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Synthesis and coordination chemistry of perfluoroalkyl-derivatised β-diketonates

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Dedicated to Professor Tatlow on the occasion of his 80th birthday.

Abstract

A series of fluorinated β-diketones, $R_fC(O)CH_2C(O)R_{f'}$ ($R_f = C_6F_{13}$, $R_{f'} = CF_3$; $R_f = R_{f'} = C_6F_{13}$, C_7F_{15}), have been prepared in reasonable yields by a two-step synthesis. On reaction with appropriate metal substrates, deprotonation and concurrent coordination of the perfluoroalkyl-derivatised β-diketonate ligands affords a range of fluorous metal complexes which have been characterised by elemental analysis, mass spectrometry, IR and NMR spectroscopies. The structures of $[Cu(L–L)_2(H_2O)_2]$ {L–L = $CF_3C(O)CHC(O)C_6F_{13}$, $C_6F_{13}C(O)CHC(O)C_6F_{13}$} and $[Cu(PPh_3)_2\{C_7F_{15}C(O)CHC(O)C_7F_{15}\}]$ have been determined by single-crystal X-ray diffraction.

Keywords: Fluorous; β-Diketonate ligands; Coordination chemistry; X-ray structure

1. Introduction

The coordination chemistry of fluorinated β-diketonate ligands, particularly the 1,1,1,5,5,5-hexafluoropentanedionato or hexafluoroacac (hfacac) ligand, has been extensively investigated for many years [1], with interest stemming from the potential application of the volatile homoleptic transition metal hexafluoroacac complexes in metal organic chemical vapour deposition. More recently, Carlini and coworkers [2] have investigated the activity and selectivity of $[Ni\{C_3F_7C(O)CHC(O)C_3F_7\}_2{\cdot}2DMF]$ in the dimerisation of propylene to 2,3-dimethylbutenes and Knochel and coworkers [3,4] have briefly introduced the application of β-diketonate ligands with long perfluoroalkyl (C_7F_{15}) groups for metal catalysed oxidations under fluorous biphase conditions. The fluorous biphase approach is an attractive solution to the catalyst/product separation issues in homogeneous catalysis, as it exploits the physical properties of many perfluorinated and conventional organic solvent mixtures, and reports on a broad spectrum of catalytic processes have appeared [5–9]. Interestingly, the first β-diketones containing long perfluoroalkyl substituents were synthesised by Tatlow and coworkers in 1971 [10], but no coordination chemistry or applications in catalysis were reported at that time. We have a long-standing interest in the coordination properties of fluorine containing ligands and have investigated a broad range of substituted phosphorus(III) ligands [11–17]. Here, we describe the synthesis of two new fluorinated diketones, alongside $C_7F_{15}C(O)CH_2C(O)C_7F_{15}$ [10], and the coordination chemistry of these pre-ligands with a range of late transition metals, including the first crystal structural characterisations of coordination compounds incorporating β-diketonate ligands with long perfluoroalkyl substituents.

2. Results and discussion

The reaction of the commercially available perfluoroalkylated carboxylic acids with three equivalents of MeMgBr readily affords the related methyl ketones [18]. Further reaction with the same or a different perfluoroalkylated ester in the presence of base gives the desired β-diketones in moderate yields (Scheme 1). These diketones have been probed by a range of spectroscopic techniques, including highly characteristic ^{19}F NMR spectra which reveal either one (**2**,**3**) or two (**1**) CF_3 signals and four or five multiplets assigned as CF_2 resonances. ^1H NMR spectroscopic studies indicates that the ketone-enol tautomerisation is highly solvent dependent; the enol proton appearing as a broad,

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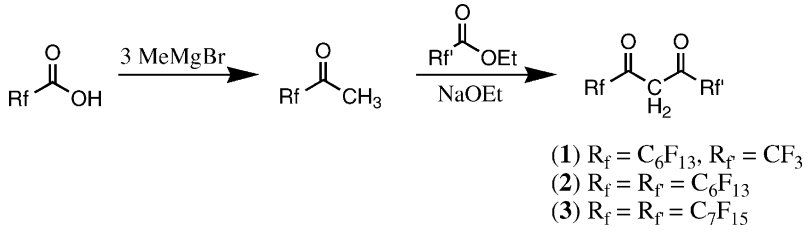


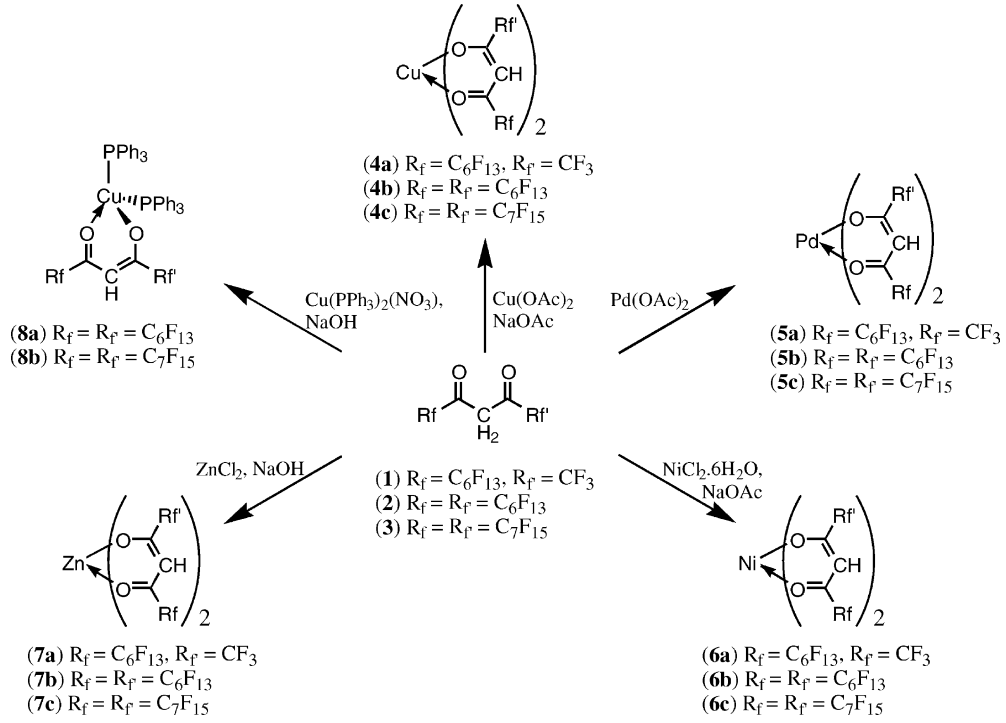
Scheme 1.

concentration dependent, singlet around 9 ppm in $CDCl_3$ [19].

