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Synthesis of Group 10 polyfluorothiolate mono- and bi-nuclear complexes. Crystal structures of [Ni(SC_6HF_4)$_2$(dppe)], [(dppe)Ni(μ-SC_6HF_4)$_2$Pd(C_6F_5)$_2$] and [(dppe)Ni(μ-SC_6F_5)$_2$Pd(C_6F_5)$_2$]

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Abstract

Complexes of the general formula *cis*-[M(2,3,5,6-SC_6HF_4)$_2$(L–L)] (M = Ni, Pd, Pt; L–L = dppm [bis(diphenylphosphino)methane], dppe [1,2-bis(diphenylphosphino)ethane]) have been synthesized (yield > 75%) by the reaction (1:2) between the corresponding *cis*-[MCl_2(L–L)] and Tl(SC_6HF_4). These compounds, when treated with *cis*-[M(C_6F_5)$_2$(THF)$_2$] (M = Pd, Pt; THF = OC_4H_8), quantitatively give rise to homo- or heterobinuclear compounds, (including two pairs of coordination position isomers). All of them have been characterized through IR, NMR and Mass spectrometries. The crystal structures of [Ni(SC_6HF_4)$_2$(dppe)], [(dppe)Ni(μ-SC_6HF_4)$_2$Pd(C_6F_5)$_2$] and [(dppe)Ni(μ-SC_6F_5)$_2$Pd(C_6F_5)$_2$] have been determined, and the different interfacial π–π interactions between aromatic rings, which depend on the nature of the polyfluorothiolate ring, are analyzed.

Keywords: Organometallic compounds; π–π Interactions; Thiolates; Group 10; Homo- and heterobinuclear; Crystal structures

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1. Introduction

In our studies [1–4] about complexes containing the SC_6F_5 ligand, we have frequently found interfacial interactions between aromatic rings, most of them intra- but sometimes intermolecular. According to Hunter and Sanders [5] such π–π interactions are of a mainly electrostatic nature and are enhanced by the presence of polarizing substituents on the rings.

In order to widen the scope of our research, we have studied the presumably similar 2,3,5,6-SC_6HF_4 ligand, and found its interfacial interactions to be markedly different from those of the SC_6F_5 ligand.

In this paper, we describe the isolation of compounds of the type *cis*-[M(SC_6HF_4)$_2$(L–L)] (M = Ni, Pd, Pt; L–L = dppm, dppe), and their reaction with the '*cis*-M′(C_6F_5)$_2$' moieties (M′ = Pd, Pt) to give binuclear [(L–L)M(μ-SC_6HF_4)$_2$M′(C_6F_5)$_2$] complexes. We also compare them with their pentafluorotiophenolato homologues.

As has repeatedly been shown [2,6,7], the tetrahydrofurane ligands in the complexes *cis*-[M(C_6F_5)$_2$(THF)$_2$] (M = Pd, Pt; THF = OC_4H_8) can readily be displaced, and the reaction proceeds with stereoretention, which makes these complexes especially valuable as reagents for the synthesis of *gem*-isomers, provided the availability of a compound with two potentially bridging ligands, preferably in a *cis*-geometry.

2. Experimental

2.1. General procedures

All reactions were carried out at room temperature (r.t.) in solvents purified by standard procedures [8]. The compounds Tl(SC_6HF_4) [9], [MCl_2(dppe)] (M = Ni [10], Pd [11], Pt [12]), [MCl_2(dppm)] (M = Pd [11], Pt [12]), and *cis*-[M(C_6F_5)$_2$(THF)$_2$] (M = Pd, Pt) [13] were prepared by previously published procedures.

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C, H and S analyses were performed with a Carlo Erba EA 1108 microanalyser. IR spectra were recorded (over the range 4000–250 cm^{-1}) on Perkin–Elmer 833 or 1730 FT spectrophotometers, using Nujol mulls between polyethylene sheets [14]. The ^{1}H, ^{19}F and ^{31}P spectra of $CDCl_3$ solutions of the compounds (except for **14**, which had to be dissolved in hexadeuteroacetone) were run on Varian UNITY-300 or Bruker ARX-300 spectrometers; chemical shifts are relative to TMS, $CFCl_3$ or, respectively, external 85% H_3PO_4.

Mass spectrometric data were obtained using FAB^{+} and FAB^{-} techniques on a VG Autospec apparatus; the matrix was 3-nitrobenzylalcohol and the samples were dissolved in CH_2Cl_2.

2.2. Syntheses

2.2.1. General procedure for the synthesis of compounds of the type $[M(SC_6HF_4)_2(L–L)]$ (L–L = dppe, M = Ni (1), Pd (2), Pt (3); L–L = dppm, M = Pd (4), Pt (5))

The corresponding dichloro(diphosphino)metal(II) complex was reacted (1:2) with $Tl(SC_6HF_4)$, and the formed TlCl was removed by filtration. The solution was evaporated to dryness and the residue was repeatedly washed with hexane or diethyl ether. A typical preparation was as follows.

*2.2.1.1. $[Ni(SC_6HF_4)_2(dppe)]$ (**1**).* To an orange suspension of 0.2643 g (0.5 mmol) of $[NiCl_2(dppe)]$ in acetone (15 cm^3) was added 0.3859 g (1.0 mmol) of $Tl(SC_6HF_4)$. The solution immediately turned red and an extremely fine, white precipitate was observed.

After 18 h stirring, the formed TlCl was filtered off, and the solvent was evaporated in vacuo. Hexane (2 ml) was added and the resulting reddish solid was filtered off, washed with a further 1 ml of hexane and vacuum dried. Yield: 78%. Anal. Found: C, 55.56; H, 3.21; S, 7.47. Calc. for $C_{38}H_{26}F_8NiP_2S_2$: C, 55.70; H, 3.20; S, 7.83%. IR (cm^{-1}): SC_6HF_4, ν(C–F) 1233m, 1217m, 1188m, 1169m; ν(C–S) 909vs. ^{1}H-NMR (δ, ppm): CH_2, 2.2 (m), SC_6HF_4, 6.4 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, −133.7 (m, F_o), −143.4 (m, F_m). $^{31}P\{^{1}H\}$-NMR (δ, ppm): 56.6 (s). MS (*m*/*z*) FAB^{+}: M, 819(3%); M–(SC_6HF_4), 637(100%); M–(C_6H_5), 741(1%); M–(SC_6HF_4+2C_6H_5+Ni), 428(8%). FAB^{-}: M, 819(3%); M–(4C_6H_5), 512(20%); M–(2C_6H_5), 666(3%); M–(2C_6H_5+SC_6HF_4+Ni), 428(14%).

