addition of the phosphine to the copper(I) carboxylate salt dissolved in benzene or toluene.^{6,9,13} However, these salts are generally air and moisture sensitive and other synthetic methods have been developed including reduction of copper(II) carboxylates with the phosphine,¹⁴ the reaction of carboxylic acids or carbon dioxide with $[\text{Cu}(\text{PR}_3)_2(\text{BH}_4)]$,^{12,14–16} and the reaction of carbon dioxide with copper(I) hydrides or arylcopper(I) complexes.^{5,17,18} For synthesis of the present series of complexes, electrochemical oxidation of copper metal to copper(I) in acetonitrile solutions of triphenylphosphine and the appropriate acid proved to be the most convenient.⁸ This approach has the advantage of obtaining complexes through a 'one pot' procedure from simple, readily available precursors without the need to preclude air or moisture from the reaction vessel. At the platinum cathode the acidic protons from the carboxylic acid are reductively coupled to give hydrogen gas with the carboxylate anion remaining in the reaction mixture. The copper anode is oxidized to Cu^+ ions which form soluble complexes with the triphenylphosphine and the carboxylate anion. The rate of corrosion of the copper anode was dependent on the acid strength of the carboxylic acid, increasing in the order $\text{CH}_2\text{F} < \text{CHF}_2 < \text{CF}_3$. For the present experiments electrolysis was continued until the molar ratio of PPh_3 to Cu^+ was 2:1 or slightly greater and the complexes were obtained by recrystallization from ethanol or toluene or as described above.

Structural Results.—The single crystal X-ray structure determinations on the three complexes crystallized from toluene show that each crystallizes as monomeric neutral molecules $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCH}_3)_n\text{F}_n]$ separated by normal van der Waals distances. The three structures are isomorphous with the parent acetate complex,⁶ adopting the basic setting of the latter in the monoclinic space group $P2_1/a$ with cell dimensions $a \approx 18.0$, $b \approx 11.0$ and $c \approx 19.3$ Å and $\beta \approx 120^\circ$. The $\text{P}_2\text{CuO}_2\text{CR}$ core geometries are presented in Table 6. The molecular structure of the monofluoroacetate complex is depicted in Fig. 1. The two triphenylphosphine ligands in each molecule in this series of compounds are crystallographically

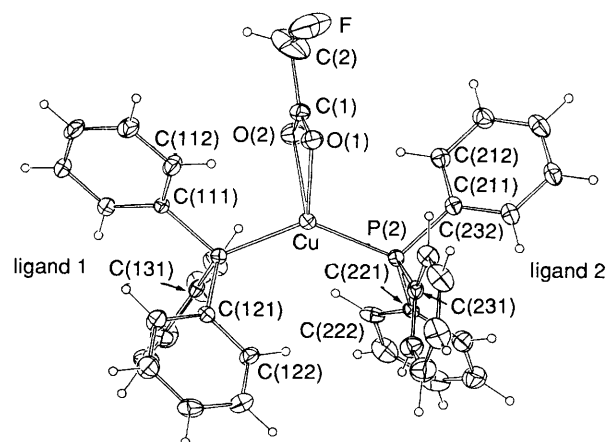
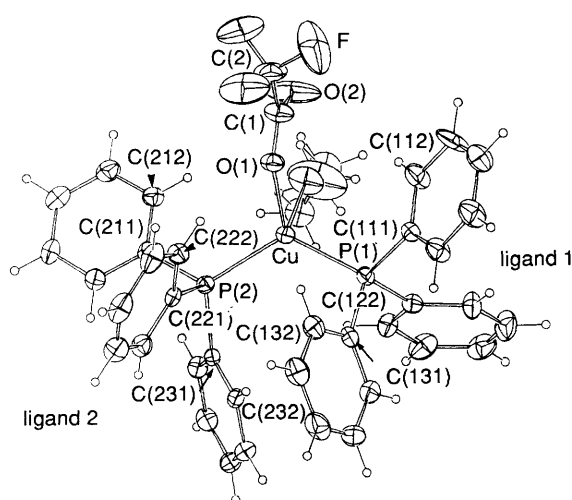
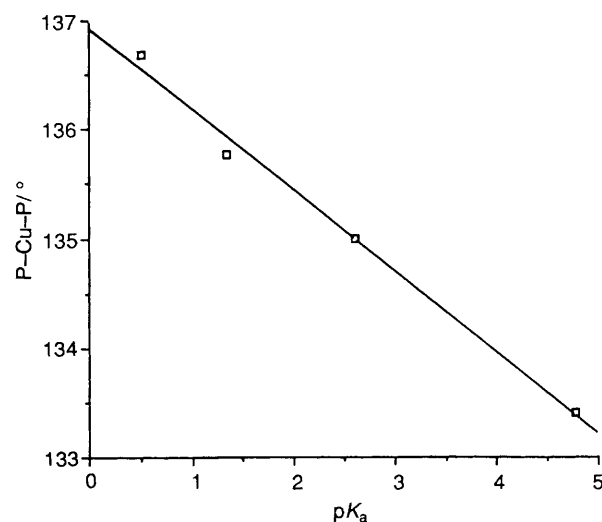