Treatment of the β-diketones with representative metal(II) salts readily affords the perfluoroalkylated analogues of well established metal acac complexes (Scheme 2) which have been characterised by elemental analysis and a range of spectroscopic techniques. However, the homoleptic complexes containing Tatlow and Knochel's perfluoroheptyl β-diketonate were difficult to characterise since they are insoluble in most common organic solvents and are only slightly soluble in ethereal solvents. The square planar palladium(II) complex with the unsymmetrical ligand (**5a**) adopts a 1:1 mixture of *cis*-/*trans*-isomers in solution with two singlets for the α-CF_3 groups, two triplets for the terminal CF_3 groups and two overlapping triplets for the α-CF_2 groups in the ^{19}F NMR spectrum. The perfluoroalkyl groups in the zinc(II) complexes (**7a–c**) are equivalent and unremarkable, indicating that these adopt regular tetrahedral geometries and are unsolvated. This is in direct contrast to the ^{19}F NMR spectroscopic studies on the closely related tetradecafluorononane-4,5-dionato-zinc(II) complexes [20] that reveal second order spectra arising from strongly coupled diastereotopic α-CF_2 fluorine atoms which indicate a *cis*-octahedral structure for the hydrated [Zn(L–L)$_2$(H$_2$O)$_2$].

Single crystal structure determinations of metal complexes with fluorous ponytails are still relatively rare in the literature. Here, we have crystallographically characterised bis aqua adducts of two of the homoleptic β-diketonate copper compounds (**4a**) and (**4b**) containing two or four C_6F_{13} units, respectively (Figs. 1 and 2, Table 1) and the heteroleptic copper compound (**8b**) which contains two C_7F_{15} units (Fig. 3, Table 2). The hydrated complexes of (**4a**) and (**4b**) were generated during the slow crystallisations from ether solutions of the complexes over a layer of chloroform. Full refinement of all three structures was complicated by considerable disorder in the perfluoroalkyl units and this is discussed later.

As expected for d^9 copper(II) metals, the coordination around the metal centres (which lie on crystallographic centres of symmetry) show tetragonally distorted octahedral arrangements of the six oxygen donors with the Cu–O bond



Scheme 2.

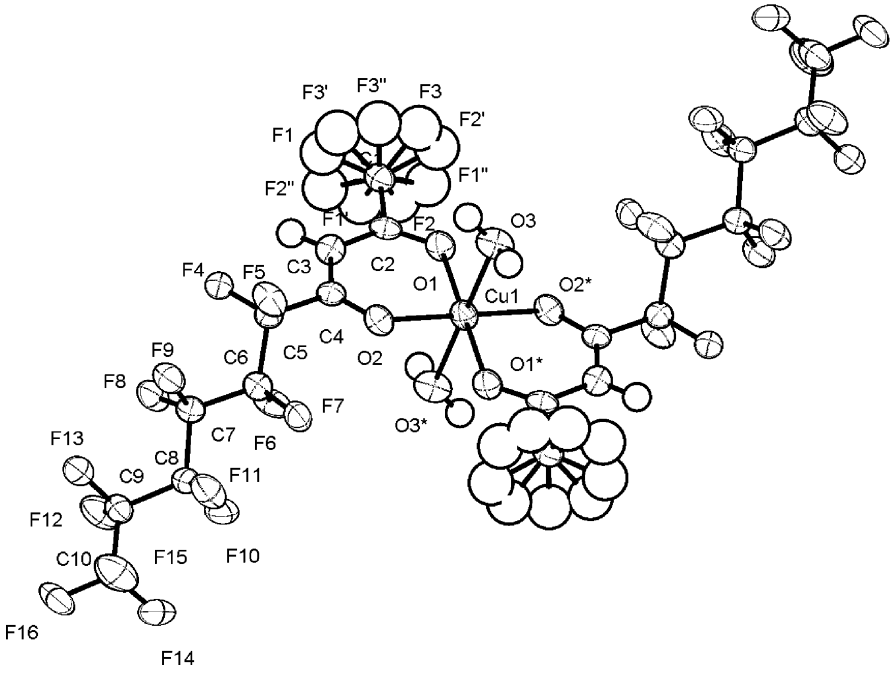


Fig. 1. Molecular structure of $[Cu\{CF_3C(O)CHC(O)C_6F_{13}\}_2(H_2O)_2]$ showing the atom labelling scheme with 50% probability ellipsoids. H atoms are shown as spheres of arbitrary radii. Primed atoms indicate disorder of the CF_3 group over three sites. The molecule is located on an inversion centre, (*) atoms are generated by symmetry $(1 - x, -y, -z)$.

distances for the more weakly bound axial water ligands approximately 20% longer than those for the β-diketonate ligands. The metal coordination environments for the two complexes are both effectively identical to that observed in the closely related $[Cu(tdf)_2(H_2O)_2]$ {tdf = tetradecafluorononane-4,6-dionato; $C_3F_7C(O)CHC(O)C_3F_7$} [20]. For the symmetrical copper complex with the pentadecanedianato ligands, both C_6F_{13} ponytails exhibit considerable disorder beyond the α-CF_2 groups. Although we have observed the same sort of disorder in other metal complexes of perfluoroalkylated ligands, the quality of the data has allowed us, for the first time, to be able to model static disorder indicating the random distribution of a series of arrangements of the ponytails throughout the crystal lattice rather than dynamic

Table 1
A direct comparison between selected bond distances (Å) and angles (°) for $[Cu\{CF_3C(O)CHC(O)C_6F_{13}\}_2(H_2O)_2]$ and $[Cu\{C_6F_{13}C(O)CHC(O)C_6F_{13}\}_2(H_2O)_2]$

$[Cu\{CF_3C(O)CHC(O)C_6F_{13}\}_2(H_2O)_2]$		$[Cu\{C_6F_{13}C(O)CHC(O)C_6F_{13}\}_2(H_2O)_2]$	
Cu–O(1)	1.942(3)	Cu–O(1)	1.9567(16)
Cu–O(2)	1.939(3)	Cu–O(2)	1.9485(16)
Cu–O(3)	2.334(3)	Cu–O(3)	2.369(2)
O(1)–C(2)	1.234(6)	O(1)–C(2)	1.257(3)
O(2)–C(4)	1.262(5)	O(2)–C(9)	1.256(3)
C(2)–C(3)	1.387(7)	C(1)–C(2)	1.382(3)
C(3)–C(4)	1.369(7)	C(1)–C(9)	1.389(3)
C(1)–C(2)	1.506(7)	C(2)–C(3)	1.544(3)
C(4)–C(5)	1.528(6)	C(9)–C(10)	1.539(3)
av. C–F	1.333	av. C–F	1.375
O(1)–Cu–O(2)	92.02(13)	O(1)–Cu–O(2)	92.38(7)
O(1)–Cu–O(3)	90.93(13)	O(1)–Cu–O(3)	88.14(7)
O(2)–Cu–O(3)	91.67(14)	O(2)–Cu–O(3)	90.08(7)
O(1)–Cu–O(2′)	87.98(13)	O(1)–Cu–O(2′)	87.62(7)
C(2)–O(1)–Cu	124.9(3)	C(2)–O(1)–Cu	124.54(16)
C(4)–O(2)–Cu	124.0(3)	C(9)–O(2)–Cu	124.68(16)
O(3)–H(3B)···O(2)	2.241 $(1 - x, 1 - y, -z)$	O(3)–H(3A)···O(2)	2.478 $(x, 1 + y, z)$
O(3)–H(3C)···O(1)	2.392 $(x, 1 + y, z)$		