*2.2.1.2. Compound **2**.* Yield: 88%. Anal. Found: C, 52.10; H, 3.21, S, 7.46. Calc. for $C_{38}H_{26}F_8P_2PdS_2$: C, 52.64; H, 3.02; S, 7.40%. IR (cm^{-1}): SC_6HF_4, ν(C–F) 1218m, 1168vs; ν(C–S) 908vs. ^{1}H-NMR (δ, ppm): CH_2, 2.4 (m), SC_6HF_4, 6.4 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, −133.6 (m, F_o), −143.2 (m, F_m). $^{31}P\{^{1}H\}$-NMR (δ, ppm): 57.5 (s). MS (*m*/*z*) FAB^{+}: M, 865(5%); M–(C_6H_5), 790(7%); M–(SC_6HF_4), 685(100%); M–(2SC_6HF_4), 504(29%); M–(2SC_6HF_4+C_6H_5), 429(38%). FAB^{-}: M, 866(5%); M–(2SC_6HF_4+2C_6H_5), 350(11%).

*2.2.1.3. Compound **3**.* Yield: 87%. Anal. Found: C, 47.62; H, 2.87; S, 6.67. Calc. for $C_{38}H_{26}F_8P_2PtS_2$: C, 47.75; H, 2.74; S, 6.71%. IR (cm^{-1}): SC_6HF_4, ν(C–F) 1219s, 1169vs; ν(C–S) 909vs. ^{1}H-NMR (δ, ppm): CH_2, 2.3 (m), SC_6HF_4, 6.4 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, −133.1 (m, F_o), −142.9 (m, F_m). $^{31}P\{^{1}H\}$-NMR (δ, ppm): 45.8 (t, $J_{Pt–P}$ = 2997 Hz). MS (*m*/*z*): FAB^{+}: M, 955(8%); M–(SC_6HF_4), 774(76%); M–(C_6H_5), 879(2%); M–(2SC_6HF_4), 592(6%); M–(2SC_6HF_4+C_6H_5), 516(6%). FAB^{-}: M, 955(4%); M–(SC_6HF_4+2C_6H_5), 620(3%); M–(dppe+SC_6HF_4), 375(7%).

*2.2.1.4. Compound **4**.* Yield: 95%. Anal. Found: C, 51.83; H, 2.78; S, 7.29. Calc. for $C_{37}H_{24}F_8P_2PdS_2$: C, 52.10; H, 2.84; S, 7.52%. IR (cm^{-1}): SC_6HF_4, ν(C–F) 1218m, 1168s; ν(C–S) 909vs; dppm, ν(chelate) 538m. ^{1}H-NMR (d, ppm): CH_2, 4.1 (t, $J_{P–H}$ = 10 Hz), SC_6HF_4, 6.4 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, −132.3 (m, F_o), −142.3 (m, F_m). $^{31}P\{^{1}H\}$-NMR (δ, ppm): −40.3 (s). MS (*m*/*z*) FAB^{+}: M, 851(7%); M–(C_6H_5), 776(9%); M–(SC_6HF_4), 670(100%); M–(2SC_6HF_4), 490(24%). FAB^{-}: M, 851(23%); M–(dppm), 468(21%); M–(2SC_6HF_4), 491(18%); M–(2SC_6HF_4+C_6H_5), 413(5%).

*2.2.1.5. Compound **5**.* Yield: 76%. Anal. Found: C, 46.90; H, 2.70; S, 6.98. Calc. for $C_{37}H_{24}F_8P_2PtS_2$: C, 47.19; H, 2.57; S, 6.81%. IR (cm^{-1}): SC_6HF_4, ν(C–F) 1220s, 1191m, 1169s; ν(C–S) 909vs; dppm, ν(chelate) 548s. ^{1}H-NMR (δ, ppm): CH_2, 4.3 (t, $J_{P–H}$ = 11, $J_{Pt–H}$ = 54 Hz), SC_6HF_4, 6.4 (m). ^{19}F-NMR (d, ppm): SC_6HF_4, −131.9 (d, F_o), −142.0 (m, F_m). $^{31}P\{^{1}H\}$-NMR (δ, ppm): −50.1 (t, $J_{Pt–P}$ = 2575 Hz). MS (*m*/*z*) FAB^{+}: M, 941(4%); M–(C_6H_5), 865(4%); M–(SC_6HF_4), 760(100%); M–(SC_6HF_4+2C_6H_5), 608(4%); M–(SC_6HF_4+dppm), 378(10%); M–(C_6H_5+2SC_6HF_4), 501(7%). FAB^{-}: M, 942(100%); M–(4C_6H_5), 634(67%); M–(4C_6H_5+SC_6HF_4+Pt), 259(82%).

2.2.2. General procedure for the synthesis of compounds of the type $[(L–L)M(\mu\text{-}SC_6HF_4)_2M'(C_6F_5)_2]$ (L–L = dppe, M′ = Pd, M = Ni (6), Pd (7), Pt (8); L–L = dppe, M′ = Pt, M = Ni (9), Pd (10), Pt (11); L–L = dppm, M′ = Pd, M = Pd (12), Pt (13); L–L = dppm, M′ = Pt, M = Pd (14), Pt (15))

The necessary bis(tetrafluorothiophenolato)diphosphino-metal(II) complex was treated (1:1) with the corresponding *cis*-$[M'(C_6F_5)_2(THF)_2]$ species. The solvent was removed and the residue washed with methanol or diethyl ether. A standard preparation is described below.

2.2.2.1. [(dppe)Ni(μ-SC_6HF_4)$_2$Pd(C_6F_5)$_2$] (**6**). *cis*-[Pd(C_6F_5)$_2$(THF)$_2$] 0.0585 g (0.1 mmol) were added to a red solution of 0.0819 g (0.1 mmol) of [Ni(SC_6HF_4)$_2$(dppe)] in dichloromethane (20 cm^3).