Fig. 1 Molecular structure of $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCH}_2\text{F})]$: 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å

Table 1 Non-hydrogen atomic coordinates for $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCH}_2\text{F})] \mathbf{1}$

Atom	$n = 1$			$n = 2$		
	x	y	z	x	y	z
Cu	0.337 15(6)	0.437 9(1)	0.234 80(6)			
P(n)	0.417 1(1)	0.508 5(2)	0.186 4(1)	0.349 9(1)	0.286 3(2)	0.315 8(1)
C($n11$)	0.361 8(5)	0.616 5(7)	0.103 4(4)	0.270 5(5)	0.289 5(8)	0.347 9(4)
C($n12$)	0.275 0(6)	0.595 9(8)	0.045 9(5)	0.239 5(5)	0.399 5(8)	0.353 8(5)
C($n13$)	0.230 5(6)	0.670 4(9)	−0.021 2(5)	0.183 7(6)	0.408 5(9)	0.382 8(5)
C($n14$)	0.270 9(6)	0.763 9(9)	−0.032 9(6)	0.159 2(6)	0.307(1)	0.406 2(5)
C($n15$)	0.356 9(6)	0.788 7(8)	0.024 4(6)	0.188 7(6)	0.195 7(9)	0.399 4(5)
C($n16$)	0.402 7(5)	0.713 9(8)	0.093 0(5)	0.245 6(5)	0.187 2(8)	0.371 9(5)
C($n21$)	0.457 7(5)	0.394 3(7)	0.146 4(4)	0.451 9(5)	0.276 8(7)	0.412 3(5)
C($n22$)	0.490 5(5)	0.288 9(8)	0.190 4(5)	0.506 5(5)	0.375 7(9)	0.436 4(5)
C($n23$)	0.526 1(6)	0.202 1(8)	0.165 5(6)	0.580 6(7)	0.378(1)	0.513 6(7)
C($n24$)	0.529 1(6)	0.219 6(9)	0.095 9(6)	0.601 5(7)	0.286(1)	0.567 0(6)
C($n25$)	0.495 0(7)	0.322 5(9)	0.050 4(6)	0.549 9(7)	0.185(1)	0.543 9(6)
C($n26$)	0.459 4(6)	0.410 0(8)	0.075 6(5)	0.474 2(6)	0.182 3(9)	0.466 9(6)
C($n31$)	0.517 4(5)	0.585 7(7)	0.262 4(4)	0.333 2(5)	0.140 3(8)	0.267 5(5)
C($n32$)	0.516 2(6)	0.654 2(9)	0.321 9(6)	0.250 4(6)	0.105 5(9)	0.209 5(6)
C($n33$)	0.589 7(8)	0.712(1)	0.380 3(6)	0.233 9(7)	−0.003(1)	0.167 4(6)
C($n34$)	0.664 8(7)	0.706(1)	0.378 8(6)	0.299 8(9)	−0.073(1)	0.179 8(8)
C($n35$)	0.666 4(6)	0.638 7(9)	0.320 5(6)	0.383 9(8)	−0.041(1)	0.235 6(8)
C($n36$)	0.593 4(5)	0.579 6(8)	0.262 1(5)	0.401 0(6)	0.068 6(9)	0.280 4(6)
O(1)	0.200 5(4)	0.469 0(6)	0.153 5(4)			
O(2)	0.269 4(4)	0.615 5(6)	0.242 3(4)			
C(1)	0.204 2(6)	0.571 6(9)	0.184 2(6)			
C(2)	0.125 8(7)	0.666(2)	0.152 5(8)			
F	0.057 1(6)	0.596 3(8)	0.098 7(7)			

**Fig. 2** Molecular structure of $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCF}_3)(\text{EtOH})]$ **Fig. 3** Plot of the P-Cu-P angle of $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCH}_3-n\text{F}_n)]$ complexes, $n = 0-3$, as a function of $\text{p}K_a$

independent with quite different conformational structures. Ligand 1 adopts quasi 3 symmetry with Cu-P(1)-C(1n1)-C(1n2) torsion angles of 39, 44 and 34° for the acetate complex, 39, 43, 36° for **1**, 39, 42, 37° for **2a** and 36, 42, 39° for **3a**. In ligand 2 the Cu-P-C(11)-C(12) torsion angle is similar to that found for ligand 1, ring 1, with the twist of ring 2 opposed to it; ring 3 lies almost at right angles to the Cu-P bond vector so that the ligand approaches m symmetry. The torsion angles Cu-P(2)-C(2n1)-(2n2) for the four complexes are 29, −10, 75 (acetate), 29, −13, 74 **1**, 28, −15, 77 **2a** and 29, −14, 78° **3a**. As expected for isomorphous complexes, the conformational structures of the ligands vary only slightly over the whole series. The Cu-P distances across the series are similar with an average value of 2.230(6) Å. For each complex, however, Cu-P(1) is marginally but consistently longer than Cu-P(2) (Table 6). By contrast, the P-Cu-P angles increase across the series from