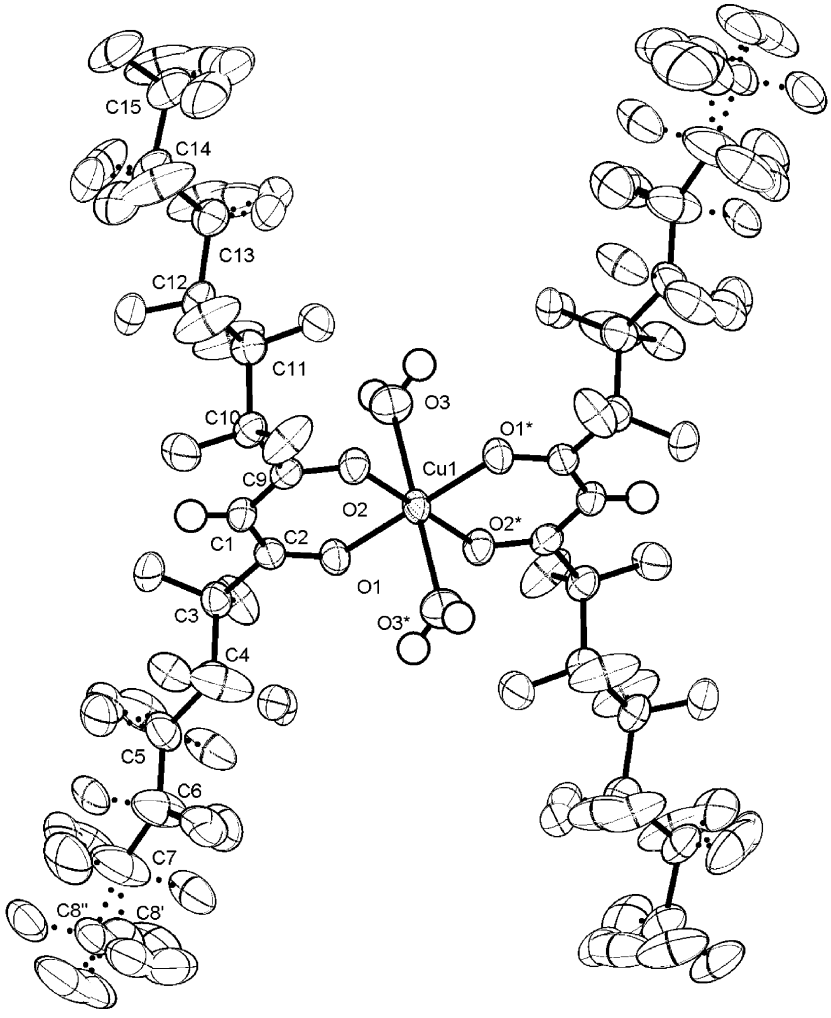


Fig. 2. Molecular structure of $[Cu\{C_6F_{13}C(O)CHC(O)C_6F_{13}\}_2(H_2O)_2]$ showing the atom labelling scheme with 50% probability ellipsoids. H atoms are shown as spheres of arbitrary radii. Primed atoms and dashed bonds indicate disorder. The molecule is located on an inversion centre, (*) atoms are generated by symmetry $(1-x, -y, 1-z)$.

thermal liberation of the CF_2 units. We have modelled the disorder of the fluorine atoms on C(4), C(5), C(6), C(7), C(13), C(14) and C(15) over two sites with 50:50 occupancy, and also the terminal CF_3 unit at C(8) {together with F(11), F(12) and F(13)} also over two sites with 50:50 occupancy. For the unsymmetrical copper complex with the decanedionato ligands, the C_6F_{13} ponytails exhibit no disorder and adopt the regular linear arrangement with torsion angles along the carbon backbone between 160 and 170°, but the α-CF_3 group is disordered across three sites (with 50:30:20 occupancies) in a well-recognised ''propeller'' pattern. For both the structures, extended views indicate that the perfluoroalkyl substituents line up in ''fluorous domains'' but, in view of the degree of disorder, the accurate identification of genuine short non-bonded F···F contacts in these structure determinations is not possible. The crystal packing diagram of $[Cu\{CF_3C(O)CHC(O)C_6F_{13}\}_2(H_2O)_2]$ also reveals that its molecules are stacked down the *b*-axis with adjacent molecules linked by four intermolecular hydrogen bonds from the water hydrogen atoms to the oxygen atoms of the perfluoroalkylated β-diketonates. A similar effect is also observed in the crystal packing diagram of $[Cu\{C_6F_{13}C(O)CHC(O)C_6F_{13}\}_2(H_2O)_2]$ but only two hydrogen bonds link the adjacent molecules.

Table 2
Selected bond distances (Å) and angles (°) for $[Cu(PPh_3)_2\{C_7F_{15}C(O)CHC(O)C_7F_{15}\}]$ (**8b**)

$[Cu(PPh_3)_2\{C_7F_{15}C(O)CHC(O)C_7F_{15}\}]$			
Cu–O(1)	2.119(2)	O(1)–Cu–O(2)	86.73(8)
Cu–O(2)	2.118(2)	O(1)–Cu–P(1)	109.68(6)
Cu–P(1)	2.2390(9)	O(2)–Cu–P(1)	106.70(7)
Cu–P(2)	2.2480(9)	O(1)–Cu–P(2)	116.01(6)
O(1)–C(1)	1.247(4)	O(2)–Cu–P(2)	98.86(7)
O(2)–C(3)	1.240(4)	P(1)–Cu–P(2)	128.34(3)
C(1)–C(2)	1.399(5)	C(1)–O(1)–Cu	125.3(2)
C(2)–C(3)	1.391(5)	C(3)–O(2)–Cu	126.1(2)
C(1)–C(4)	1.546(4)		
C(3)–C(11)	1.547(5)		
av. C–F	1.346		

The structure of $[Cu(PPh_3)_2\{C_7F_{15}C(O)CHC(O)C_7F_{15}\}]$ (Fig. 3) shows that this compound adopts a distorted tetrahedral geometry. The structure is not as distorted as $[Cu(PCy_3)_2(hfacac)]$ which contains the bulky tricyclohexylphosphine ligand [21], but has a similar P–Cu–P bond angle to $[Cu(PPh_3)_2(tfac)]$ (tfac = trifluoroacetylacetone; 127°) [22]. The Cu–P bond lengths are virtually the same as those in both $[Cu(PPh_3)_2(ttfac)]$ (ttfac = 2-thenoyltrifluoroacetone) [23] and $[Cu(PCy_3)_2(hfacac)]$, and although the Cu–O bond length is nearly identical to $[Cu(PPh_3)_2(hfacac)]$ (2.120 Å), the full structural data for this compound are not available [24]. Similar to $[Cu\{C_6F_{13}C(O)CHC(O)C_6F_{13}\}_2(H_2O)_2]$, one of the C_7F_{15} chains exhibits considerable disorder beyond the α-CF_2 group and this static disorder was modelled for the fluorine atoms on C(12), C(13) and C(15) over two sites with 50:50 occupancy and the central carbon atom C(14) which was similarly modelled over two sites with 50:50 occupancy. However, this disorder prevented the identification of genuine short non-bonded F···F contacts, even although fluorous layers are observed in the solid-state packing diagram demonstrating the preference for the fluorous ponytails to align.