After 6 h stirring, the solution was evaporated to dryness; methanol (1 ml) was added and the red solid was filtered off, washed with methanol (2 × 0.5 ml) and dried in vacuo, over P_2O_5. Yield: 72%. Anal. Found: C, 47.21; H, 2.07; S, 5.04. Calc. for $C_{50}H_{26}F_{18}NiP_2PdS_2$: C, 47.67; H, 2.08; S, 5.09%. IR (cm^{-1}): C_6F_5 and SC_6HF_4, ν(C–F) 1222m, 1168m, 1055s; ν(C–S) 913s; ν(X-sensitive) 787m, 777m. ^{1}H-NMR (δ, ppm): CH_2, 2.2 (m), SC_6HF_4, 6.5 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, −130.4 (m, F_o), −140.0 (m, F_m); C_6F_5, −116.7 (d, $J_{om} = 26$ Hz, F_o), −165.2 (m, F_m), −163.2 (t, $J_{mp} = 19$ Hz, F_p). $^{31}P\{^1H\}$-NMR (δ, ppm): 54.7 (s). MS (*m/z*) FAB^+: M–($2C_6H_5$), 1105(5%); M–(C_6F_5), 1092(5%); M–(SC_6HF_4), 1078(4%); M–($2C_6F_5$), 925(16%); M–(dppe), 861(9%); M–(dppe + Ni + SC_6HF_4), 622(74%); M–($2C_6F_5$ + SC_6HF_4), 745(33%). FAB^-: M, 1258(5%); M–(dppe + Ni + SC_6HF_4), 622(100%); M–($2C_6F_5$ + SC_6HF_4 + $3C_6H_5$), 513(19%); M–($2C_6F_5$ + SC_6HF_4 + $3C_6H_5$ + Ni), 455(44%); M–(C_6F_5 + $2SC_6HF_4$ + $4C_6H_5$ + Pd + Ni), 259(59%).

2.2.2.2. Compound **7**. Yield: 60%. Anal. Found: C, 45.49; H, 1.94; S, 4.89. Calc. for $C_{50}H_{26}F_{18}P_2Pd_2S_2$: C, 45.93; H, 2.00; S, 4.90%. IR (cm^{-1}): C_6F_5 and SC_6HF_4, ν(C–F) 1226m, 1168s, 1054s; ν(C–S) 913vs; ν(X-sensitive) 786s, 776s. ^{1}H-NMR (δ, ppm): CH_2, 2.4 (m), SC_6HF_4, 6.5 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, −131.4 (m, F_o), −140.4 (m, F_m); C_6F_5, −117.1 (d, $J_{om} = 33$ Hz, F_o), −165.2 (m, F_m), −163.2 (t, $J_{mp} = 19$ Hz, F_p). $^{31}P\{^1H\}$-NMR (δ, ppm): 59.2 (s). MS (*m/z*) FAB^+: M–(C_6F_5), 1140(4%); M–($2C_6F_5$), 973(10%); M–($2C_6F_5$ + Pd), 867(7%); M–($2C_6F_5$ + SC_6HF_4 + Pd), 686(57%); M–($2C_6F_5$ + SC_6HF_4), 792(47%); M–($2C_6F_5$ + SC_6HF_4 + C_6H_5), 715(12%). FAB^-: M–(dppe + Pd + SC_6HF_4), 622(100%); M–($2C_6F_5$ + SC_6HF_4 + $3C_6H_5$ + Pd), 455(47%); M–(C_6F_5 + $2SC_6HF_4$ + $4C_6H_5$ + 2Pd), 259(26%).

2.2.2.3. Compound **8**. Yield: 54%. Anal. Found: C, 42.79; H, 1.73; S, 4.72. Calc. for $C_{50}H_{26}F_{18}P_2PdPtS_2$: C, 43.01; H, 1.88; S, 4.59%. IR (cm^{-1}): C_6F_5 and SC_6HF_4, ν(C–F) 1221s, 1174vs, 1056vs, 1000m; ν(C–S) 916s; ν(X-sensitive) 785s, 778s. ^{1}H-NMR (δ, ppm): CH_2, 2.2 (m), SC_6HF_4, 6.5 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, −131.0 (m, F_o), −140.3 (m, F_m); C_6F_5, −117.5 (d, $J_{om} = 29$ Hz, F_o), −165.2 (m, F_m), −162.9 (t, $J_{mp} = 19$ Hz, F_p). $^{31}P\{^1H\}$-NMR (δ, ppm): 44.4 (s $J_{Pt-P} = 3061$ Hz). MS (*m/z*) FAB^+: M, 1395(3%); M–($2C_6F_5$), 1061(4%); M–($2C_6F_5$ + SC_6HF_4), 881(65%); M–($2C_6F_5$ + SC_6HF_4 + Pd), 774(100%); M–($2C_6F_5$ + SC_6HF_4 + Pt), 686(20%). FAB^-: M, 1396(3%); M–(dppe + Pt + SC_6HF_4), 622(100%); M–($2C_6F_5$ + SC_6HF_4 + $3C_6H_5$ + Pt), 455(25%); M–(C_6F_5 + $2SC_6HF_4$ + $4C_6H_5$ + Pd + Pt), 258(15%).

2.2.2.4. Compound **9**. Yield: 60%. Anal. Found: C, 44.13; H, 1.93; S, 4.47. Calc. for $C_{50}H_{26}F_{18}NiP_2PtS_2$: C, 44.53; H, 1.94; S, 4.76%. IR (cm^{-1}): C_6F_5 and SC_6HF_4, ν(C–F) 1257s, 1221s, 1174s, 1060vs; ν(C–S) 916vs; ν(X-sensitive) 802s, 792s. ^{1}H-NMR (δ, ppm): CH_2, 2.3 (m), SC_6HF_4, 6.5 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, −129.9 (m, F_o), −139.6 (m, F_m); C_6F_5, −120.1 (d, $J_{om} = 23$ Hz, $J_{Pt-F} = 445$ Hz, F_o), −166.3 (m, F_m), −164.5 (t, $J_{mp} = 19$ Hz, F_p). $^{31}P\{^1H\}$-NMR (δ, ppm): 55.2 (s). MS (*m/z*) FAB^+: M, 1348(5%); M–(C_6F_5), 1181(7%); M–($2C_6F_5$ + SC_6HF_4), 833(9%); M–(SC_6HF_4 + C_6F_5), 1000(8%); M–($2C_6F_5$ + SC_6HF_4 + Ni), 774(14%); M–(SC_6HF_4 + $2C_6F_5$ + Pt), 637(100%). FAB^-: M, 1348(8%); M–($2C_6F_5$ + $2C_6H_5$ + Ni), 802(12%); M–($2C_6F_5$ + $4C_6H_5$ + SC_6HF_4), 525(55%); M–(C_6F_5 + $2SC_6HF_4$ + $4C_6H_5$ + Pt + Ni), 258(51%).