133.4(1) to 135.0(1) to 135.8(1) to 136.7(1)°, this last angle being the greatest yet recorded for a $[\text{Cu}(\text{PPh}_3)_2]^+$ complex. Empirically, correlation of the P-Cu-P angle with $\text{p}K_a$ values for the carboxylic acids (Fig. 3) yields a good linear relationship (1) with $R^2 = 0.993$, reflecting quite well the influence of

$$\text{P-Cu-P} = 136.93 - 0.744\text{p}K_a \quad (1)$$

decreasing donor capacity of the anion on the cation geometry, either directly or *via* changes in the steric profile of the anion.

A striking structural feature of this series of compounds is the effect of increasing the number of substituents on the co-ordination of the carboxylate anion. As the donor strength of the anion decreases the co-ordination of the anion becomes

Table 2 Non-hydrogen atomic coordinates for $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCHF}_2)] \mathbf{2a}$

Atom	$n = 1$			$n = 2$		
	x	y	z	x	y	z
Cu	0.336 59(5)	0.428 26(7)	0.232 32(5)			
P(n)	0.416 48(9)	0.504 1(1)	0.185 51(9)	0.352 0(1)	0.281 1(1)	0.315 75(9)
C(n 11)	0.360 7(4)	0.610 2(5)	0.102 6(3)	0.274 0(3)	0.283 6(5)	0.348 7(3)
C(n 12)	0.275 0(4)	0.587 7(5)	0.043 7(4)	0.241 3(4)	0.392 3(5)	0.352 7(4)
C(n 13)	0.229 2(4)	0.661 5(7)	−0.024 6(4)	0.185 6(4)	0.402 1(6)	0.381 4(4)
C(n 14)	0.269 4(5)	0.756 9(6)	−0.033 2(4)	0.161 5(4)	0.301 0(8)	0.405 2(4)
C(n 15)	0.353 8(5)	0.782 5(6)	0.025 7(5)	0.192 5(4)	0.192 8(6)	0.400 8(4)
C(n 16)	0.400 2(4)	0.708 9(5)	0.094 2(4)	0.249 1(4)	0.183 5(5)	0.373 1(4)
C(n 21)	0.458 8(3)	0.394 7(5)	0.145 6(3)	0.455 6(3)	0.275 7(6)	0.412 6(3)
C(n 22)	0.492 3(4)	0.290 1(6)	0.189 3(4)	0.508 1(4)	0.373 6(6)	0.437 1(4)
C(n 23)	0.530 0(4)	0.205 7(6)	0.165 4(4)	0.584 4(5)	0.380 3(7)	0.514 9(6)
C(n 24)	0.534 4(4)	0.225 9(7)	0.098 0(5)	0.606 9(5)	0.288(1)	0.567 5(5)
C(n 25)	0.499 6(5)	0.328 4(7)	0.051 8(4)	0.556 2(6)	0.187 7(8)	0.544 5(5)
C(n 26)	0.462 1(4)	0.411 9(5)	0.076 2(4)	0.479 8(5)	0.181 5(6)	0.467 6(5)
C(n 31)	0.514 8(3)	0.581 7(5)	0.262 2(3)	0.337 2(4)	0.135 6(5)	0.269 2(3)
C(n 32)	0.511 5(4)	0.648 2(6)	0.320 6(4)	0.252 7(4)	0.096 6(6)	0.213 1(4)
C(n 33)	0.585 3(6)	0.709 5(7)	0.379 2(5)	0.239 4(5)	−0.009 6(8)	0.172 8(5)
C(n 34)	0.661 1(5)	0.704 8(7)	0.380 3(5)	0.308 9(7)	−0.076 2(7)	0.186 7(5)
C(n 35)	0.664 3(4)	0.638 3(7)	0.322 3(5)	0.392 5(6)	−0.038 6(7)	0.239 3(5)
C(n 36)	0.592 0(4)	0.577 3(6)	0.264 8(4)	0.406 8(4)	0.068 1(6)	0.281 2(4)
O(1)	0.201 9(3)	0.466 5(4)	0.152 7(3)			
O(2)	0.267 6(3)	0.612 1(4)	0.240 7(3)			
C(1)	0.203 1(4)	0.565 1(7)	0.182 3(5)			
C(2)	0.117 8(7)	0.633 4(9)	0.138(1)			
F(1)*	0.079 6(7)	0.601 6(8)	0.190 6(9)			
F(2)*	0.053 9(6)	0.584 5(9)	0.091 2(7)			
F(3)*	0.122 1(5)	0.741 5(7)	0.146 9(5)			

* Population 0.667.