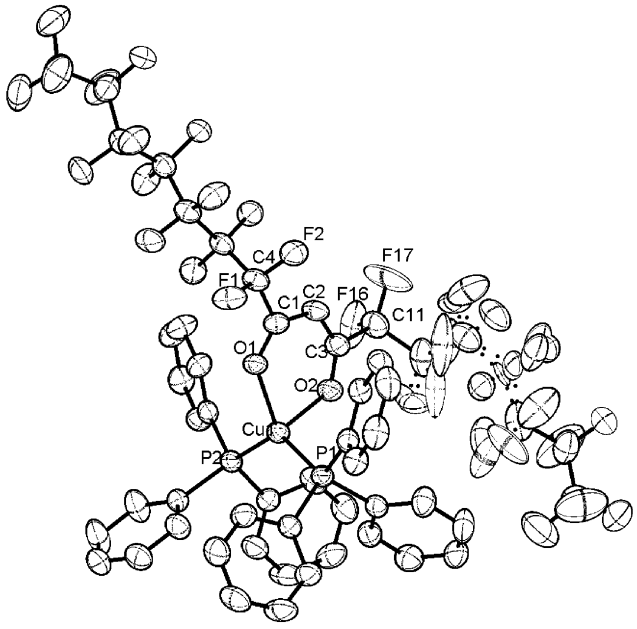


Fig. 3. Molecular structure of $[Cu(PPh_3)_2\{C_7F_{15}C(O)CHC(O)C_7F_{15}\}]$ showing part of the atom label scheme with 50% probability ellipsoids. H atoms are omitted for clarity. One of the C_7F_{15} chains shows disorder.

3. Conclusions

Perfluoroalkylated analogues of 2,4-pentanedione (hfacac), readily prepared by a two step reaction sequence, undergo straightforward reactions with metal salts to generate stable perfluoroalkyl-β-diketonate metal complexes. X-ray structural determinations reveal tetragonal distorted octahedrally coordinated metal centres for $[Cu(L–L)_2(H_2O)_2]$ {L–L = $CF_3C(O)CHC(O)C_6F_{13}$, $C_6F_{13}C(O)CHC(O)C_6F_{13}$} and distorted tetrahedral geometry for $[Cu(PPh_3)_2\{C_7F_{15}C(O)CHC(O)C_7F_{15}\}]$. All the three structures possess disordered perfluoroalkyl substituents and the disorder has been modelled for the first time.

4. Experimental

4.1. General experimental procedures

Proton, ^{13}C and ^{19}F NMR spectroscopies were carried out on a Bruker ARX250 spectrometer at 250.13, 62.90 and 235.34 MHz. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ^1H and ^{13}C NMR spectra were referenced to external $SiMe_4$ and ^{19}F NMR spectra to external $CFCl_3$. The infrared spectra were recorded on a Digilab FTS40 Fourier transform spectrometer at 4 cm^{-1} resolution for compounds as Nujol mulls held between KBr discs. Elemental analyses were performed either by Butterworth Laboratories Ltd. or the Elemental Analysis Service at the University of North London. Mass spectra were recorded on a Kratos concept 1H mass spectrometer.

Dichloromethane, dried by heating to reflux over CaH_2, diethyl ether and THF, dried by refluxing over sodium metal, were distilled under nitrogen, stored in closed ampoules over molecular sieves and freezed/pumped/thawed three times to remove all the dissolved gases before use. The $[Cu(PPh_3)_2(NO_3)]$ was prepared by the literature route [25] whilst dry methanol (Aldrich), methyl magnesium bromide (3 mol dm^{-3} in diethyl ether, Aldrich) and trifluoroacetic, perfluoroheptanoic and perfluorooctanoic acids and their ethyl esters (Fluorochem) were used as supplied.

4.1.1. 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-octan-2-one [$C_6F_{13}COCH_3$]

A solution of perfluoroheptanoic acid (25 g, 0.069 mol) in diethyl ether (23 cm^3) was added dropwise over 1 h to methyl magnesium bromide (3.0 mol dm^{-3} solution; 69 cm^3, 0.206 mol) in diethyl ether (36 cm^3) and the reaction mixture refluxed for 2 h. On cooling, the reaction was quenched with ice (62.5 g) followed by hydrochloric acid (6 mol dm^{-3}, 63 cm^3), the aqueous layer extracted with diethyl ether (3 × 30 cm^3) and the organic fractions combined. The resulting yellow solution was washed with a saturated sodium chloride solution, dried over magnesium sulfate and the solvent removed in vacuo to leave a pale yellow slightly viscous liquid. The product was isolated from the tertiary alcohol ($C_6F_{13}C(CH_3)_2OH$) by distillation under vacuum (23.1 mmHg, 46–49 °C) to give the product as a clear colourless liquid. Yield 14.75 g, 59%. ^1H NMR ($CDCl_3$): δ 2.45 [3H, s, CH_3]. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −81.44 [3F, t, $^4J_{F-F}$ = 9.3 Hz, CF_3], −120.90 [2F, t, $^4J_{F-F}$ = 12.1 Hz, α-CF_2],

−122.90 [2F, m, CF_2], −122.16 [2F, m, CF_2], −124.09 [2F, m, CF_2], −126.74 [2F, m, CF_2]. ^{13}C NMR ($CDCl_3$): δ 25.36 [s, CH_3], 105–120 [m's, C_6F_{13}], 191.32 [t, $^2J_{C-F} = 27.1$ Hz, C=O]. MS (ES) *m/z*: 362 [M^+], 361 [M–H]$^+$, 319 [C_6F_{13}]$^+$ (100%), 169 [C_3F_7]$^+$. IR: 1746 cm^{-1} ν(C=O). Analytically calculated for $C_8H_3OF_{13}$: C, 26.5; H, 0.8; F, 68.2. Found: C, 26.8; H, 0.9; F, 68.7.

4.1.2. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-nonan-2-one [$C_7F_{15}COCH_3$]

3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-nonan-2-one [$C_7F_{15}COCH_3$] was prepared similarly as a clear colourless liquid (20 mmHg, 55–56 °C) in 52% yield. ^1H NMR ($CDCl_3$): δ 2.4 [3H, s, CH_3]. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −81.41 [3F, t, $^4J_{F-F} = 9.3$ Hz, CF_3], −120.86 [2F, t, $^4J_{F-F} = 12.1$ Hz, α-CF_2], −121.94 [2F, m, CF_2], −122.56 [2F, m, CF_2], −122.80 [2F, m, CF_2], −122.84 [2F, m, CF_2], −126.69 [2F, m, CF_2]. MS (ES) *m/z*: 413 [MH]$^+$, 393 [M–F]$^+$, 333 [M–2F]$^+$ (100%), 150 [C_3F_6]$^+$, 69 [CF_3]$^+$. IR: 1765 cm^{-1} ν(C=O).

