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# Synthesis and characterization of rhenium carbonyltrifluoroacetate complexes with phosphites, phosphonites and phosphinites

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## 1. Introduction

Transition metal carbonyl complexes are widely studied in chemistry because they have many different applications ranging from catalysts [1] to biochemistry [2]. Many properties of the complexes, such as redox potential of the metal centre, lability of the ligands, etc., are related to the synergistic effects of  $\sigma$  and  $\pi$  bonds between the metal centre and the CO ligands [3]. On the other hand, phosphines are also very common ligands with tuneable electronic properties that allow them to mimic those of CO ligands. Moreover, the possibility of modifying their steric properties explains their wide use in many coordination compounds. Replacement of the R groups from PR3 compounds by OR groups to form mixed phosphites  $(PR_n(OR)_{3-n}; n = 0-2)$  modifies the electronic character of the ligand, enhancing its  $\pi$ -acceptor character and reducing its  $\sigma$ -donor behaviour [4]. These changes, in turn, modify the properties of the metal complex. We are interested in analysing the properties of carbonyl complexes that bear mono- and bidentate mixed phosphites and we have previously reported on the properties of [ReX(CO)<sub>3</sub>L] [5] and [ReBr(CO)<sub>2</sub>LL'] [6] (X = Br, OTf; L = diphosphinite; L' = mixed phosphite). Substitution of the bromo ligand by the potentially bidentate OTf ligand, did not produce relevant differences on the properties of the complex. Thus, we report here the carbonyl rhenium complexes  $[Re(O_2CCF_3)(CO)_3(L)]$  and [ $\operatorname{Re}(O_2\operatorname{CCF}_3)(\operatorname{CO})_2\operatorname{LL'}$ ] (L = Ph<sub>2</sub>POCH<sub>2</sub>CH<sub>2</sub>OPPh<sub>2</sub>; L' = PPh<sub>n</sub>(OR)<sub>3-n</sub>; R = Me, Et; n = 0-2) bearing the more basic trifluoroacetate ligand to investigate its influence on the properties of the new complexes.

### ABSTRACT

The rhenium(I) complexes  $[Re(O_2CCF_3)(CO)_3(L)]$  (1) and  $[Re(O_2CCF_3)(CO)_2LL']$  (L = Ph<sub>2</sub>POCH<sub>2</sub>CH<sub>2</sub>OPPh<sub>2</sub>; L' = PPh<sub>n</sub>(OR)<sub>3-n</sub>; R = Me, Et; n = 0-2) (**2a**-**f**) have been synthesised by the reaction of the parent bromo derivatives with AgO<sub>2</sub>CCF<sub>3</sub>. These compounds have been characterized by microanalysis, IR, NMR, mass spectrometry and, in the cases of 1 and 2a, by X-ray diffraction. The metal is in a distorted octahedral environment with the trifluoroacetate ligand acting in a monodentate manner.

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#### 2. Experimental

#### 2.1. General methods and instrumentation

All experimental manipulations were carried out under an argon atmosphere using Schlenk techniques. Solvents were purified by conventional procedures [7] and distilled prior to use. The complexes [ReBr(CO)<sub>3</sub>(L)] and [ReBr(CO)<sub>2</sub>LL'] (L = Ph<sub>2</sub>POCH<sub>2</sub>CH<sub>2</sub>OPPh<sub>2</sub>; L' = PPh<sub>n</sub>(OR)<sub>3-n</sub>, R = Me, Et; n = 0-2) were prepared by previously described methods [6].

The <sup>1</sup>H, <sup>31</sup>P(<sup>1</sup>H), <sup>13</sup>C(<sup>1</sup>H) and <sup>19</sup>F(<sup>1</sup>H) NMR ( $\delta$  in ppm) spectra were obtained on a Bruker ARX-400 spectrometer operating at frequencies of 400, 161, 100 and 376 MHz, respectively. <sup>1</sup>H and <sup>13</sup>C(<sup>1</sup>H) chemical shifts are referred to internal TMS. <sup>19</sup>F(<sup>1</sup>H) and <sup>31</sup>P(<sup>1</sup>H) chemical shifts are reported with respect to CFCl<sub>3</sub> and 85% H<sub>3</sub>PO<sub>4</sub>, respectively, with downfield shifts considered positive. Infrared spectra were recorded as KBr discs on a Bruker VECTOR IFS28 FT spectrophotometer. Mass spectra were recorded in the LSIMS (FAB<sup>+</sup>), Cs<sup>+</sup> mode on a Micromass Autospec M instrument, using 3-nitrobenzyl alcohol as the matrix material. The conductivity values of 10<sup>-3</sup> mol dm<sup>-3</sup> solutions of the complexes in MeNO<sub>2</sub> at 25 °C were measured with a Crison GLP 32 conductimeter. Elemental analyses (C, H) were performed using a Fisons EA-1108 microanalyzer. Melting points were determined on a GallenKamp MFB-595 and are uncorrected.