Table 3 Non-hydrogen atomic coordinates for $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCF}_3)] \mathbf{3a}$

Atom	$n = 1$			$n = 2$		
	x	y	z	x	y	z
Cu	0.337 30(4)	0.424 56(6)	0.232 83(4)			
P(n)	0.415 34(8)	0.503 8(1)	0.185 89(8)	0.353 38(8)	0.278 0(1)	0.316 36(8)
C(n 11)	0.358 5(3)	0.609 5(4)	0.102 5(3)	0.276 0(3)	0.280 5(4)	0.349 8(3)
C(n 12)	0.270 9(3)	0.589 2(5)	0.044 4(3)	0.244 3(3)	0.389 1(4)	0.355 1(3)
C(n 13)	0.226 2(4)	0.661 1(5)	−0.022 7(3)	0.188 3(3)	0.397 9(5)	0.384 1(3)
C(n 14)	0.267 8(4)	0.755 3(5)	−0.031 9(3)	0.163 8(3)	0.297 2(6)	0.406 6(3)
C(n 15)	0.353 8(4)	0.779 1(5)	0.026 0(3)	0.193 8(4)	0.190 3(5)	0.400 5(3)
C(n 16)	0.398 8(3)	0.705 6(4)	0.093 8(3)	0.250 2(3)	0.179 7(5)	0.372 9(3)
C(n 21)	0.459 0(3)	0.396 1(4)	0.146 8(3)	0.457 4(3)	0.272 8(5)	0.414 3(3)
C(n 22)	0.494 3(3)	0.293 1(5)	0.191 6(3)	0.509 1(3)	0.371 8(5)	0.437 1(3)
C(n 23)	0.532 3(4)	0.210 4(5)	0.167 8(3)	0.584 7(4)	0.379 8(6)	0.513 6(4)
C(n 24)	0.536 0(4)	0.229 1(5)	0.099 5(4)	0.608 1(4)	0.288 5(6)	0.566 9(3)
C(n 25)	0.500 0(4)	0.330 4(5)	0.054 2(4)	0.558 5(4)	0.188 2(6)	0.544 5(3)
C(n 26)	0.461 7(4)	0.413 6(5)	0.077 6(3)	0.482 8(4)	0.179 8(5)	0.468 1(3)
C(n 31)	0.512 3(3)	0.582 2(4)	0.263 2(3)	0.339 2(3)	0.133 8(4)	0.269 9(3)
C(n 32)	0.508 7(4)	0.648 9(5)	0.320 2(3)	0.255 1(4)	0.094 2(5)	0.214 4(3)
C(n 33)	0.580 9(4)	0.708 9(6)	0.379 2(4)	0.241 4(4)	−0.011 7(6)	0.173 4(4)
C(n 34)	0.657 0(4)	0.704 4(6)	0.381 7(4)	0.310 9(5)	−0.077 5(6)	0.187 2(4)
C(n 35)	0.661 6(4)	0.638 7(6)	0.325 2(4)	0.394 2(4)	−0.039 5(5)	0.239 8(4)
C(n 36)	0.590 5(3)	0.577 9(5)	0.266 5(3)	0.408 5(4)	0.066 0(5)	0.281 5(3)
O(1)	0.203 3(2)	0.464 5(3)	0.158 7(2)			
O(2)	0.267 1(2)	0.611 9(4)	0.243 9(2)			
C(1)	0.204 5(3)	0.561 0(5)	0.188 0(3)			
C(2)	0.115 7(4)	0.623 1(5)	0.150 0(4)			
F(1)	0.085 0(3)	0.605 5(4)	0.198 3(3)			
F(2)	0.056 9(2)	0.581 7(4)	0.080 4(3)			
F(3)	0.119 5(3)	0.736 3(3)	0.144 2(3)			

increasingly unsymmetrical with the differences between Cu–O(1) and Cu–O(2) increasing from 0.09₃ Å for acetate⁶ to 0.43₂ Å for the trifluoroacetate. In the fluoroacetate species, Cu–O(1) decreases from 2.162(5) to 2.113(4) Å while Cu–O(2) increases from 2.257(7) to 2.545(5) Å. These results are consistent with increasing double-bond character in the C–O(2)

bond with decreasing p*K*_a and a corresponding localization of the anion charge on O(1). From the perspective of the anion, the results show nicely a transition of the cation from co-ordination to both donor oxygen atoms to co-ordination to a single oxygen (Scheme 1) with the C–O(2) bond being shortest for the trifluoroacetate complex. Shifts in the asymmetric

Table 4 Non-hydrogen atomic coordinates for $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCHF}_2)(\text{EtOH})]$ **2b**