*4.1.3. 1,1,1,5,5,6,6,7,7,8,8,9,9,10,10,10-Hexadecafluorodecan-2,4-dione [$CF_3C(O)CH_2C(O)C_6F_{13}$] (**1**)*

A solution of ethyl trifluoroacetate (1.64 cm^3, 0.0138 mol) in diethyl ether (5 cm^3) was added dropwise to a stirred solution of sodium ethoxide (1.03 g, 0.0152 mol) in diethyl ether (20 cm^3) at 0 °C, followed by a solution of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-one (5 g, 0.0138 mol) in diethyl ether (5 cm^3) over 1 h. The reaction was maintained at 0 °C for 12 h, allowed to warm to room temperature and stirred for a further 48 h. The mixture was hydrolysed with glacial ethanoic acid (1 g, 0.0166 mol) in water (5 cm^3), before the addition of copper(II) acetate (3.94 g, 0.0197 mol) in water (22 cm^3), which generated an iridescent green colour. The ethereal layer was removed in vacuo, to leave the insoluble green copper complex in the aqueous layer. The crystalline solid was filtered, washed with ice-cold water and light petroleum (40–60 °C), and dried under vacuum. This copper bis(1,1,1,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-decane-2,4-dionate) complex was then dissolved in diethyl ether and hydrogen sulphide gas was passed over the stirred solution for 25 min, during this time the solution turned from green to dark black (CuS). The vessel was then flushed with nitrogen for 1 h to remove the excess hydrogen sulphide. Evaporation of the diethyl ether followed by vacuum distillation (11.25 mmHg, 48–50 °C) afforded the products as a pale yellow viscous oil. Yield 2.0 g, 32%. ^1H NMR ($CDCl_3$): δ 6.25 [1H, s, C=C–H], 9.95 [1H, br s, C–OH]. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −76.93 [3F, s, α-CF_3], −81.29 [3F, m, terminal CF_3], −119.64 [2F, t, $^4J_{F-F} = 11.3$ Hz, α-CF_2], −121.26 [2F, m, CF_2], −122.73 [2F, m, CF_2], −123.36 [2F, m, CF_2], −126.76 [2F, m, CF_2]. ^{13}C NMR ($CDCl_3$): δ 95.51 [s, C_3], 105 – 121 [m's, C_6F_{13}], 117.45 [q, $^1J_{C-F} = 281.3$ Hz, CF_3], 175.83 [q, $^2J_{C-F} = 38.6$ Hz, C_2=O], 179.53 [t, $^2J_{C-F} = 27.9$ Hz, C_4=O]. MS (ES) *m/z*: 458 [M^+], 457 [M–H]$^+$ (100%), 439 [M–F]$^+$. IR: 1682 cm^{-1} ν(C=O), 1622 cm^{-1} ν(C–O–H). Analytically calculated for $C_{10}H_2O_2F_{16}$: C, 26.2; H, 0.4; F, 66.4. Found: C, 25.9; H, 0.5; F, 66.4.

*4.1.4. 1,1,1,2,2,3,3,4,4,5,5,6,6,10,10,11,11,12,12,13,13,14,14,15,15,15-Hexacosafluoro-pentadecane-7,9-dione [$C_6F_{13}C(O)CH_2C(O)C_6F_{13}$] (**2**)*

1,1,1,2,2,3,3,4,4,5,5,6,6,10,10,11,11,12,12,13,13,14,14,15,15,15-Hexacosafluoro-pentadecane-7,9-dione [$C_6F_{13}C(O)CH_2C(O)C_6F_{13}$] (**2**) was prepared similarly as a colourless viscous oil (15 mmHg, 52–55 °C) in 74% yield from ethyl perfluoroheptanoate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-one. ^1H NMR ($CDCl_3$): δ 6.45 [1H, s, C=C–H], 9.2 [1H, br s, C–OH]. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −81.28 [3F, t, $^4J_{F-F} = 9.6$ Hz, CF_3], −120.30 [2F, t, $^4J_{F-F} = 13.4$ Hz, α-CF_2], −122.07 [2F, m, CF_2], −122.75 [2F, m, CF_2], −123.21 [2F, m, CF_2], −126.55 [2F, m, CF_2]. ^{13}C NMR (d^6-acetone): δ 98.31 [s, C_8], 105 – 121 [m's, C_6F_{13}], 176.07 [t, $^2J_{C-F} = 27.2$ Hz, $C_{7,9}$]. MS (EI) *m/z*: 708 [M^+] (trace), 689 [M–F]$^+$, 389 [$CO(CH_2)COC_6F_{12}$]$^+$ (100%), 319 [C_6F_{13}]$^+$, 169 [C_3F_7]$^+$, 69 [CF_3]$^+$. IR: 1663 cm^{-1} ν(C=O), 1616 cm^{-1} ν(C–OH). Analytically calculated for $C_{15}H_2O_2F_{26}$: C, 25.4; H, 0.3. Found: C, 25.1; H, 0.4.

*4.1.5. 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-Triacontafluoro-heptadecane-8,10-dione [$C_7F_{15}C(O)CH_2C(O)C_7F_{15}$] (**3**)*

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-Triacontafluoro-heptadecane-8,10-dione [$C_7F_{15}C(O)CH_2C(O)C_7F_{15}$] (**3**) was prepared similarly as a cream solid (128–130 °C, 20 mmHg) in 30% yield from ethyl perfluorooctanoate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-nonan-2-one. ^1H NMR ($CDCl_3$): δ 6.45 [1H, s, C=C–H], ∼6–9 (position variable) [1H, br s, C–OH]. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −80.81 [3F, t, $^4J_{F-F} = 9.8$ Hz, CF_3], −120.10 [2F, t, $^4J_{F-F} = 12.2$ Hz, α-CF_2], −121.08 [2F, m, CF_2], −121.64 [2F, m, CF_2], −122.00 [2F, m, CF_2], −122.37 [2F, m, CF_2], −125.84 [2F, m, CF_2]. ^{13}C NMR ($CDCl_3$): δ 96.99 [s, C_9], 105 – 121 [m's, C_7F_{15}], 177.96 [t, $^2J_{C-F}$28.3 Hz, $C_{8,10}$]. MS (ES) *m/z*: 808 [M^+] (100%), 413 [$C_7F_{15}CO_2$]$^+$, 369 [C_7F_{15}]$^+$, 169 [C_3F_7]$^+$. IR: 1705, 1696, 1653, 1617 cm^{-1}.

*4.1.6. Copper bis(1,1,1,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-decane-2,4-dionate) [$Cu\{CF_3C(O)CHC(O)C_6F_{13}\}_2$] (**4a**)*

Copper(II) acetate (0.102 g, 5.11 × 10^{-4} mol) dissolved in methanol (10 cm^3) was added dropwise to a stirred solution of sodium acetate (0.084 g, 1.022 × 10^{-3} mol) and 1,1,1,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-decane-2,4-dione (**1**) (0.468 g, 1.022 × 10^{-3} mol) in methanol (10 cm^3) and the reaction mixture stirred for 1 h. The solvent was removed to yield the product as a pale green powdery solid, which was washed with hexane and dried in vacuo over silica gel. Yield 0.41 g, 82%. IR: 1636, 1527 cm^{-1}. Analytically calculated for $CuC_{20}H_2O_4F_{32}$: C, 24.5; H, 0.2. Found: C, 23.9; H, 0.3.

*4.1.7. Copper bis(1,1,1,2,2,3,3,4,4,5,5,6,6,10,10,11 ,11,12,12,13,13,14,14,15,15,15-hexacosafluoro-pentadecane-7,9-dionate) [Cu{$C_6F_{13}C(O)CHC(O)C_6F_{13}$}$_2$] (**4b**)*

Copper bis(1,1,1,2,2,3,3,4,4,5,5,6,6,10,10,11,11,12,12, 13,13,14,14,15,15,15-hexacosafluoro-pentadecane-7,9-dionate) [Cu{$C_6F_{13}C(O)CHC(O)C_6F_{13}$}$_2$] (**4b**) was prepared similarly, but precipitated out of solution and was filtered off as a fine green powder which was dried in vacuo over silica gel (88% yield). IR: 1635, 1526 cm^{-1}. Analytically calculated for $CuC_{30}H_2O_4F_{52}$: C, 24.4; H, 0.1. Found: C, 24.6; H, 0.2.