### 2.2. Synthesis of the complexes

AgO<sub>2</sub>CCF<sub>3</sub> was added to a dichloromethane solution of the precursor complex [ReBr(CO)<sub>2</sub>(X)(L)] (X = CO or L') in a 1.5:1 molar





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ratio. The mixture was heated under reflux for 2–3 h and the AgBr formed was removed from the resulting grey suspension by filtration through Celite. In the case of complex **1**, the concentration of the resulting solution afforded an oil, which was triturated with diethyl ether (5 mL) to give a beige solid. This solid was filtered off, washed with diethyl ether (2 × 3 mL), dried under vacuum and recrystallised from a mixture of  $CH_2CI_2$ /diethyl ether. In the case of compounds **2**, white solids were obtained and these were recrystallised from a mixture of  $CH_2CI_2$ /hexane.

#### 2.2.1. $[Re(O_2CCF_3)(CO)_3(L)]$ (1)

AgO<sub>2</sub>CCF<sub>3</sub> (42.4 mg, 0.192 mmol) was added to a solution of [ReBr(CO)<sub>3</sub>(L)] (100 mg, 0.128 mmol) in dichloromethane (20 mL). Yield ≥ 58%. M.p. 211 °C.  $\Lambda_{M(nitromethane)} = 3.5 \Omega^{-1} cm^2 mol^{-1}$ . Anal. Calc. for C<sub>31</sub>H<sub>24</sub>O<sub>7</sub>P<sub>2</sub>F<sub>3</sub>Re: C, 45.7; H, 3.0. Found: C, 46.0; H, 3.1%. IR (cm<sup>-1</sup>)  $v_{CO}$ : 2041, 1967, 1932;  $v_{asym(OCO)}$ : 1692,  $v_{sym(OCO)}$ : 1420. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  7.56–7.21 (m, 20H, Ph), 4.33–4.07 (m, 4H, –CH<sub>2</sub>CH<sub>2</sub>–). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm):  $\delta$  116.5 (s). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm):  $\delta$  –74.8 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$  66.5 (s, br, –CH<sub>2</sub>–), 114.7 (q, *J*<sub>CF</sub> = 288 Hz, CF<sub>3</sub>), 128.8–138.3 (Ph), 162.2 (qt, *J*<sub>CF</sub> = 37 Hz, *J*<sub>CP</sub> = 2 Hz, O<sub>2</sub>CCF<sub>3</sub>), 191.2 (m, 2CO *cis* to O<sub>2</sub>CCF<sub>3</sub>), 191.5 (t, *J*<sub>CP</sub> = 7 Hz, CO *trans* to O<sub>2</sub>CCF<sub>3</sub>).

#### 2.2.2. $[Re(O_2CCF_3)(CO)_2(L)(L')]$ (2)

 $AgO_2CCF_3$  (33 mg, 0.15 mmol) was added to [ReBr(CO)<sub>2</sub>LL'] (0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL).

Compound **2a**, L' = P(OMe)<sub>3</sub>: Yield  $\ge$  37%. M.p. 202 °C.  $\Lambda_{M(nitromethane)} = 3.0 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ . *Anal.* Calc. for  $C_{33}H_{33}O_9P_3F_3Re:$ C, 43.6; H, 3.7. Found: C, 43.4; H, 3.7%. FAB MS: *m/z* (referred to the most abundant isotopes): 910 (48.5%) [M]; 882 (35.7%) [M–CO]; 797 (100%) [M–O<sub>2</sub>CCF<sub>3</sub>]; 758 (95.6%) [M–CO–L']; 645 (6.0%) [M–CO–L'–O<sub>2</sub>CCF<sub>3</sub>]. IR (cm<sup>-1</sup>)  $\nu_{CO}$ : 1962, 1882;  $\nu_{asym(OCO)}$ : 1697;  $\nu_{sym(OCO)}$ : 1418. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  7.64–7.19 [m, 20H, Ph (L)], 4.50 (m, 1H, –CH<sub>2</sub>CH<sub>2</sub>–), 4.00 (m, 3H, –CH<sub>2</sub>CH<sub>2</sub>–), 3.39 [d, 9H, *J*<sub>HP</sub> = 10 Hz, –CH<sub>3</sub> (L')]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm) (see Scheme 1 for labelling):  $\delta$  115.2 (dd, *J*<sub>AB</sub> = 33 Hz, *J*<sub>BC</sub> = 299 Hz, P<sub>B</sub>), 118.2 (dd, *J*<sub>AC</sub> = 32 Hz, P<sub>A</sub>), 124.3 (dd, P<sub>C</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm):  $\delta$  –75.1 (s).