Atom	$n = 1$			$n = 2$		
	x	y^a	z	x	y	z
Cu	0.415 57(5)	0.500 0	0.260 9(1)			
P(n)	0.394 6(1)	0.386 9(2)	0.184 4(3)	0.342 6(1)	0.583 3(2)	0.275 8(3)
C(n 11)	0.452 5(5)	0.345 6(6)	0.071(1)	0.359 4(5)	0.666 0(6)	0.378(1)
C(n 12)	0.512 3(6)	0.355 6(8)	0.115(1)	0.419 0(5)	0.675 9(7)	0.435(1)
C(n 13)	0.557 1(6)	0.324(1)	0.031(2)	0.432 1(6)	0.740 5(8)	0.508(1)
C(n 14)	0.546 7(7)	0.283(1)	−0.096(2)	0.391 2(7)	0.793 2(7)	0.518(2)
C(n 15)	0.489 3(7)	0.276 1(9)	−0.136(2)	0.333 7(6)	0.786 7(7)	0.461(1)
C(n 16)	0.441 9(5)	0.305 3(7)	−0.053(1)	0.318 7(5)	0.721 4(6)	0.392(1)
C(n 21)	0.379 2(4)	0.320 0(6)	0.327(1)	0.321 4(5)	0.619 7(6)	0.092(1)
C(n 22)	0.351 2(6)	0.342 4(6)	0.459(1)	0.367 1(5)	0.626 3(6)	−0.012(1)
C(n 23)	0.340 0(6)	0.293 0(9)	0.572(1)	0.356 5(8)	0.657 4(8)	−0.148(2)
C(n 24)	0.354 9(7)	0.221 1(9)	0.556(2)	0.297 8(8)	0.680 8(8)	−0.183(1)
C(n 25)	0.382 8(8)	0.199 0(8)	0.428(2)	0.252 4(8)	0.673 3(6)	−0.082(1)
C(n 26)	0.394 5(6)	0.247 5(7)	0.316(1)	0.263 7(6)	0.640 8(6)	0.059(1)
C(n 31)	0.329 3(5)	0.386 7(7)	0.063(1)	0.272 3(4)	0.550 4(5)	0.356(1)
C(n 32)	0.329 3(5)	0.434 3(7)	−0.053(1)	0.233 9(4)	0.507 0(7)	0.275(1)
C(n 33)	0.279 2(8)	0.442 1(9)	−0.140(2)	0.182 0(5)	0.479 3(7)	0.336(2)
C(n 34)	0.229 7(8)	0.399(1)	−0.117(2)	0.166 1(5)	0.494 8(8)	0.473(2)
C(n 35)	0.229 2(6)	0.350 5(8)	0.000(2)	0.202 4(6)	0.537 3(7)	0.560(1)
C(n 36)	0.278 9(6)	0.343 8(7)	0.088(2)	0.255 5(6)	0.566 0(6)	0.498(1)
O(1)	0.485 9(3)	0.538 6(5)	0.130 8(8)			
O(2)	0.562 0(4)	0.533(1)	0.285(1)			
C(1)	0.536 9(6)	0.546 5(9)	0.159(2)			
C(2)	0.577 8(7)	0.573(2)	0.039(3)			
F(1) ^b	0.555 3(9)	0.598(2)	−0.076(2)			
F(2) ^b	0.614(1)	0.618(1)	0.076(3)			
F(3) ^b	0.620(2)	0.535(1)	0.024(4)			
O(11)	0.476 9(4)	0.492 1(7)	0.448 6(9)			
C(11)	0.479(1)	0.475(3)	0.602(2)			
C(12a) ^c	0.498(2)	0.475(2)	0.706(4)			
C(12b) ^c	0.444(2)	0.487(2)	0.666(4)			

^a Defines origin. ^b Population 0.667. ^c Population 0.5.**Table 5** Non-hydrogen atomic coordinates for $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CCF}_3)(\text{EtOH})]$ **3b**