*4.1.8. Copper bis(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,11,11, 12,12,13,13,14,14,15,15,16,16,17,17,17-Triacontafluoro-heptadecane-8,10-dionate) [Cu{$C_7F_{15}C(O)CHC(O)C_7F_{15}$}$_2$] (**4c**)*

Copper bis(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,11,11,12,12,13, 13,14,14,15,15,16,16,17,17,17-Triacontafluoro-heptadecane-8,10-dionate) [Cu{$C_7F_{15}C(O)CHC(O)C_7F_{15}$}$_2$] (**4c**) was prepared similarly, but precipitated out of solution and was filtered off as a fine green powder which was dried in vacuo over silica gel (78% yield). IR: 1626, 1528 cm^{-1}. Analytically calculated for $CuC_{34}H_2O_4F_{60}$: C, 24.3; H, 0.1. Found: C, 22.4; H, 0.1.

*4.1.9. Palladium bis(1,1,1,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-decane-2,4-dionate) [Pd{$CF_3C(O)CHC(O)C_6F_{13}$}$_2$] (**5a**)*

Palladium acetate (0.0881 g, 3.92×10^{-4} mol) was added to a solution of 1,1,1,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-decane-2,4-dione (**1**) (0.359 g, 7.85×10^{-4} mol) in THF and dichloromethane (1:1, 30 cm^3) and the reaction mixture stirred for 1 h. The solvent was removed in vacuo to yield a thick, black tar from which the product was recrystallised as a powdery yellow solid from refluxing toluene and then dried in vacuo. Yield 0.21 g, 52%. ^{1}H NMR ($CDCl_3$): δ 6.4 [C–H]. ^{19}F{^{1}H} NMR ($CDCl_3$): δ −73.42 [3F, s, *cis*/*trans*-α-CF_3], −73.56 [3F, s, *cis*/*trans*-α-CF_3], −81.18 [3F, t, $^4J_{F-F} = 11.3$ Hz, *cis*/*trans*-terminal CF_3], −81.32 [3F, t, $^4J_{F-F} = 8.5$ Hz, *cis*/*trans*-terminal CF_3] −116.8 [2 × 2F, 2× overlapping triplets, $^4J_{F-F} = 12.7$ and 12.8 Hz, α-CF_2's], −121.91 [4F, m, CF_2], −122.29 [4F, m, CF_2], −123.30 [4F, m, CF_2], −126.60 [4F, m, CF_2]. MS (FAB) *m*/*z*: 1043 $[M + Na]^+$, 1020 $[M]^+$. IR: 1598 cm^{-1} ν(C=O). Analytically calculated for $PdC_{20}H_2O_4F_{32}$: C, 23.6; H, 0.2. Found: C, 22.9; H, 0.2.

*4.1.10. Palladium bis(1,1,1,2,2,3,3,4,4,5,5,6,6, 10,10,11,11,12,12,13,13,14,14,15,15,15-hexacosafluoro-pentadecane-7,9-dionate) [Pd{$C_6F_{13}C(O)CHC(O)C_6F_{13}$}$_2$] (**5b**)*

Palladium acetate (0.0591 g, 2.63×10^{-4} mol) was added to a solution of 1,1,1,2,2,3,3,4,4,5,5,6,6,10,10,-11,11,12, 12,13,13,14,14,15,15,15-hexacosafluoro-pentadecane-7,9-dione (**2**) (0.373 g, 5.26×10^{-4} mol) in THF and dichloromethane (1:1, 30 cm^3) and the reaction mixture stirred for 1 h when a powdery, yellow/orange solid was formed. The complex was isolated by filtration, washed with cold THF/dichloromethane and dried in vacuo. Yield 0.326 g, 81.5%. ^{1}H NMR ($CDCl_3$): δ 6.4 [C–H]. ^{19}F{^{1}H} NMR ($CDCl_3$): δ −81.31 [3F, t, $^4J_{F-F} = 9.8$ Hz, CF_3], −116.76 [2F, t, $^4J_{F-F} = 12.7$ Hz, α-CF_2], −121.81 [2F, m, CF_2], −122.25 [2F, m, CF_2], −123.28 [2F, m, CF_2], −126.64 [2F, m, CF_2]. MS (FAB) m/z: 1517 $[M]^+$. IR: 1595 cm^{-1} ν(C=O). Analytically calculated for $PdC_{30}H_2O_4F_{52}$: C, 23.7; H, 0.1. Found: C, 23.6; H, 0.3.

*4.1.11. Palladium bis(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7, 11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-triacontafluoro-heptadecane-8,10-dionate) [Pd{$C_7F_{15}C(O)CHC(O)C_7F_{15}$}$_2$] (**5c**)*

Palladium bis(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,11,11,12,12, 13,13,14,14,15,15,16,16,17,17,17-triacontafluoro-heptadecane-8,10-dionate) [Pd{$C_7F_{15}C(O)CHC(O)C_7F_{15}$}$_2$] (**5c**) was prepared similarly with 82% yield. ^{19}F{^{1}H} NMR (C_6D_6): δ −81.24 [3F, t, $^4J_{F-F} = 9.8$ Hz, CF_3], −117.17 [2F, m, CF_2], −121.52 [2F, m, CF_2], −121.97 [2F, m, CF_2], −122.40 [2F, m, CF_2], −123.13 [2F, m, CF_2], −126.57 [2F, m, CF_2]. MS (FAB) *m*/*z*: 1721 $[M]^+$. IR: 1594 cm^{-1} ν(C=O).

*4.1.12. Nickel bis(1,1,1,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-decane-2,4-dionate) [Ni{$CF_3C(O)CHC(O)C_6F_{13}$}$_2$] (**6a**)*

Nickel dichloride hexahydrate (0.0977 g, 4.11×10^{-4} mol) was dissolved in methanol (5 cm^3) and added to a stirred solution of sodium acetate (0.067 g, 8.22×10^{-4} mol) and 1,1,1,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-decane-2,4-dione (**1**) (0.377 g, 8.22×10^{-4} mol) in methanol (25 cm^3). The reaction mixture was stirred for 1 h and the solvent removed to give the product as a pale green powdery solid, which was washed with hexane and dried in vacuo over silica gel. Yield 0.34 g, 85%. MS (FAB) *m*/*z*: 974 $[MH]^+$. IR: 1639, 1527, 1495 cm^{-1}. Analytically calculated for $NiC_{20}H_2O_4F_{32}$: C, 24.7; H, 0.1. Found: C, 24.6; H, 0.2.