Compound **2b**,  $L' = P(OEt)_3$ : Yield  $\geq 36\%$ . M.p. 190 °C.  $\Lambda_{M(nitromethane)} = 2.9 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ . *Anal.* Calc. for  $C_{36}H_{39}O_9P_3F_3Re$ : C, 45.4; H, 4.2. Found: C, 45.2; H, 4.1%. FAB MS: m/z (referred to the most abundant isotopes): 952 (58.5%) [M]; 924 (52.7%) [M–CO]; 839 (99.9%) [M–O<sub>2</sub>CCF<sub>3</sub>]; 758 (100%) [M–CO–L']; 645 (6.2%) [M–CO–L'–O<sub>2</sub>CCF<sub>3</sub>]. IR (cm<sup>-1</sup>)  $\nu_{CO}$ : 1975, 1876;  $\nu_{asym(OCO)}$ : 1696;  $\nu_{sym(OCO)}$ : 1410. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  7.66–7.19 [m, 20H, Ph (L)], 4.50 (m, 1H, -CH<sub>2</sub>CH<sub>2</sub>–), 4.20–3.80 [m, 3H, -CH<sub>2</sub>CH<sub>2</sub>–(L)], 3.76 [m, 6H, -CH<sub>2</sub>–(L')], 1.01 [t, 9H,  $J_{HH} = 7$  Hz,  $-CH_3(L')$ ]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm) (see Scheme 1 for labelling):  $\delta$  114.6 (dd,  $J_{AB} = 49$  Hz,  $J_{BC} = 308$  Hz,  $P_B$ ), 119.1 (dd,  $J_{AC} = 32$  Hz,  $P_A$ ), 119.9 (dd,  $P_C$ ). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm):  $\delta$  –74.9 (s).



C<sub>38</sub>H<sub>35</sub>O<sub>8</sub>P<sub>3</sub>F<sub>3</sub>Re: C, 47.7; H, 3.7. Found: C, 48.1; H, 3.7%. FAB MS: *m/z* (referred to the most abundant isotopes): 956 (42.0%) [M]; 928 (45.9%) [M–CO]; 843 (88.7%) [M–O<sub>2</sub>CCF<sub>3</sub>]; 758 (100%) [M–CO–L']; 645 (5.0%) [M–CO–L'–O<sub>2</sub>CCF<sub>3</sub>]. IR (cm<sup>-1</sup>)  $v_{CO}$ : 1974, 1877;  $v_{asym(OCO)}$ : 1697;  $v_{sym(OCO)}$ : 1403. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 7.64–7.26 [m, 25H, Ph (L+L')], 4.54 [m, 1H, –CH<sub>2</sub>CH<sub>2</sub>–(L)], 4.06 [m, 2H, –CH<sub>2</sub>CH<sub>2</sub>–(L)], 3.94 [m, 1H, –CH<sub>2</sub>CH<sub>2</sub>–(L)], 3.40 [d, 3H,  $J_{HP}$  = 11 Hz, –CH<sub>3</sub>(L')], 3.31 [d, 3H,  $J_{HP}$  = 11 Hz, –CH<sub>3</sub> (L')]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm) (see Scheme 1 for labelling): δ 116.3 (dd,  $J_{AB}$  = 34 Hz,  $J_{BC}$  = 251 Hz, P<sub>B</sub>), 117.8 (dd,  $J_{AC}$  = 33 Hz, P<sub>A</sub>), 143.9 (dd, P<sub>C</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm): δ –74.8 (s).