2.2.2.5. Compound **10**. Yield: 71%. Anal. Found: C, 42.62; H, 1.81; S, 4.19. Calc. for $C_{50}H_{26}F_{18}P_2PdPtS_2$: C, 43.01; H, 1.88; S, 4.59%. IR (cm^{-1}): C_6F_5 and SC_6HF_4, ν(C–F) 1222s, 1191m, 1173vs; ν(C–S) 915vs; ν(X-sensitive) 802s, 791s. ^{1}H-NMR (δ, ppm): CH_2, 2.4 (m), SC_6HF_4, 6.5 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, −131.2 (m, F_o), −140.1 (m, F_m); C_6F_5, −120.3 (d, $J_{om} = 26$ Hz, $J_{Pt-F} = 474$ Hz, F_o), −166.3 (m, F_m), −164.6 (t, $J_{mp} = 19$ Hz, F_p). $^{31}P\{^1H\}$-NMR (δ, ppm): 58.5 (s). MS (*m/z*) FAB^+: M, 1396(7%); M–(C_6F_5), 1228(8%); M–($2C_6F_5$), 1061(6%); M–(SC_6HF_4), 1215(5%); M–(SC_6HF_4 + $2C_6F_5$), 881(41%); M–($2C_6F_5$ + SC_6HF_4 + Pd), 774(13%); M–(SC_6HF_4 + $2C_6F_5$ + Pt), 685(100%); M–(C_6F_5 + SC_6HF_4), 1047(11%). FAB^-: M, SC_6HF_4(7%); M–($2C_6H_5$), 1240(16%); M–($2C_6H_5$ + $2C_6F_5$), 908(5%); M–(dppe + Pd + $2SC_6HF_4$), 530(25%); M–($2C_6F_5$ + $4C_6H_5$ + SC_6HF_4), 573(5%); M–(C_6F_5 + $2SC_6HF_4$ + $4C_6H_5$ + Pd + Pt), 259(100%).

2.2.2.6. Compound **11**. Yield: 79%. Anal. Found: C, 39.97; H, 1.78; S, 4.00. Calc. for $C_{50}H_{26}F_{18}P_2Pt_2S_2$: C, 40.44; H, 1.76; S, 4.32%. IR (cm^{-1}): C_6F_5 and SC_6HF_4, ν(C–F) 1223m, 1174s, 1060vs; ν(C–S) 917vs; ν(X-sensitive) 802m, 792m. ^{1}H-NMR (δ, ppm): CH_2, 2.2 (m), SC_6HF_4, 6.5 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, −131.1 (m, F_o), −139.9 (m, F_m); C_6F_5, −120.5 (d, $J_{om} = 25$ Hz, $J_{Pt-F} = 419$ Hz, F_o), −166.1 (m, F_m), −164.2 (t, $J_{mp} = 20$ Hz, F_p). $^{31}P\{^1H\}$-NMR (δ, ppm): 46.3 (s, $J = 3016$ Hz). MS (*m/z*) FAB^+: M, 1486(6%); M–(C_6F_5), 1317(11%); M–($2C_6F_5$), 1150(17%); M–($2C_6F_5$ + SC_6HF_4), 969(30%); M–($2C_6F_5$ + SC_6HF_4 + Pt), 774(100%); M–(dppe + Pt), 892(18%). FAB^-: M, 1484(6%); M–($2C_6F_5$ + SC_6HF_4 + dppe), 572(8%); M–(C_6F_5 + $2SC_6HF_4$ + $4C_6H_5$ + 2Pt), 258(100%).

2.2.2.7. Compound ***12***. Yield: 66%. Anal. Found: C, 45.10; H, 1.73; S, 4.56. Calc. for $C_{49}H_{24}F_{18}P_2Pd_2S_2$: C, 45.50; H, 1.87; S, 4.96%. IR (cm^{-1}): C_6F_5 and SC_6HF_4, *v*(C–F) 1230m, 1173m, 1057s, 998m; *v*(C–S) 914vs; *v*(X-sensitive) 786s, 777s; dppm, *v*(chelate) 542s. ^{1}H-NMR (d, ppm): CH_2, 4.3 (t, J_{P-H} 11 Hz), SC_6HF_4, 6.5 (m). ^{19}F-NMR (d, ppm): SC_6HF_4, -129.3 (m, F_o), -139.2 (m, F_m); C_6F_5, -116.1 (d, $J_{om} = 28$ Hz, F_o), -164.9 (m, F_m), -162.8 (t, $J_{mp} = 19$ Hz, F_p). $^{31}P\{^1H\}$-NMR (δ, ppm): -41.4 (s). MS (*m*/*z*) FAB$^+$: $M-(C_6F_5+SC_6HF_4)$, 945(2%); $M-(2C_6F_5+SC_6HF_4)$, 779(20%); $M-(2C_6F_5+SC_6HF_4+Pd)$, 671(58%). FAB$^-$: M, 1292(7%); $M-(dppm+Pd+SC_6HF_4+C_6F_5)$, 454(17%); $M-(SC_6HF_4+2C_6F_5+2C_6H_5)$, 623(100%).

