Electronic Supplementary Information

Taking TiF_4 complexes to extremes – the first examples with phosphine co-ligands

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Synthesis of N- and O-donor ligand complexes

Experimental

[TiF_4(2,2'-bipy)]: [$TiF_4(thf)_2$] (0.265 g, 1.0 mmol) was dissolved in CH_2Cl_2 (5 mL) and a solution of 2,2'-bipyridyl (0.155 g, 1.0 mmol) in CH_2Cl_2 (5 mL) added via a syringe. The solution was stirred for 30 min, concentrated to ~5 mL and refrigerated overnight. The white solid which deposited was filtered off and dried *in vacuo*. Yield: 0.13 g, 46%. Required for $C_{10}H_8F_4N_2Ti$ (280.1): C, 42.9; H, 2.9; N, 10.0. Found: C, 42.6; H, 2.7; N, 9.8%. ^{1}H NMR (CD_2Cl_2): δ 7.65 (m) [2H], 8.15 (m) [4H], 8.65 (t) [2H]. $^{19}F\{^1H\}$ NMR (CH_2Cl_2) 293 K: 207.7 (s) [2F], 140.3 (s) [2F]; 223 K: 204.3 (t) [2F], 136.9 (t) [2F] $^2J_{FF}$ = 35 Hz. IR (Nujol/cm^{-1}): 664, 622, 592, 560 ν(TiF). UV/vis (diffuse reflectance) E_{max}/cm^{-1}: 38700, 30700(sh). Small colourless crystals were grown by refrigerating (260 K) the filtrate, and also by vapour diffusion of diethyl ether into a CH_2Cl_2 solution of the complex. The following complexes were made similarly.

[TiF_4(1,10-phen)]: White powder. Yield: 56%. Required for $C_{12}H_8F_4N_2Ti$ (304.1): C, 47.4; H, 2.7; N, 9.2. Found: C, 47.6; H, 2.5; N, 9.6%. ^{1}H NMR (CD_2Cl_2): δ 7.63 (m) [2H], 7.85 (s) [2H], 8.25 (dd) [2H], 9.19 (t) [2H]. $^{19}F\{^1H\}$ NMR (CH_2Cl_2) 293 K: 210.4 (s) [2F], 141.6 (s)

[2F]; 243 K: 208.2 (t) [2F], 140.1 (t) [2F] $^2J_{FF}$ = 33 Hz. IR (Nujol/cm^{-1}): 645, 618, 569 TiF. UV/vis (diffuse reflectance) E_{max}/cm^{-1}: 38600, 33000(sh).

***Cis*-[TiF$_4$(py)$_2$]:** White powder. Yield: 60%. Required for $C_{10}H_{10}F_4N_2Ti$ (282.1): C, 42.6; H, 3.6; N, 9.9. Found: C, 43.4; H, 3.7; N, 10.1%. ^{1}H NMR (CD_2Cl_2): δ 7.45 (s) [2H], 7.90 (s) [H], 8.93 (s) [2H]. ^{19}F{^{1}H}NMR (CH_2Cl_2) 293 K: 218.3 (s) [2F], 150.8 (s) [2F]; 243 K: 213.8 (t) [2F], 151.6 (t) [2F] $^2J_{FF}$ = 28 Hz. IR (Nujol/cm^{-1}): 654, 638, 631, 570 ν(TiF). UV/vis (diffuse reflectance) E_{max}/cm^{-1}: 38600, 33000(sh).

[TiF$_4${Me$_2$N(CH$_2$)$_2$NMe$_2$}]: The reaction solution was filtered and then reduced to dryness *in vacuo* and the white residue washed with diethyl ether. Yield: 75%. Required for $C_6H_{16}F_4N_2Ti$ (240.1): C, 30.0; H, 6.7; N, 11.7. Found: C, 30.1; H, 7.0; N, 11.3%. ^{1}H NMR (CD_2Cl_2): δ 2.71 (s) [3H], 2.80 (s) [H]. ^{19}F{^{1}H} NMR (CH_2Cl_2) 293 K: 199.1 (t) [2F], 145.2 (t) [2F] $^2J_{FF}$ = 37 Hz. IR (Nujol/cm^{-1}): 630, 604(br) ν(TiF). UV/vis (diffuse reflectance) E_{max}/cm^{-1}: 45500, 35700(sh).