Compound **2d**, L' = PPh(OEt)<sub>2</sub>: Yield  $\geq$  59%. M.p. 177 °C.  $\Lambda_{M(nitromethane)} = 4.1 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ . Anal. Calc. for C<sub>40</sub>H<sub>39</sub>O<sub>8</sub> P<sub>3</sub>F<sub>3</sub>Re: C, 48.8; H, 4.00. Found: C, 48.7; H, 3.95%. FAB MS: *m/z* (referred to the most abundant isotopes): 984 (43.9%) [M]; 956 (46.2%) [M–CO]; 871 (82.6%) [M–O<sub>2</sub>CCF<sub>3</sub>]; 758 (100%) [M–CO–L']; 645 (3.9%) [M–CO–L'–O<sub>2</sub>CCF<sub>3</sub>]. IR (cm<sup>-1</sup>)  $\nu_{co}$ : 1993, 1888;  $\nu_{asym(OCO)}$ : 1694;  $\nu_{sym(OCO)}$ : 1406. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  7.76– 7.16 [m, 25H, Ph (L+L')), 4.55 [m, 1H, –CH<sub>2</sub>CH<sub>2</sub>–(L)], 4.05 [m, 1H, –CH<sub>2</sub>CH<sub>2</sub>–(L)], 3.88 [m, 2H, –CH<sub>2</sub>CH<sub>2</sub>–(L)], 3.40–3.70 [m, 4H, –CH<sub>2</sub>–(L')], 1.07 [t, 3H, J<sub>HH</sub> = 7 Hz, –CH<sub>3</sub> (L')], 1.00 [t, 3H, J<sub>HH</sub> = 7 Hz, –CH<sub>3</sub> (L')]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm) (see Scheme 1 for labelling):  $\delta$  115.4 (dd, J<sub>AB</sub> = 37 Hz, J<sub>BC</sub> = 269 Hz, P<sub>B</sub>), 118.6 (dd, J<sub>AC</sub> = 33 Hz, P<sub>A</sub>), 138.2 (dd, P<sub>C</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm):  $\delta$  –74.8 (s).

Compound **2e**,  $L' = PPh_2(OMe)$ : Yield  $\geq 40\%$ . M.p. 174 °C.  $\Lambda_{M(nitromethane)} = 3.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . *Anal.* Calc. for  $C_{43}H_{37}O_7P_3F_3Re$ : C, 51.5; H, 3.7. Found: C, 51.4; H, 3.7%. FAB MS: m/z (referred to the most abundant isotopes): 1003 (11.7%) [M+1]; 974 (7.7%) [M–CO]; 889 (32.2%) [M–O\_2CCF\_3]; 758 (100%) [M–CO–L']; 645 (7.6%) [M–CO–L'–O\_2CCF\_3]. IR (cm<sup>-1</sup>)  $\nu_{CO}$ : 1973, 1872;  $\nu_{asym(OCO)}$ : 1695;  $\nu_{sym(OCO)}$ : 1406. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  7.65–7.19 [m, 30H, Ph (L+L')], 4.31 [m, 1H, -CH<sub>2</sub>CH<sub>2</sub>-(L)], 3.91 [m, 3H, -CH<sub>2</sub>CH<sub>2</sub>-(L)], 2.88 [t, 3H,  $J_{HP} = 6$  Hz, -CH<sub>3</sub>(L')]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm) (see Scheme 1 for labelling):  $\delta$  115.2 (d<sub>app</sub>,  $J_{app} = 33$  Hz,  $P_B+P_C$ ), 117.2 (t<sub>app</sub>, P<sub>A</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm):  $\delta$  –75.0 (s).

Compound **2f**,  $L' = PPh_2(OEt)$ : Yield  $\ge 44\%$ . M.p. 170 °C.  $\Lambda_{M(nitromethane)} = 3.2 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ . *Anal.* Calc. for  $C_{44}H_{39}O_7P_3F_3Re$ : C, 52.0; H, 3.97. Found: C, 49.2; H, 3.97%. FAB MS: m/z (referred to the most abundant isotopes): 1017 (31.5%) [M+1]; 988 (11.1%) [M–CO]; 903 (65.3%) [M–O\_2CCF\_3]; 758 (100%) [M–CO–L']; 645 (3.8%) [M–CO–L'–O\_2CCF\_3]. IR (cm<sup>-1</sup>)  $v_{CO}$ : 1979, 1881;  $v_{sym(OCO)}$ : 1693;  $v_{asym(OCO)}$ : 1408. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  7.75–7.16 [m, 30H, Ph (L+L')], 4.46 [m, 1H, –CH<sub>2</sub>CH<sub>2</sub>–(L)], 4.03–3.89 [m, 3H, –CH<sub>2</sub>CH<sub>2</sub>–(L)], 3.23 [m, 2H, –CH<sub>2</sub>–(L')], 0.81 [t, 3H,  $J_{HH}$  = 7 Hz, –CH<sub>3</sub> (L')]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm) (see Scheme 1 for labelling):  $\delta$  113.8 (m, P<sub>B</sub>+P<sub>C</sub>), 117.5 (t<sub>app</sub>,  $J_{app}$  = 32 Hz, P<sub>A</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm):  $\delta$  –75.0 (s).