2.2.2.8. Compound ***13***. Yield: 69%. Anal. Found: C, 42.05; H, 1.53; S, 4.07. Calc. for $C_{49}H_{24}F_{18}P_2PdPtS_2$: C, 42.58; H, 1.75; S, 4.64%. IR (cm^{-1}): C_6F_5 and SC_6HF_4, *v*(C–F) 1226s, 1170s, 1055vs,999s; *v*(C–S) 915vs; *v*(X-sensitive) 786s, 778s; dppm, *v*(chelate) 555vs. ^{1}H-NMR (δ, ppm): CH_2, 4.6 (t, J_{P-H} 11 Hz), SC_6HF_4, 6.5 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, -129.0 (m, F_o), -139.2 (m, F_m); C_6F_5, -116.6 (d, $J_{om} = 26$ Hz, F_o), -165.1 (m, F_m), -162.8 (t, $J_{mp} = 19$ Hz, F_p). $^{31}P\{^1H\}$-NMR (δ, ppm): -52.4 (s, $J_{Pt-P} = 2667$ Hz). MS (*m*/*z*) FAB$^+$: $M-(C_6F_5+SC_6HF_4)$, 1034(8%); $M-(2C_6F_5+SC_6HF_4)$, 867(27%); $M-(2C_6F_5+SC_6HF_4+Pd)$, 760(82%); $M-(2C_6F_5+SC_6HF_4+Pt)$, 672(13%). FAB$^-$: M, 1381(5%); $M-(C_6F_5)$, 1214(16%); $M-(C_6F_5+SC_6HF_4)$, 1032(7%); $M-(SC_6HF_4+2C_6F_5+3C_6H_5)$, 635(100%); $M-(SC_6HF_4+2C_6F_5+3C_6H_5+Pd)$, 529(20%).

2.2.2.9. Compound ***14***. Yield: 69%. Anal. Found: C, 41.97; H, 1.70; S, 4.61. Calc. for $C_{49}H_{24}F_{18}P_2PdPtS_2$: C, 42.58; H, 1.75; S, 4.64%. IR (cm^{-1}): C_6F_5 and SC_6HF_4, *v*(C–F) 1249m, 1230m, 1173s, 1060vs, 1014m; *v*(C–S) 914s; *v*(X-sensitive) 800m, 791s; dppm, *v*(chelate) 542m. ^{1}H-NMR (δ, ppm, d^6-acetone): CH_2, 5.2 (t, J_{P-H} 11 Hz), SC_6HF_4, 6.5 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, -129.8 (m, F_o), -139.8 (m, F_m); C_6F_5, -117.6 (d, $J_{om} = 27$ Hz, $J_{Pt-F} = 440$ Hz, F_o), -166.6 (m, F_m), -165.3 (t, $J_{mp} = 19$ Hz, F_p). $^{31}P\{^1H\}$-NMR (δ, ppm): -32.5 (s). MS (*m*/*z*) FAB$^+$: M, 1381(6%); $M-(C_6F_5)$, 1213(11%); $M-(2C_6F_5)$, 1048(9%); $M-(2C_6F_5+SC_6HF_4)$, 865(21%); $M-(2C_6F_5+SC_6HF_4+Pt)$, 671(65%); $M-(2C_6F_5+SC_6HF_4+Pd)$, 761(14%); $M-(C_6F_5+SC_6HF_4)$, 1034(23%); $M-(SC_6HF_4)$, 1199(3%). FAB$^-$: M, 1381(19%); $M-(dppm+SC_6HF_4+Pd)$, 709(100%); $M-(C_6F_5+2SC_6HF_4+4C_6H_5+Pt)$, 349(18%).

2.2.2.10. Compound ***15***. Yield: 69%. Anal. Found: C, 39.87; H, 1.67; S, 4.29. Calc. for $C_{49}H_{24}F_{18}P_2Pt_2S_2$: C, 40.01; H, 1.64; S, 4.36%. IR (cm^{-1}): C_6F_5 and SC_6HF_4, *v*(C–F) 1254m, 1228s, 1177s, 1059vs, 1000m; *v*(C–S) 916vs; *v*(X-sensitive) 801s, 791s; dppm, *v*(chelate) 555vs. ^{1}H-NMR (δ, ppm): CH_2, 4.6 (t, $J_{P-H} = 11$ Hz), SC_6HF_4, 6.5 (m). ^{19}F-NMR (δ, ppm): SC_6HF_4, -129.6 (m, F_o), -139.1 (m, F_m); C_6F_5, -120.2 (d, $J_{om} = 22$ Hz, $J_{Pt-F} = 443$ Hz, F_o), -166.2 (m, F_m), -164.2 (t, $J_{mp} = 19$ Hz, F_p). $^{31}P\{^1H\}$-NMR (δ, ppm): -52.4 (s, $J_{Pt-P} = 2635$ Hz). MS (*m*/*z*) FAB$^+$: M, 1470(3%); $M-(C_6F_5)$, 1303(4%); $M-(2C_6F_5)$, 1136(5%); $M-(2C_6F_5+SC_6HF_4)$, 955(5%); $M-(2C_6F_5+SC_6HF_4+Pt)$, 760(100%). FAB$^-$: M, 1470(7%); $M-(dppm+SC_6HF_4+Pt)$, 709(100%); $M-(C_6F_5+2SC_6HF_4+4C_6H_5+Pt)$, 348(20%).

2.3. Crystal structure determination of [Ni(SC

Crystal data, and data collection and refinement parameters, are summarized in Table 1. Single crystals (reddish parallelepipeds, in every case) were grown by slow diffusion of diethyl ether into a diluted dichloromethane solution of the respective compounds, at r.t. A fragment was mounted on top of a glass fibre, in a drop of HMP lithium grease, and rapidly cooled down to 200 K.

Heavy atom methods [15], were used to locate the transition metal(s), sulfur and phosphorus atoms, while subsequent cycles of full-matrix least-squares refinement [16] and difference Fourier maps were used to locate the remaining non-hydrogen atoms; all non-H atoms, anisotropic. Hydrogen atoms were placed at geometrically calculated positions, and their positional coordinates were constrained (taking into account the temperature) to ride on those of the corresponding carbon atoms, with dependent isotropic displacement parameters. Selected bond lengths and angles are given in Tables 2–4; other crystallographic data are available as supplementary material.

3. Results and discussion

3.1. Mononuclear complexes

Addition (2:1) of thallium *p*-tetrafluorobenzenethiolate to a slurry of *cis*-[MCl_2(L–L)] in acetone leads to the formation of the corresponding bis(tetrafluorothiophenolato) complex.

$$cis[MCl_2(L\text{–}L)] + 2Tl(SC_6HF_4) \rightarrow cis[M(SC_6HF_4)_2(L\text{–}L)] + 2TlCl\downarrow \qquad (1)$$

L–L = dppe; M = Ni (**1**), Pd (**2**), Pt (**3**); L–L = dppm; M = Pd (**4**), Pt (**5**).