*4.1.13. Nickel bis(1,1,1,2,2,3,3,4,4,5,5,6,6,10,10,11,11,12, 12,13,13,14,14,15,15,15-hexacosafluoro-pentadecane-7,9-dionate) [Ni{$C_6F_{13}C(O)CHC(O)C_6F_{13}$}$_2$] (**6b**)*

Nickel bis(1,1,1,2,2,3,3,4,4,5,5,6,6,10,10,11,11,12,12,13, 13,14,14,15,15,15-hexacosafluoro-pentadecane-7,9-dionate) [Ni{$C_6F_{13}C(O)CHC(O)C_6F_{13}$}$_2$] (**6b**) was prepared similarly as an apple green solid in 92% yield. MS (FAB) *m*/*z*: 1472 $[M]^+$, 1153 $[M–C_6F_{13}]^+$, 319 $[C_6F_{13}]^+$. IR: 1638, 1528, 1490 cm^{-1}. Analytically calculated for $NiC_{30}H_2O_4F_{52}$: C, 24.5; H, 0.1. Found: C, 24.3; H, <0.3.

*4.1.14. Nickel bis(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,11,11, 12,12,13,13,14,14,15,15,16,16,17,17,17-triacontafluoro-heptadecane-8,10-dionate) [Ni{$C_7F_{15}C(O)CHC(O)C_7F_{15}$}$_2$] (**6c**)*

Nickel bis(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,11,11,12,12,13, 13,14,14,15,15,16,16,17,17,17-triacontafluoro-hepta-

decane-8,10-dionate) [Ni{$C_7F_{15}C(O)CHC(O)C_7F_{15}$}$_2$] (**6c**) was prepared similarly as an apple green solid in 94% yield. MS (FAB) *m/z*: 1672 $[M]^+$. IR: 1638, 1533, 1499 cm^{-1}.

4.1.15. Zinc bis(1,1,1,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-decane-2,4-dionate) [Zn{$CF_3C(O)CHC(O)C_6F_{13}$}$_2$] (**7a**)

Sodium hydroxide (0.033 g, 8.17×10^{-4} mol) was added to a stirred solution of 1,1,1,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-decane-2,4-dione (**1**) (0.374 g, 8.17×10^{-4} mol) in methanol (25 cm^3). On complete dissolution, zinc dichloride (0.0557 g, 4.083×10^{-4} mol) was added and the reaction mixture stirred for 2 h. After removing the solvent in vacuo the product was dried in vacuo over silica gel. Yield: 0.34 g, 85%. ^{1}H NMR ($CDCl_3$): δ 6.15 [s, C–H]. ^{19}F{^{1}H} NMR (C_6D_6): δ −76.24 [3F, s, α-CF_3], −81.77 [3F, t, $^4J_{F-F} = 10.0$ Hz, CF_3], −120.01 [2F, t, $^4J_{F-F} = 13.5$ Hz, α-CF_2], −122.07 [2F, m, CF_2], −122.52 [2F, m, CF_2], −123.28 [2F, m, CF_2], −126.74 [2F, m, CF_2]. MS (FAB) *m/z*: 979 $[M]^+$. IR: 1645 cm^{-1} ν(C=O).

4.1.16. Zinc bis(1,1,1,2,2,3,3,4,4,5,5,6,6,10,10,11,11,12,12,13,13,14,14,15,15,15-hexacosafluoro-pentadecane-7,9-dionate) [Zn{$C_6F_{13}C(O)CHC(O)C_6F_{13}$}$_2$] (**7b**)

Zinc bis(1,1,1,2,2,3,3,4,4,5,5,6,6,10,10,11,11,12,12,13,13,14,14,15,15,15-hexacosafluoro-pentadecane-7,9-dionate) [Zn{$C_6F_{13}C(O)CHC(O)C_6F_{13}$}$_2$] (**7b**) was prepared similarly. The white powdery product was filtered from the reaction mixture, washed with methanol and dried in vacuo over silica gel. Yield: 65%. ^{1}H NMR ($CDCl_3$): δ 5.3 [s, C–H].^{19}F{^{1}H} NMR (C_6D_6): δ −81.80 [3F, t, $^4J_{F-F} = 10.1$ Hz, CF_3], −120.23 [2F, t, $^4J_{F-F} = 13.5$ Hz, α-CF_2], −122.12 [2F, m, CF_2], −122.63 [2F, m, CF_2], −123.29 [2F, m, CF_2], −126.73 [2F, m, CF_2]. MS (FAB) *m/z*: 979 $[M]^+$, 1002 $[MNa]^+$, 910 $[M–CF_3]^+$, 69 $[CF_3]^+$. IR: 1646 cm^{-1} ν(C=O). Analytically calculated for $ZnC_{30}H_2O_4F_{52}$: C, 24.4; H, 0.1. Found: C, 23.9; H, <0.3.

4.1.17. Zinc bis(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-triacontafluoro-heptadecane-8,10-dionate) [Zn{$C_7F_{15}C(O)CHC(O)C_7F_{15}$}$_2$] (**7c**)

Zinc bis(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-triacontafluoro-heptadecane-8,10-dionate) [Zn{$C_7F_{15}C(O)CHC(O)C_7F_{15}$}$_2$] (**7c**) was prepared similarly. The white powdery product was filtered from the reaction mixture, washed with methanol and dried in vacuo over silica gel. Yield: 79%. ^{19}F{^{1}H} NMR (C_6D_6): δ −82.91 [3F, t, $^4J_{F-F} = 9.5$ Hz, CF_3], −121.38 [2F, m, CF_2], −122.82 [2F, m, CF_2], −123.50 [2F, m, CF_2], −124.08 [2F, m, CF_2], −124.72 [2F, m, CF_2], −127.80 [2F, m, CF_2]. MS (FAB) *m/z*: 1680 $[M]^+$, 1660 $[M\text{-}F,H]^+$. IR: 1642 cm^{-1} ν(C=O). Analytically calculated for $ZnC_{34}H_2O_4F_{60}$: C, 24.3; H, 0.1. Found: C, 24.3; H, 0.1.

4.1.18. Copper bis(triphenylphosphine)(1,1,1,2,2,3,3,4,4,5,5,6,6,10,10,11,11,12,12,13,13,14,14,15,15,15-hexacosafluoro-pentadecane-7,9-dionate) [Cu(PPh_3)$_2${$C_6F_{13}C(O)CHC(O)C_6F_{13}$}] (**8a**)

Sodium hydroxide (0.0185 g, 3.09×10^{-4} mol) and 1,1,1,2,2,3,3,4,4,5,5,6,6,10,10,11,11,12,12,13,13,14,14,15,15,15-hexacosafluoro-pentadecane-7,9-dione (**2**) (0.219 g, 3.09×10^{-4} mol) were dissolved in methanol (20 cm^3) and [$Cu^I(PPh_3)_2NO_3$] (0.201 g, 3.09×10^{-4} mol) added. After stirring for 30 min, the orange precipitate was filtered, washed with methanol and dried in vacuo over silica gel. Yield: 0.38 g, 95%. ^{1}H NMR ($CDCl_3$): δ 5.65 [1H, s, C–H], 7.6 [30H, br s, C_6H_5]. ^{19}F{^{1}H} NMR ($CDCl_3$): δ −81.23 [3F, t, $^4J_{F-F} = 9.7$ Hz, CF_3], −119.91 [2F, t, $^4J_{F-F} = 13.0$ Hz, α-CF_2], −122.20 [2F, m, CF_2], −122.80 [2F, m, CF_2], −123.26 [2F, m, CF_2], −126.57 [2F, m, CF_2]. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −3.2 [br s]. IR: 1646 cm^{-1} ν(C=O). Analytically calculated for $CuC_{51}H_{31}O_2F_{26}P_2$: C, 47.3; H, 2.4. Found: C, 47.3; H, 2.4.