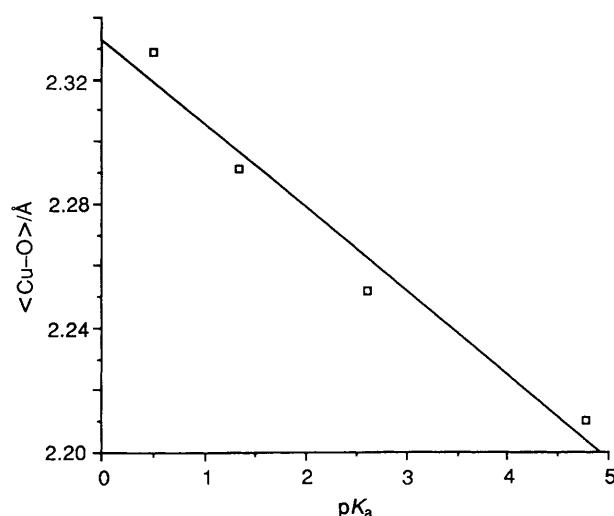
Atom	$n = 1$			$n = 2$		
	x	y^a	z	x	y	z
Cu	0.584 76(3)	0.500 0	0.736 3(1)			
P(n)	0.606 08(9)	0.612 6(1)	0.813 5(2)	0.656 80(8)	0.415 7(1)	0.722 5(2)
C(n 11)	0.548 3(4)	0.654 5(5)	0.927 9(9)	0.639 6(4)	0.332 1(4)	0.621 3(9)
C(n 12)	0.489 8(5)	0.645 1(6)	0.882(1)	0.581 2(4)	0.322 8(5)	0.564 7(9)
C(n 13)	0.444 5(4)	0.676 3(9)	0.967(2)	0.566 4(5)	0.258 9(6)	0.494(1)
C(n 14)	0.455 4(6)	0.715 1(7)	1.091(1)	0.607 8(5)	0.205 1(6)	0.483(1)
C(n 15)	0.513 1(6)	0.723 3(7)	1.133(1)	0.664 2(5)	0.213 1(5)	0.536(1)
C(n 16)	0.559 5(4)	0.693 5(5)	1.053(1)	0.680 2(4)	0.277 4(5)	0.605 0(9)
C(n 21)	0.621 7(4)	0.679 2(5)	0.670(1)	0.677 4(4)	0.379 2(4)	0.906 8(9)
C(n 22)	0.649 9(4)	0.655 5(5)	0.542(1)	0.632 9(4)	0.372 2(5)	1.010 9(9)
C(n 23)	0.662 2(5)	0.705 5(7)	0.428(1)	0.644 3(6)	0.341 2(6)	1.145(1)
C(n 24)	0.647 1(6)	0.777 1(8)	0.442(1)	0.702 4(6)	0.317 9(6)	1.180(1)
C(n 25)	0.619 0(6)	0.799 9(6)	0.569(1)	0.746 1(5)	0.325 6(6)	1.078(1)
C(n 26)	0.607 7(5)	0.752 2(5)	0.682(1)	0.735 3(4)	0.356 0(5)	0.940(1)
C(n 31)	0.671 8(4)	0.612 3(5)	0.933(1)	0.728 0(3)	0.447 2(4)	0.642 2(8)
C(n 32)	0.671 5(4)	0.564 7(5)	1.049(1)	0.764 8(3)	0.490 2(5)	0.725 4(8)
C(n 33)	0.720 7(6)	0.558 1(7)	1.139(1)	0.817 0(4)	0.518 7(5)	0.662(1)
C(n 34)	0.771 8(6)	0.601 1(8)	1.114(2)	0.832 7(4)	0.503 6(6)	0.521(1)
C(n 35)	0.772 2(5)	0.648 1(6)	0.999(2)	0.795 0(4)	0.460 9(5)	0.436(1)
C(n 36)	0.722 2(5)	0.654 7(5)	0.910(1)	0.742 6(4)	0.432 6(5)	0.494 6(9)
O(1)	0.513 9(3)	0.460 7(3)	0.868 4(6)			
O(2)	0.437 3(3)	0.463 8(8)	0.720(1)			
C(1)	0.461 5(5)	0.452 7(7)	0.835(1)			
C(2)	0.422 6(6)	0.429(1)	0.961(2)			
F(1)	0.446 4(5)	0.402 2(8)	1.075(1)			
F(2)	0.387 5(5)	0.377 7(7)	0.926(1)			
F(3)	0.386 5(7)	0.475 3(7)	1.002(2)			
O(11)	0.523 6(3)	0.508 6(6)	0.550 6(7)			
C(11)	0.520 3(9)	0.522(2)	0.408(2)			
C(12a) ^b	0.508(2)	0.527(2)	0.295(4)			
C(12b) ^b	0.558(1)	0.510(2)	0.327(3)			

^a Defines origin. ^b Population 0.5.

Table 6 Relevant geometric parameters (lengths in Å, angles in °) for bidentate compounds [Cu(PPh₃)₂(O₂CR)]