The reaction being driven by the scarce solubility of the thallium chloride, which forms as a very fine

Table 1
Crystal data and structure refinement for $[Ni(SC_6HF_4)_2(dppe)]$, $[(dppe)Ni(\mu\text{-}SC_6HF_4)_2Pd(C_6F_5)_2]$ and $[(dppe)Ni(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$

Formula	$C_{38}H_{26}F_8NiP_2S_2$	$C_{50}H_{26}F_{18}NiP_2PdS_2$	$C_{50}H_{22}F_{20}NiP_2PdS_2$
Formula weight	819.36	1259.88	1295.86
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (number 2)	$P2_1/c$ (number 14)	$P2_1/n$ (number 14)
a (Å)	10.082(2)	14.3715(11)	13.5461(14)
b (Å)	11.264(3)	13.4324(9)	23.303(2)
c (Å)	16.936(4)	24.826(2)	15.3644(14)
α (°)	93.63(2)	90	90
β (°)	104.828(15)	100.622(8)	98.716(11)
γ (°)	109.845(14)	90	90
V (Å^3)	1724.8(8)	4710.3(6)	4794.1(8)
Z	2	4	4
D_{calc} (g cm^{-3})	1.578	1.777	1.795
Crystal size (mm^3)	0.27 × 0.27 × 0.19	0.57 × 0.27 × 0.23	0.57 × 0.48 × 0.46
μ (mm^{-1})	0.849	1.047	1.037
Transm factors: max/min	0.992, 0.806	0.703, 0.632	1.000, 0.930
Data collection instrument	Stoe-Siemens AED2	Stoe-Siemens AED2	Stoe-Siemens AED2
Radiation (Å)	Mo–K$_\alpha$, $\lambda = 0.71073$	Mo–K$_\alpha$, $\lambda = 0.71073$	Mo–K$_\alpha$, $\lambda = 0.71073$
Temperature (K)	200	200	200
Scan method	$\omega - \theta$	$\omega - \theta$	$\omega - \theta$
θ Collection range (°)	1.95–25.00	1.67–24.52	1.60–25.51
Measured reflections	6441	9012	9328
Unique data [R_{int}]	6062 [0.0383]	7837 [0.0110]	8934 [0.1083]
Number of parameters refined	460	667	685
R_1 [a] [$I > 2\sigma(I)$], (number of data)	0.0506 (3748)	.0299 (6145)	.0512 (6657)
wR_2 [b] (all data)	0.0891	0.0655	0.1474
Weighting parameters: g_1, g_2 [c]	0.0272, 0.0000	0.0332, 1.2770	0.0739, 10.7980
Quality-of-fit [d] (on F^2)	0.991	0.985	1.062
Largest shift/estimated S.D., final cycle	−0.001	−0.001	−0.001
Largest peak, hole (e Å^{-3})	0.406, −0.347	0.377, −0.439	1.154, −1.630

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma\ w(F_o^2)^2]]^{0.5}$.

[c] $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max(F_o^2; 0) + 2F_c^2]/3$.

[d] Quality-of-fit $= [\Sigma[w(F_o^2 - F_c^2)^2/(N_{observations} - N_{parameters})]^{0.5}$.

Table 2
Selected bond lengths (Å) and angles (°) for $[Ni(SC_6HF_4)_2(dppe)]$ (**1**)

Bond lengths	
Ni1–P1	2.1714(14)
Ni1–P2	2.1817(14)
Ni1–S1	2.2041(14)
Ni1–S2	2.2182(15)
S1–C31	1.751(5)
S2–C41	1.762(4)
Bond angles	
P1–Ni1–P2	85.78(5)
P1–Ni1–S1	97.74(5)
P2–Ni1–S1	175.29(6)
P1–Ni1–S2	161.10(5)
P2–Ni1–S2	85.20(5)
S1–Ni1–S2	92.31(6)
C31–S1–Ni1	113.66(15)
C41–S2–Ni1	113.09(15)

precipitate that must be carefully filtered off. Evaporation of the clear solution to dryness, and addition of diethyl ether or hexane, affords the desired complex.

The IR spectra of the solids show, along with other typical absorptions of the polyfluorophenyl ring [17–19] and those due to the neutral bidentate ligand, a strong band in the 910–915 cm^{-1} region which, by comparison with the homologous pentafluorothiophenolate complexes [7], can be tentatively assigned to the ν(C–S) vibrations of the tetrafluorothiolato groups [19,20].

Complexes **4** and **5** show a strong band at 538 or, 548 cm^{-1}, respectively, characteristic [21] of the dppm ligand acting as a chelate.

The ^{31}P-NMR spectra of complexes **1**–**5** show a single signal (along with the expected platinum satellites in the case of compounds **3** and **5**) indicating that in solution both phosphorus nuclei are equivalent. The negative value (to low frequencies from 85% H_3PO_4, as the reference) of the chemical shift in complexes **4** and **5** proves [21] the chelate character of the bis(diphenylphosphino)methane ligand.

The ^{19}F-NMR spectra of complexes **1**–**5** show (in the −125 to −135 ppm region, assignable to the *ortho*-fluorine nuclei of the tetrafluorothiophenolato groups, see ref. [22]) a multiplet, as expected from the coupling to both *meta*-fluorine and the *para* proton nuclei. No

Table 3
Selected bond lengths (Å) and angles (°) for [(dppe)Ni(μ-$SC_6HF_4)_2Pd(C_6F_5)_2$] (**6**)

Bond lengths	
Ni–P1	2.1849(9)
Ni–P2	2.1966(9)
Ni–S2	2.2640(9)
Ni–S1	2.2826(8)
Pd–C61	2.015(3)
Pd–C51	2.024(3)
Pd–S2	2.3796(8)
Pd–S1	2.3818(8)
S1–C31	1.762(3)
S2–C41	1.771(3)
Bond angles	
P1–Ni–P2	85.28(3)
P1–Ni–S2	173.10(3)
P2–Ni–S2	98.64(3)
P1–Ni–S1	88.56(3)
P2–Ni–S1	173.62(3)
S2–Ni–S1	87.65(3)
C61–Pd–C51	87.15(12)
C61–Pd–S2	93.62(8)
C51–Pd–S2	177.83(9)
C61–Pd–S1	171.72(9)
C51–Pd–S1	96.18(9)
S2–Pd–S1	82.79(3)
C31–S1–Ni	110.68(11)
C31–S1–Pd	110.60(10)
Ni–S1–Pd	90.65(3)
C41–S2–Ni	113.96(12)
C41–S2–Pd	100.36(10)
Ni–S2–Pd	91.16(3)