#### 2.3. X-ray crystallography

Single crystals of compounds **1** and **2a** were mounted on a glass fibre and studied on a Bruker Smart CCD area-detector diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\Lambda$  = 0.71073 Å). The crystal parameters and experimental details for data collection are summarized in Table 1. Absorption corrections were carried out using sADABS [8]. The structures were solved with the oscAL program [9] by the Patterson method and refined by full-matrix least-squares based on  $F^2$  [10]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from the International Tables for X-ray Crystallography [11]. Details of crystal data and structural refinement are given in Table 1.

Table 1	
Crystal data and structure refinement for compounds 1	and <b>2a</b> .

	1	2a
Empirical formula	$C_{62}H_{48}F_6O_{14}P_4Re_2$	$C_{33}H_{33}F_{3}O_{9}P_{3}Re$
Formula weight	1627.28	909.70
Crystal size (mm)	$0.67 \times 0.39 \times 0.12$	$0.22\times0.08\times0.07$
T (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	ΡĪ	$P2_1/c$
a (Å)	10.1231(5)	12.0956(10)
b (Å)	17.9762(9)	17.4771(15)
<i>c</i> (Å)	18.5233(9)	17.1160(14)
α (°)	67.5350(10)	90
β (°)	87.8420(10)	90.309(2)
γ (°)	89.5730(10)	90
$V(Å^3)$	3112.7(3)	3618.2(5)
Ζ	2	4
Density (calc.) (Mg/m <sup>3</sup> )	1.736	1.670
$\mu ({ m mm^{-1}})$	4.070	3.557
F(0 0 0)	1592	1800
$\theta$ Range for data collection (°)	2.01-28.01	1.67-17.99
Index ranges	$-13 \leqslant h \leqslant 11, \ -23 \leqslant k \leqslant 23, \ -20 \leqslant l \leqslant 24$	$-10\leqslant h\leqslant 10,-11\leqslant k\leqslant 15,-13\leqslant l\leqslant 14$
Reflections collected	18 666	8412
Independent reflections (R <sub>int</sub> )	13 127(0.0762)	2468(0.0660)
Reflections observed (> $2\sigma$ )	9663	1767
Data completeness	0.871	0.990
Max. and min. transmission	1.000 and 0.234	1.000 and 0.719
Data/restraints/parameters	13 127/0/793	2468/0/445
Goodness-of-fit on $F^2$	0.961	0.771
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0681, wR_2 = 0.1721$	$R_1 = 0.0282, wR_2 = 0.0435$
R indices (all data)	$R_1 = 0.0853, wR_2 = 0.1819$	$R_1 = 0.0551, wR_2 = 0.0480$
Largest difference in peak and hole ( $e \text{ Å}^{-3}$ )	4.241 and -3.922	0.309 and -0.355

#### 3. Results and discussion

#### 3.1. Synthesis

The bromo complexes [ReBr(CO)<sub>3</sub>(L)] [5a] and [ReBr(CO)<sub>2</sub>LL'] [6] [L = Ph<sub>2</sub>POCH<sub>2</sub>CH<sub>2</sub>OPPh<sub>2</sub>, L' = PPh<sub>n</sub>(OR)<sub>3-n</sub> n = 0-2] reacted with an excess of AgO<sub>2</sub>CCF<sub>3</sub> in refluxing dichloromethane to give [Re(O<sub>2</sub>CCF<sub>3</sub>)(CO)<sub>3</sub>L] (1) and [Re(O<sub>2</sub>CCF<sub>3</sub>)(CO)<sub>2</sub>LL'] (2), respectively, as beige (1) or white (2) solids (Scheme 1). The new complexes are air-stable in the solid state and in solution at room temperature, and were characterized by elemental analysis, IR spectroscopy, mass spectrometry and, in the cases of compounds 1 and 2a, by X-ray diffraction. Conductivity measurements on nitromethane solutions of the compounds show values that are consistent with nonelectrolyte behaviour, in agreement with the coordination of the trifluoroacetate anion to the rhenium atom. The compounds were also studied in solution by NMR spectroscopy.