R =	H ref. 5	Me ref. 6	CH ₂ F 1	CHF ₂ 2a	CF ₃ 3a
Cu-P(1)	2.247(1)	2.240(3)	2.232(3)	2.234(2)	2.235(2)
Cu-P(2)	2.247(1)*	2.233(2)	2.222(3)	2.219(2)	2.228(2)
Cu-O(1)	2.226(3)	2.162(5)	2.144(6)	2.118(4)	2.113(4)
Cu-O(2)	2.226(3)*	2.257(7)	2.363(7)	2.465(6)	2.545(5)
C(1)-O(1)	1.224(4)	1.26(1)	1.27(1)	1.24(1)	1.228(7)
C(1)-O(2)	1.224(4)*	1.28(1)	1.22(1)	1.228(7)	1.219(6)
C(1)-C(2)	—	1.52(1)	1.60(2)	1.51(1)	1.542(8)
P(1)-Cu-P(2)	128.3(4)	133.4(1)	135.0(1)	135.8(1)	136.7(1)
P(1)-Cu-O(1)	114.6(1)*	107.5(2)	112.8(2)	111.6(2)	112.6(1)
P(1)-Cu-O(2)	110.3(1)	116.4(2)	101.7(2)	99.3(2)	98.6(1)
P(2)-Cu-O(1)	114.6(1)	112.4(2)	106.8(2)	109.3(2)	108.3(1)
P(2)-Cu-O(2)	110.3(1)*	104.3(2)	117.0(2)	117.0(2)	116.3(1)
O(1)-Cu-O(2)	58.05(8)	59.4(2)	58.4(2)	56.7(2)	55.4(1)
O(1)-C-O(2)	124.0(5)	121.8(8)	125(1)	125.6(7)	127.8(5)

* Symmetry related.

**Fig. 4** Plot of the average Cu-O distance for [Cu(PPh₃)₂(O₂CC-H_{3-n}F_n)] complexes, *n* = 0-3, as a function of p*K*_a**Scheme 1**

carbonyl-stretching frequency in the infrared spectra measured in Nujol mulls are consistent with increasing strength of the C-O(2) bond with values increasing smoothly from 1566 cm⁻¹ for the acetate,¹⁴ 1595 cm⁻¹ for the fluoroacetate, 1636 cm⁻¹ for the difluoroacetate to 1666 cm⁻¹ for the trifluoroacetate. Overall, as the complexes undergo the transition towards monodentate co-ordination, the average Cu-O bond length increases and, as for the P-Cu-P angle, empirical correlation with p*K*_a (Fig. 4) shows a linear relationship (2) with *R*² = 0.965.

$$\langle \text{Cu-O} \rangle = 2.33 - 0.027\text{p}K_a \quad (2)$$

It is interesting to compare the results for these complexes with those reported for the formate complex.⁵ The acid strength of formic acid is between that of acetic and monofluoroacetic acid with a p*K*_a value of 3.75.⁷ From equation (2) the average Cu-O bond length is predicted to be 2.228 Å which is in good

Table 7 Relevant geometric parameters (lengths in Å, angles in °) for [Cu(PPh₃)₂(O₂CR)L] complexes with monodentate carboxylate anions

R =	CHF ₂ 2b	CF ₃ 3b	C ₆ H ₄ NO ₂ -4 L = H ₂ O, ref. 12
Cu-P(1)	2.248(3)	2.248(2)	2.252(1)
Cu-P(2)	2.236(3)	2.240(2)	2.246(1)
Cu-O(1)	2.074(8)	2.104(6)	2.067(3)
Cu...O(2)	3.308(10)	3.353(8)	3.318(3)
Cu-O(11)	2.169(8)	2.160(6)	2.227(3)
C(1)-O(1)	1.17(2)	1.21(1)	1.249(5)
C(1)-O(2)	1.29(2)	1.19(1)	1.243(5)
C(1)-C(2)	1.50(3)	1.49(2)	1.518(6)
P(1)-Cu-P(2)	120.5(1)	120.8(1)	126.9(1)
P(1)-Cu-O(1)	107.7(2)	107.7(2)	n.a.
P(1)-Cu-O(2)	107.7(4)	107.7(3)	n.a.
P(2)-Cu-O(1)	109.9(2)	109.1(2)	n.a.
P(2)-Cu-O(2)	116.9(3)	117.3(2)	n.a.
O(1)-Cu-O(11)	89.4(2)	89.4(2)	93.7(1)
O(1)-C-O(2)	126(1)	129(1)	n.a.

n.a. = Not available.

agreement with the observed value of 2.226(3) Å. However, from equation (1), the P-Cu-P angle is predicted to be 134° or nearly 6° greater than the observed value of 128.3(4)°, suggesting that considerable differences exist in the nature and extent of the interactions between the formate and acetate/fluoroacetate anions and the [Cu(PPh₃)₂]⁺ cation. In addition, the C2/c crystallographic lattice adopted by the formate is a common isomorphous one for small anions, being found previously for the nitrate,¹⁹ tetrahydroborate²⁰ and iodide⁴ complexes and it might be reasonable to expect that the lattice-packing interactions between the phenyl substituents may play a role in the determination of the structure of these complexes.