Table 4
Selected bond lengths (Å) and angles (°) for [(dppe)Ni(μ-$SC_6F_5)_2Pd(C_6F_5)_2$] (**6**)

Bond lengths	
Ni–P2	2.1817(14)
Ni–P1	2.1819(14)
Ni–S1	2.2592(14)
Ni–S2	2.2654(14)
Pd–C61	2.007(5)
Pd–C51	2.021(5)
Pd–S2	2.3719(13)
Pd–S1	2.3780(13)
S1–C31	1.749(6)
S2–C41	1.763(6)
Bond angles	
P2–Ni–P1	85.72(5)
P1–Ni–S1	171.60(6)
P1–Ni–S1	94.69(5)
P2–Ni–S2	92.16(5)
P1–Ni–S2	170.88(6)
S1–Ni–S2	88.71(5)
C61–Pd–C51	91.7(2)
C61–Pd–S2	92.79(14)
C51–Pd–S2	174.12(14)
C61–Pd–S1	174.98(14)
C51–Pd–S1	92.24(14)
S2–Pd–S1	83.51(4)
C31–S1–Ni	114.0(2)
C31–S1–Pd	99.64(18)
Ni–S1–Pd	93.76(5)
C41–S2–Ni	112.0(2)
C41–S2–Pd	101.65(18)
Ni–S2–Pd	93.77(5)

coupling to ^{31}P or ^{195}Pt is observed (i.e. $^{5}J_{P-F}$ and $^{4}J_{Pt-F} \cong 0$).

All these data support a mononuclear nature for complexes **1**–**5** and a *cis* configuration, as proposed in Eq. (1).

3.2. Molecular structure of [$Ni(SC_6HF_4)_2(dppe)$]

Amongst the above described mononuclear complexes which gave single crystals suitable for an X-ray diffraction study, [$Ni(SC_6HF_4)_2$(dppe)] (**1**) was chosen (see Fig. 1 for structure and numbering scheme) since its structure could be compared with that of the analogous compound with pentafluorothiophenolate as a ligand, which has already been established by Torrens et al. [23]. For the sake of comparison, the positional parameters for this last compound have been retrieved from the Cambridge Structural Database [24].

Coordination around the nickel centre in compound (**1**) is distorted square-planar (the angles around Ni1 add to 361.0°, and the mean deviation for the best plane defined by the Ni1, S1, S2, P1 and P2 atoms is 0.176 Å). The bonding angles vary between 85.20(5) and 97.74(6)° although the widest angle is not that opposite to the P1–Ni–P2 which, due to the chelate bite, is necessarily the smallest one. The five-membered NiP_2C_2 chelate ring is puckered [25] (28% twist with axis through Ni1 and P1 and 72% envelope with flap at C1).

The nickel–phosphorus distances (2.171(1) and 2.182(1) Å) are similar and comparable with those of the homologous compound with perfluorobenzenethiolato (2.182(3) and 2.193(3) Å). On the other hand, the Ni–S bond distances in compound (**1**) (2.218(1) and 2.204(1) Å) are close to those found for the pentafluorobenzenethiolato complex (2.216(3) and 2.218(3) Å).

The sulfur–carbon bonds in compound (**1**), (1.751(5) and 1.762(4) Å) are not very different to those found for the pentafluorothiophenolato complex (1.766(10) and 1.761(10) Å). This may appear in clear contrast with the wavenumber of the IR band assigned to mainly the $\nu(C_{ipso}-S)$ stretching [7,19,20]: 858 cm^{-1} for the SC_6F_5 compound against 909 cm^{-1} for the SC_6HF_4 complex (**1**); however, as has already been stated [18,19,26], the so called 'X-sensitive' vibration of C_6F_5-X groups is not a 'pure' carbon-X stretching, but includes the contributions of other motions of the same symmetry species.

A striking difference between both homologous compounds is the absence of interfacial interactions [5] between the aromatic tetrafluorotiophenolato rings of compound **1**, which has been observed before in many pentafluorobenzenetiolato compounds [1–4]. For in-