#### 3.2. Description of the structures

#### 3.2.1. $[Re(O_2CCF_3)(CO)_3(L)]$ (1)

An ORTEP [12] drawing of the two molecules in the asymmetric unit, along with the numbering scheme adopted, is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 2. The asymmetric unit contains two different molecules with identical formulae. Both consist of a rhenium(I) atom coordinated in an octahedral arrangement by three *facially* disposed carbonyl ligands, two phosphorus atoms of the chelating phosphinite ligand Ph<sub>2</sub>POCH<sub>2</sub>CH<sub>2</sub>OPPh<sub>2</sub>, and an oxygen atom of a trifluoroacetate ion acting as a monodentate ligand. The main differences between the two molecules in the asymmetric unit are: (i) the seven-membered chelate ring adopts a twisted boat conformation [13] in molecule 1 whereas it adopts a twisted chair conformation [13] in molecule 2; (ii) the chelate angles are  $86.5(1)^{\circ}$  [Re(1)] and  $90.0(1)^{\circ}$  [Re(2)]; (iii) molecule 1 has surrounding Re(1) parameters that are more distorted from the ideal octahedral geometry than those for molecule 2; (iv) the orientation of the carboxylate moiety  $[C-CO_2]$  is different in the two molecules, being directed towards the bisector of the two CO ligands in molecule 1 [torsion angles 38.3(4) and 52.8(4)°] and almost parallel to one of them [torsion angle 1.3(6)°] and perpendicular to the other in molecule 2.

The Re–P bond lengths span from 2.431(2) to 2.456(2) Å, a narrower range than that found in the closely related triflato complex [Re(OSO<sub>2</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(L)] [5b]. The Re–C bond lengths range from 1.87(1) to 2.00(1) Å, and they are similar to those of the triflato complex [5b]. The Re–C bond distances *trans* to the phosphorus atoms are, on average, 0.08 Å longer than that *trans* to the oxygen atom, a greater but comparable difference, than that observed for the triflato complex (0.06 Å) [5b]. Those values are also in a comparable range to that found for other *fac*-tricarbonyl Re(I) complexes bearing related diphosphinite ligands [5c].

The trifluoroacetate group acts as a monodentate ligand in a similar way to other rhenium(I) compounds bearing this group as a ligand [14]. The OCO angle ( $\sim$ 129°) and the O–C bond lengths of the carboxylate moiety (1.20–1.23 Å), which are near to the ionic limit (1.250 Å) as defined by Hocking and Hambley [15], are indicative of a high ionic character (>90%) for the carboxylate–rhenium interaction.

#### 3.2.2. $[Re(O_2CCF_3)(CO)_2(L){P(OMe)_3}]$ (**2a**)

An ORTEP [12] drawing of the molecule, along with the numbering scheme adopted, is shown in Fig. 2. Selected bond lengths and bond angles are listed in Table 3. The compound consists of a rhenium(I) atom coordinated by two *cis* carbonyl ligands, two phosphorus atoms of the chelating bidentate phosphinite ligand Ph<sub>2</sub>POCH<sub>2</sub>CH<sub>2</sub>OPPh<sub>2</sub>, another phosphorus atom from a trimethylphosphite ligand and an oxygen atom of a trifluoroacetate group, which acts as a monodentate ligand. This arrangement results in an octahedral arrangement around the metal atom. The three phosphorus atoms are in meridional positions. The Re–C



Fig. 1. Molecular structure of molecules 1 (left) and 2 (right) of compound 1.

bond distances are 1.864(12) and 1.914(13) Å, with the shorter one corresponding to that trans to the trifluoroacetate ion. The bidentate phosphinite ligand shows two different Re-P bond lengths, 2.402(3) and 2.467(3) Å, with the shorter one corresponding to that *trans* to the phosphite ligand. The geometrical parameters for the trifluoroacetate ligand are similar to those observed for 1 and are consistent with its monodentate behaviour. The *cis* angles range from 82.2(2) to 95.9(4)°. It is noteworthy that the most distorted values are those of the trifluoroacetate ligand, probably due to the steric requirements of the phenyl groups of the bidentate phosphinite ligand in the direction of the position occupied by the trifluoromethyl group. In fact, the carboxylate moiety of the trifluoroacetate ligand is not parallel to any other ligand, but is directed towards the free space between a carbonyl and the phosphite ligand with very different torsion angles: 21.8(4)° with the carbonyl ligand and 69.9(3)° with the phosphite ligand [vectors defined as O(4)-O(3) versus Re-O(2) and Re-P(3)]. The sevenmembered chelate ring adopts a twisted boat conformation [13] with a chelate P(1)-Re-P(2) angle of 87.8(1)°.