4.1.19. Copper bis(triphenylphosphine)(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-triacontafluoro-heptadecane-8,10-dionate) [Cu(PPh_3)$_2${$C_7F_{15}C(O)CHC(O)C_7F_{15}$}] (**8b**)

Copper bis(triphenylphosphine)(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-triacontafluoro-heptadecane-8,10-dionate) [Cu(PPh_3)$_2${$C_7F_{15}C(O)CHC(O)C_7F_{15}$}] (**8b**) was prepared similarly with 92% yield. ^{1}H NMR ($CDCl_3$): δ 5.91 [1H, s, C–H], 7.4 [30H, br s, C_6H_5]. ^{19}F{^{1}H} NMR ($CDCl_3$): δ −81.25 [3F, t, $^4J_{F-F} = 9.3$ Hz, CF_3], −119.93 [2F, t, $^4J_{F-F} = 11.8$ Hz, α-CF_2], −122.00 [2F, m, CF_2], −122.50 [2F, m, CF_2], −122.77 [2F, m, CF_2], −123.18 [2F, m, CF_2], −126.57 [2F, m, CF_2]. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −3.4 [br s]. IR: 1646 cm^{-1} ν(C=O). MS (FAB) *m/z*: 1395 $[M]^+$. Analytically calculated for $CuC_{53}H_{31}O_2F_{30}P_2$: C, 45.6; H, 2.2. Found: C, 45.5; H, 2.2.

4.1.20. Crystal structures of [Cu{$CF_3C(O)CHC(O)C_6F_{13}$}$_2$(H_2O)$_2$], [Cu{$C_6F_{13}C(O)CHC(O)C_6F_{13}$}$_2$($H_2O$)$_2$] and [Cu($PPh_3$)$_2$($C_7F_{15}C(O)CHC(O)C_7F_{15}$)]

Crystals of (**4a**·$2H_2O$) and (**4b**·$2H_2O$) were grown by slow evaporation from ether solutions of the complexes over a layer of chloroform. Crystals of (**8b**) were grown by slow evaporation from acetone.

4.1.21. Crystal data

$C_{20}H_6CuF_{32}O_6$ (**4a**·$2H_2O$), $M = 1013.78$, monoclinic, space group $P2_1/n$, $a = 13.917(7)$ Å, $b = 5.375(3)$ Å, $c = 20.678(11)$ Å, $\beta = 103.704(8)^\circ$, $U = 1502.7(13)$ Å^3 (by least squares refinement of 2336 reflections), $T = 150(2)$ K, graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, $Z = 2$, $D_c = 2.240$ g cm^{-3}, $F(000) = 982$, dimensions 0.32 mm × 0.09 mm × 0.08 mm, μ (Mo Kα) = 0.966 mm^{-1}, empirical absorption correction, maximum and minimum transmission factors of 0.928 and

0.407, respectively (the minimum transmission factor is smaller than that calculated since the empirical absorption correction compensates for absorption by the glass mounting fibre), Bruker APEX 2000 diffractometer, data collection range $\lambda = 1.6$–25.0°, $-16 \leq h \leq 16$, $-6 \leq k \leq 6$, $-24 \leq l \leq 24$, no crystal decay was detected; 7865 reflections were measured and 2651 were unique ($R_{int} = 0.0674$), final $R_1 = 0.0598$, $wR_2 = 0.1518$ (0.0810 and 0.1595, respectively for all the data) for 277 variables. The final residual Fourier map showed peaks of 0.766 and –1.234 eÅ^{-3}.

$C_{30}H_6CuF_{52}O_6$ (**4b**·2H_2O), $M = 1513.89$, monoclinic, space group $P2/c$, $a = 14.6481(10)$ Å, $b = 5.5300(4)$ Å, $c = 28.947(2)$ Å, $\beta = 95.093(1)^\circ$, $U = 2335.5(3)$ Å^3 (by least squares refinement of 5604 reflections), $T = 160(2)$ K, graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, $Z = 2$, $D_c = 2.153$ g cm^{-3}, $F(0\,0\,0) = 1462$, dimensions 0.30 mm × 0.14 mm × 0.12 mm, μ (Mo Kα) = 0.719 mm^{-1}, empirical absorption correction, maximum and minimum transmission factors of 0.93 and 0.83, respectively, Bruker APEX 2000 diffractometer, data collection range $\theta = 1.4$–26.0°, $-18 \leq h \leq 18$, $-6 \leq k \leq 6$, $-35 \leq l \leq 35$, no crystal decay was detected, 17270 reflections were measured and 4591 were unique ($R_{int} = 0.0237$), final $R_1 = 0.0453$, $wR_2 = 0.1214$ (0.0568 and 0.1281, respectively for all the data) for 565 variables. The final residual Fourier map showed peaks of 0.697 and –0.357 eÅ^{-3}.

$C_{53}H_{31}CuF_{30}O_2P_2$ (**8b**), $M = 1395.26$, monoclinic, space group $C2/c$, $a = 36.773(2)$ Å, $b = 13.222(1)$ Å, $c = 22.532(1)$ Å, $\beta = 93.729(1)^\circ$, $U = 10932.0(8)$ Å^3 (by least squares refinement of 12843 reflections), $T = 150(2)$ K, graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, $Z = 8$, $D_c = 1.695$ g cm^{-3}, $F(0\,0\,0) = 5552$, dimensions 0.32 mm × 0.29 mm × 0.15 mm, μ (Mo Kα) = 0.603 mm^{-1}, empirical absorption correction, maximum and minimum transmission factors of 0.746 and 0.655, respectively, Bruker APEX 2000 diffractometer, data collection range $\theta = 1.6$–25.0°, $-42 \leq h \leq 43$, $-15 \leq k \leq 15$, $-26 \leq l \leq 26$, no crystal decay was detected; 38861 reflections were measured and 9618 were unique ($R_{int} = 0.028$), final $R_1 = 0.0515$, $wR_2 = 0.135$ (0.0619 and 0.142, respectively, for all the data) for 862 variables. The final residual Fourier map showed peaks of 1.13 (0.92 Å from C14′) and −0.60 eÅ^{-3}.

4.1.22. Structure solution and refinement

Structure solution by Patterson methods and structure refinement on F^2 employed SHELXTL/PC Version 5.0 [26]. The C–H hydrogen atoms were included in calculated positions (C–H = 0.96 Å) with isotropic displacement parameters set to 1.2 U_{eq} of the bonded atom. The aqua hydrogen atoms of (**4a**·2H_2O) and (**4b**·2H_2O) were located from difference Fourier maps and included in refinement cycles riding on the oxygen atoms with isotropic displacement parameters set to 1.5 U_{eq} of the oxygen atoms. The fluorine atoms of the disordered trifluoromethyl groups in (**4a**·2H_2O) were refined with isotropic displacement parameters. All other non-hydrogen atoms were refined with anisotropic displacement parameters. The data were corrected for Lorentz and polarisation effects. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 192861–192863. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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