***Cis*-[TiF$_4$(pyNO)$_2$]:** White powder. Yield: 75%. Required for $C_{10}H_{10}F_4N_2O_2Ti$ (314.1): C, 38.2; H, 3.2; N, 8.9. Found: C, 38.0; H, 2.6; N, 8.7%. ^{1}H NMR (CD_2Cl_2): δ 7.40 (s) [2H], 8.23 (br) [3H]. ^{19}F{^{1}H} NMR (CH_2Cl_2) 293 K: 170.7 (s) [2F], 136.9 (s) [2F]; 223 K: 162.4 (t) [2F], 134.2 (t) [2F] $^2J_{FF}$ = 35 Hz. IR (Nujol/cm^{-1}): 1223, 1208 ν(NO), 630, 580(br) ν(TiF). UV/vis (diffuse reflectance) E_{max}/cm^{-1}: 45500, 40000, 33000(sh).

***Cis*-[TiF$_4$(Ph$_3$PO)$_2$]:** Colourless crystals. Yield: 56%. Required for $C_{36}H_{30}F_4O_2P_2Ti$ (680.5): C, 63.6; H, 4.4. Found: C, 62.9; H, 3.9%. ^{1}H NMR (CD_2Cl_2): δ 7.3–7.7 (m). ^{19}F{^{1}H} NMR (CH_2Cl_2) 293 K: 200.7 (s) [2F], 140.7 (s) [2F]; 243 K: 195.7 (t) [2F], 137.9 (t) [2F] $^2J_{FF}$ = 38

Hz. $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2) 293 K: 40.2 (s); 200 K: 41.7 (s). IR (Nujol/cm^{-1}): 1152, 1067 ν(PO), 640, 620, 596 ν(TiF). UV/vis (diffuse reflectance) E_{max}/cm^{-1}: 43100, 38500. Crystals were obtained directly from the reaction filtrate after isolating the bulk material.

***Cis*-[$TiF_4(Me_3PO)_2$]:** Colourless powder. Yield: 73%. Required for $C_6H_{18}F_4O_2P_2Ti$ (308.0): C, 23.4; H, 5.9. Found: C, 22.6; H, 6.2%. ^{1}H NMR (CD_2Cl_2): δ 2.15 (s). $^{19}F\{^{1}H\}$ NMR (CH_2Cl_2) 293 K: 188.2 (s) [2F], 127.4 (s) [2F]; 243 K: 179.5 (t) [2F], 127.5 (t) [2F] $^{2}J_{FF}$ = 38 Hz. $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2) 293 K: 63.1 (s). IR (Nujol/cm^{-1}): 1155(m), 1075(br) ν(PO), 640(sh), 620, 580 ν(TiF). UV/vis (diffuse reflectance) E_{max}/cm^{-1}: 44100, 38600.

***Cis*-[$TiF_4(Ph_3AsO)_2$]**: Colourless crystals. Yield: 59%. Required for $C_{36}H_{30}As_2F_4O_2Ti{\cdot}CH_2Cl_2$ (853.3): C, 52.1; H, 3.8. Found: C, 51.7; H, 3.7%. ^{1}H NMR (CD_2Cl_2): δ 7.3–7.7 (m). $^{19}F\{^{1}H\}$ NMR (CH_2Cl_2) 293 K: 160.8 (t) [2F], 121.2 (t) [2F] $^{2}J_{FF}$ = 35 Hz. IR (Nujol/cm^{-1}): 845(br) ν(AsO), 640(sh), 616, 595, 570 ν(TiF). UV/vis (diffuse reflectance) E_{max}/cm^{-1}: 45500, 36400. Crystals were grown by vapour diffusion of diethyl ether into a CH_2Cl_2 solution of the complex.

[TiF_4{$Ph_2P(O)CH_2P(O)Ph_2$}]: Colourless crystals. Yield: 48%. Required for $C_{25}H_{22}F_4O_2P_2Ti$ (540.3): C, 55.6; H, 4.1. Found: C, 55.2; H, 4.2%. ^{1}H NMR (CD_2Cl_2): δ 7.3–7.7 (m), 5.2 (s,br). $^{19}F\{^{1}H\}$ NMR (CH_2Cl_2) 293 K: 218.8 (t) [2F], 135.7 (t) [2F] $^{2}J_{FF}$ = 35 Hz. $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2) 293 K: 40.1 (s). IR (Nujol/cm^{-1}): 1156, 1100 ν(PO), 657, 639, 622, 600(sh) ν(TiF). UV/vis (diffuse reflectance) E_{max}/cm^{-1}: 45000, 39100, 36400(sh).