Table 2	
Selected bond lengths [Å] and angles [°] for co	mpound 1

Re(1)-C(3)	1.874(10)	Re(2)-C(103)	1.909(10)
$\operatorname{Re}(1) - C(4)$	1.981(11)	Re(2)-C(104)	1.937(10)
Re(1)-C(5)	1.954(11)	Re(2)-C(105)	1.999(11)
Re(1)-P(1)	2.456(2)	Re(2)-P(101)	2.449(2)
Re(1)-P(2)	2.433(2)	Re(2)-P(102)	2.431(2)
Re(1)-O(3)	2.175(6)	Re(2)-O(103)	2.185(7)
C(3)-O(4)	1.179(11)	C(103)-O(104)	1.123(12)
C(5)-O(6)	1.150(12)	C(105)-O(106)	1.115(12)
C(4) - O(5)	1.106(12)	C(104)-O(105)	1.137(12)
O(3) - C(6)	1.214(11)	O(103)-C(106)	1.218(13)
O(7)-C(6)	1.230(12)	O(107)-C(106)	1.205(16)
C(3)-Re(1)-C(5)	89.6(4)	C(103)-Re(2)-C(105)	88.1(5)
C(3)-Re(1)-C(4)	87.1(4)	C(103)-Re(2)-C(104)	91.9(4)
C(3) - Re(1) - P(1)	96.5(3)	C(103)-Re(2)-P(102)	92.5(3)
C(5)-Re(1)-C(4)	90.5(4)	C(104)-Re(2)-C(105)	88.6(4)
C(5)-Re(1)-O(3)	91.2(3)	C(105)-Re(2)-O(103)	93.5(4)
C(4) - Re(1) - O(3)	91.7(3)	C(104)-Re(2)-O(103)	89.4(4)
C(3) - Re(1) - P(2)	88.5(3)	C(103)-Re(2)-P(101)	86.5(3)
C(5)-Re(1)-P(2)	92.3(3)	C(105)-Re(2)-P(101)	89.7(3)
O(3) - Re(1) - P(1)	82.76(17)	O(103)-Re(2)-P(102)	85.81(19)
O(3) - Re(1) - P(2)	92.64(19)	O(103)-Re(2)-P(101)	92.3(2)
C(4) - Re(1) - P(1)	91.2(3)	C(104)-Re(2)-P(102)	91.7(3)
P(2)-Re(1)-P(1)	86.50(8)	P(102)-Re(2)-P(101)	90.00(8)
C(4) - Re(1) - P(2)	174.8(3)	C(104)-Re(2)-P(101)	177.7(3)
C(3)-Re(1)-O(3)	178.6(3)	C(103)-Re(2)-O(103)	178.0(3)
C(5)-Re(1)-P(1)	173.7(3)	C(105)-Re(2)-P(102)	179.2(3)

#### 3.3. Spectroscopic studies

The IR spectrum of compound **1** shows three strong v(CO) bands that are characteristic of the *fac*-Re<sup>I</sup>(CO)<sub>3</sub> fragment [16] at 2041, 1967 and 1932 cm<sup>-1</sup>. These bands are displaced to higher wavenumbers with respect to the precursor complex  $[ReBr(CO)_3(L)]$ [5a], in agreement with a minor electronic back-donation of the



Fig. 2. Molecular structure of compound 2a.

Table 3		
Selected bond lengths	[Å] and angles [°]	for compound 2a.