The structural results for the difluoro- and trifluoro-acetate complexes recrystallized from ethanol, **2b** and **3b**, show the two complexes to be isostructural. Unlike the above complexes, however, the carboxylate anions co-ordinate as mono- rather than bi-dentate ligands with Cu-O(1) distances of 2.074(8) and 2.104(6) Å and Cu...O(2) distances of 3.30(1) and 3.353(8) Å respectively (Table 7). The fourth copper co-ordination site is occupied by an ethanol molecule with Cu-O(11) distances of 2.169(8) and 2.160(6) Å providing, to our knowledge, the first structural characterization of any copper(I) species with co-ordinated ethanol. The molecular structure of the difluoro complex is shown in Fig. 2. Monodentate carboxylate co-

ordination has been reported for $[\text{Cu}(\text{PPh}_3)_2(\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2-4)(\text{H}_2\text{O})]$ with a molecule of water occupying the fourth co-ordination site¹² interestingly at an appreciably longer distance $[\text{Cu}-\text{O} \ 2.227(3) \text{ \AA}]$ despite the $\text{Cu}-\text{O}$ carboxylate distance being comparable with that of the difluoroacetate **2b**. As for **2a** and **3a**, the PPh_3 ligands adopt quasi *3* and *m* conformations with $\text{Cu}-\text{P}(1)-\text{C}(1n1)-\text{C}(1n2)$ 42, 33, 51 and $-43, -33, -52^\circ$ and $\text{Cu}-\text{P}(2)-\text{C}(2n1)-\text{C}(2n2)$ 4, $-35, -75$ and $-4, 35, 75^\circ$ for **2b** and **3b** respectively. The $\text{Cu}-\text{P}(1)$ distances remain slightly longer than the $\text{Cu}-\text{P}(2)$, as for ligands of similar conformation in the unsolvated complexes. The $\text{P}-\text{Cu}-\text{P}$ angles decrease to $120.5(1)$ and $120.8(1)^\circ$ in these complexes, reflecting the increase in steric crowding resulting from the increase in the number of co-ordinated ligands from three to four. For comparison, the $\text{P}-\text{Cu}-\text{P}$ angles in the series of complexes $[\text{Cu}(\text{PPh}_3)_2(\text{py})\text{X}]$ (py = pyridine) are $126, 124$ and 126° for $\text{X} = \text{Cl}, \text{Br}$ and I respectively.²¹ It is interesting, however, that despite the strength of the ethanol co-ordination, recrystallization of the monofluoroacetate from ethanol yielded only the non-solvated complex.

Acknowledgements

We acknowledge support of this work by grants from the Australian Research Grants Scheme. We thank Ms. Michelle Peake for assistance with the electrochemistry experiments.

References

- 1 F. H. Jardine, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 115.
- 2 B. J. Hathaway, *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 5, p. 533.
- 3 S. J. Lippard and G. J. Palenik, *Inorg. Chem.*, 1971, **10**, 1322.
- 4 G. A. Bowmaker, J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1987, 1089.
- 5 N. Marsich, A. Camus and G. Nardin, *J. Organomet. Chem.*, 1982, **239**, 429.
- 6 M. G. B. Drew, A. H. bin Othman, D. A. Edwards and R. Richards, *Acta Crystallogr., Sect. B*, 1975, **31**, 2695.
- 7 J. J. Christensen, L. D. Hansen and R. M. Izatt, *Handbook of Proton Ionization Heats*, Wiley, New York, 1976.
- 8 M. Khan, C. Oldham and D. G. Tuck, *Can. J. Chem.*, 1981, **59**, 2714.
- 9 M. D. Dines, *Inorg. Chem.*, 1972, **11**, 2949.
- 10 J. A. Ibers and W. C. Hamilton (Editors), *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol 4.
- 11 S. R. Hall, H. D. Flack and J. M. Stewart, *XTAL 3.2 Reference Manual*, Universities of Western Australia, Geneva and Maryland, 1992.
- 12 M. A. Cabras, L. Naldini, M. A. Zoroddu, F. Cariati, F. Demartin, N. Masciocchi and M. Sansoni, *Inorg. Chim. Acta*, 1985, **104**, L19.
- 13 D. A. Edwards and R. Richards, *J. Chem. Soc., Dalton Trans.*, 1975, 637.
- 14 B. Hammond, F. H. Jardine and A. G. Vohra, *J. Inorg. Nucl. Chem.*, 1971, **33**, 1017.
- 15 F. Cariati, L. Naldini, A. Panzanelli, F. Demartin and M. Manessero, *Inorg. Chim. Acta*, 1983, **69**, 117.
- 16 C. Bianchini, C. A. Ghilardi, A. Moli, S. Midollini and A. Orlandini, *Inorg. Chem.*, 1985, **24**, 924.
- 17 A. Miyashita and A. Yamamoto, *J. Organomet. Chem.*, 1976, **113**, 187.
- 18 B. Beguin, B. Denise and R. P. A. Sneed, *J. Organomet. Chem.*, 1981, **208**, C18.
- 19 G. G. Messmer and G. J. Palenik, *Inorg. Chem.*, 1969, **8**, 2751.
- 20 S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1967, **6**, 2223.
- 21 L. M. Engelhardt, P. C. Healy, J. D. Kildea and A. H. White, *Aust. J. Chem.*, 1989, **42**, 895.

Received 13th September 1993; Paper 3/054651