Re(1)–C(1)	1.864(12)	Re(1)-C(2)	1.914(13)
Re(1)-O(3)	2.175(8)	Re(1)-P(3)	2.362(3)
Re(1)-P(1)	2.402(3)	Re(1)-P(2)	2.467(3)
C(1) - O(1)	1.174(11)	C(2)-O(2)	1.164(12)
O(3)-C(3)	1.264(13)	O(4)-C(3)	1.218(13)
C(1)-Re(1)-C(2)	86.7(5)	C(1)-Re(1)-O(3)	175.0(4)
C(2) - Re(1) - O(3)	95.9(4)	C(1)-Re(1)-P(3)	87.2(3)
C(2) - Re(1) - P(3)	91.2(3)	O(3) - Re(1) - P(3)	88.5(2)
C(1)-Re(1)-P(1)	88.8(3)	C(2)-Re(1)-P(1)	90.2(3)
O(3) - Re(1) - P(1)	95.4(2)	P(3)-Re(1)-P(1)	175.71(11)
C(1)-Re(1)-P(2)	95.4(4)	C(2)-Re(1)-P(2)	177.1(4)
O(3) - Re(1) - P(2)	82.2(2)	P(3)-Re(1)-P(2)	90.95(11)
P(1)-Re(1)-P(2)	87.79(11)		



Scheme 2. Fragmentation pathways for compounds 2a-f.

rhenium atom to the CO ligands due to the replacement of Br by the trifluoroacetate ligand. Similarly, the IR spectra of compounds **2** display two strong v(CO) bands, characteristic of *cis*-dicarbonyl compounds [6,17], and these are also displaced to higher energy with respect to the [ReBr(CO)<sub>2</sub>(L)(L')] compounds [6]. On the other hand, compounds **1** and **2** display a strong band at 1692– 1697 cm<sup>-1</sup> and a medium band at 1403–1418 cm<sup>-1</sup> due to the asymmetric and symmetric modes of the carboxylate group of the O<sub>2</sub>CCF<sub>3</sub> ligand [18]. The energy difference between the two bands is related to the coordination type of the carboxylate ligand and, in our case, this is in accordance (~290 cm<sup>-1</sup>) with a monodentate behaviour of the ligand in all the complexes [19]. The X-ray diffraction studies of complexes **1** and **2a** confirm this behaviour.

The <sup>1</sup>H NMR spectrum of compound **1** does not show any relevant differences compared with that of the precursor. However, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** shows a singlet at a lower field ( $\delta$  = 116.5 ppm) than that of the precursor ( $\delta$  = 105.3 ppm), as expected because of the electron-withdrawing characteristics of the trifluoromethyl group. In the case of compounds 2, the  $^{1}$ H NMR signals of the -CH<sub>2</sub>CH<sub>2</sub>- group of the bidentate phosphinite ligand (which appear as three multiplets with intensities 1:1:2 in the spectra of the parent bromide complexes), are two multiplets with intensities 1:3, except for compounds 2c and 2d in which they appear as three 1:2:1 and 1:1:2 multiplets, respectively. In all cases, these multiplets span in a similar but narrower region than those of the bromide precursors. On the other hand, the signals of the OR groups of the monodentate mixed-phosphite ligands, are similar to those of the parent bromide complexes but slightly upfield shifted. Compounds **2a-d** display <sup>31</sup>P{<sup>1</sup>H} NMR spectra that are consistent with an ABM spin system (three double doublets), but compounds **2e-f** show signals corresponding to ABC and A<sub>2</sub>B spin systems [20], respectively, reflecting the similarity between the P nuclei of both bidentate and monodentate phosphinite ligands. In all cases the signals are shifted downfield when compared to their bromide analogues. These shifts are consistent with the IR data discussed above and are in accordance with the presence of the more electron-withdrawing trifluoroacetate group, which reduces the rhenium  $\pi$ -back-donation to the phosphorus ligands. The mass spectra of compounds 2a-f show, in all cases, five sets of peaks (see Section 2) displaying the rhenium isotope pattern. This allows us to propose possible fragmentation pathways for these compounds that would give rise to the identified fragments (Scheme 2).

The most abundant peak is, in all cases (except for **2a** – although in this case its abundance is also very high, 95.6%), that at m/z = 758, corresponding to loss of a carbonyl and the monodentate L' ligand.

#### 4. Conclusions

The synthesis and structural characterization of trifluoroacetatecarbonylrhenium(I) complexes bearing different mono- and bidentate mixed-phosphite ligands are described. The new complexes were prepared by the reaction of the parent bromo-complexes with silver trifluoroacetate. All the complexes were studied by spectroscopic techniques and, in the cases of complexes **1** and **2a**, structures in the solid state were determined by X-ray diffraction. In all cases the trifluoroacetate ligand behaves in a monodentate manner.

#### Supplementary data

CCDC 719369 and 719370 contains the supplementary crystallographic data for compounds **1** and **2a**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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