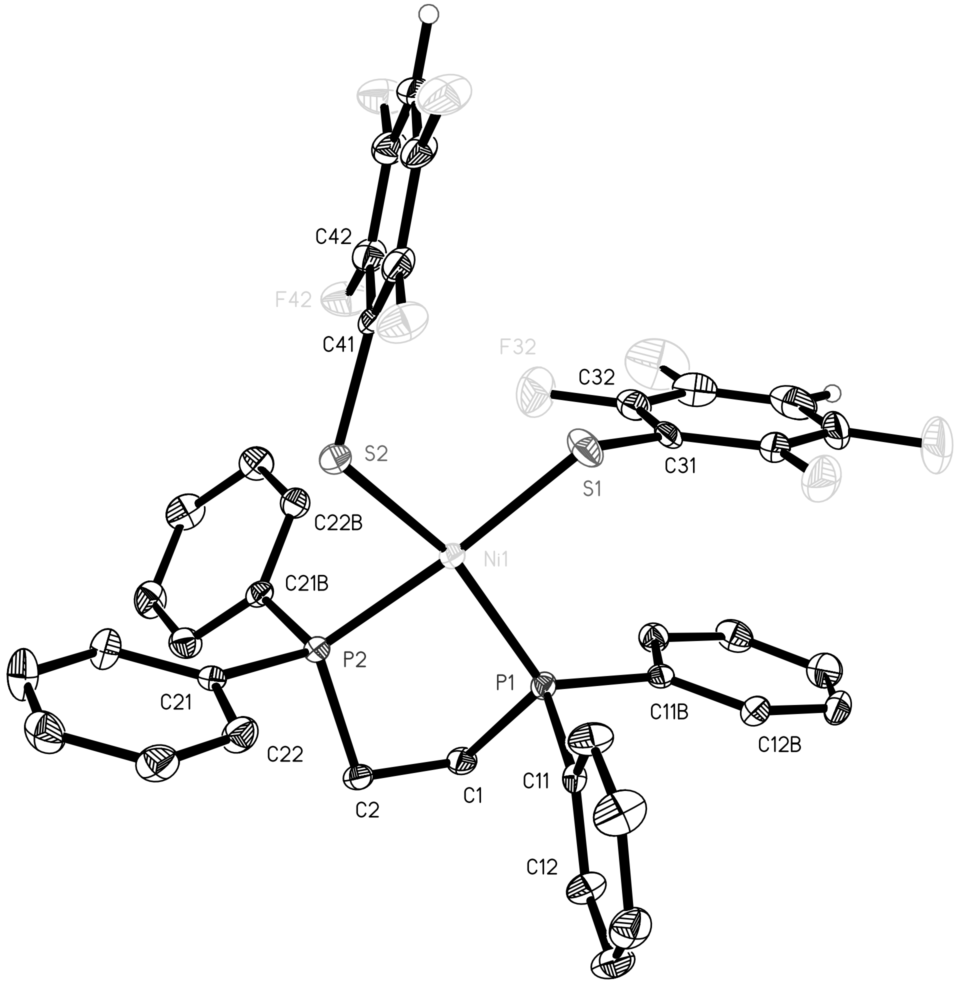


Fig. 1. Molecular structure and numbering scheme for [Ni(SC_6HF_4)$_2$(dppe)] (**1**); ellipsoids at 30% probability.

stance, in [Ni(SC_6F_5)$_2$(dppe)], both rings are almost parallel: they form an angle of only 4.9°, they are set off [5] by 1.781 Å and the mean distance between planes is just 3.226 Å. In compound (**1**), one of the tetrafluorotiophenolato rings is not so parallel to one of the phenylic rings of the diphosphine, with a dihedral angle of 7.1(3)°, a distance between planes (calculated as the mean of the separations of each C_6-centroid to the opposite plane) of 3.322 Å and the offset of the rings is 0.924 Å, while the polyfluorothiolate rings form an angle of 82.00(13)°.

3.3. Binuclear complexes

The *cis*-geometry of the mononuclear complexes, together with the ability of thiolato groups to act as bridging ligands [27], make them especially adequate for the synthesis of *geminal* homo- or heterobinuclear compounds. Selection of the reactants permited the isolation of two pairs of binuclear coordination position isomers.

Thus, when a dichloromethane or acetone solution of *cis*-[M(SC_6HF_4)$_2$(L–L)] is treated with an equivalent amount of *cis*-[M′(C_6F_5)$_2$(THF)$_2$], the two labile tetrahydrofurane groups are readily displaced and the desired dinuclear compound is formed, according to Eq. (2).

$$\begin{aligned} &cis[\mathrm{M(SC_6HF_4)_2(L{-}L)}] + cis[M'(\mathrm{C_6F_5})_2(\mathrm{THF})_2] \\ &\quad \rightarrow [\mathrm{(L{-}L)M(\mu SC_6HF_4)_2}M'(\mathrm{C_6F_5})_2] + 2\mathrm{THF} \end{aligned} \qquad (2)$$

L–L = dppe, M′ = Pd, M = Ni (**6**), Pd (**7**), Pt (**8**); L–L = dppe, M′ = Pt, M = Ni (**9**), Pd (**10**), Pt (**11**); L–L = dppm, M′ = Pd, M = Pd (**12**), Pt (**13**); L–L = dppm, M′ = Pt, M = Pd (**14**), Pt (**15**).

For compounds **6**–**15**, the solvent was evaporated and the residue was washed with diethyl ether and methanol.

The IR spectra of these binuclear complexes (besides other absorptions, which arise from the tetrafluorobenzenethiolato and the pentafluorophenyl rings [17–19]) show two bands in the 805–760 cm^{-1} region (‘X-sensitive vibration’ [18,26]) indicative of a *cis* geometry of the pentafluorophenyl groups, and a somewhat broad peak around 910 cm^{-1} assignable to the $\nu(C_{ipso}-S)$ vibrations of the thiolate moieties.

Amongst other bands due to the neutral ligands, a strong one around 550 cm^{-1}, indicative [21] of chelating dppm, can be observed for compounds **12**–**15**.

The $^{31}P\{^1H\}$-NMR spectra in solution consist of a single peak (flanked by platinum satellites in the case of compounds **8**, **11**, **13**, **15**) the phosphorus nuclei being, thus, magnetically equivalent. Again, the high field position of the resonance (relative to 85% H_3PO_4) in compounds **12**–**15** proves [21] the chelating rôle of the bidentate dppm ligand.

Complexes **6**–**15** show, in the *ortho*-fluorine region, two doublets: one in the −110 to −122 range (pentafluorophenyl) and another between −125 and −135 ppm (tetrafluorobenzenethiolate ligand) [22]; in the case of compounds **8**, **11**, **13**, **15**, the doublet at higher frequency is escorted by ^{195}Pt satellites, as expected.

Due to the scarce solubility of compound **14** in chloroform, its ^{19}F-NMR spectrum was recorded using hexadeuteroacetone as the solvent; at room temperature, a doublet with ^{195}Pt satellites ($\delta = -117.6$ ppm, $^4J_{Pt-F} = 440$ Hz, C_6F_5) and a broad peak ($\delta = -129.8$ ppm, SC_6HF_4) were observed in the *ortho*-fluorine region, the later pointing to an exchange process.

The *meta* fluorine nuclei can be assigned (−139.8 ppm, SC_6HF_4; −166.6 ppm, C_6F_5), since the former signal shows some broadening while the latter multiplet presents a residual coupling to ^{195}Pt in the base of the signal.

In the $^{31}P\{^1H\}$-NMR spectrum, a broad signal was observed at −32.5 ppm, comfirming a dynamic process. Hence, a variable temperature (−85 to +55 °C) $^{31}P\{^1H\}$-NMR study was undertaken, to no avail since always a more or less broad signal is observed, with no splitting nor coalescence. We suppose that various exchange processes coexist (e.g. restricted rotation around the C–S bonds, along with interconversion between the *syn*–*exo*, *syn*–*endo* and *anti* conformers through inversion at the sulfur centres), as commonly encountered [28] in doubly thiolato-bridged binuclear compounds.

Such fluxional behavior has already been described [7] for the homologous perfluorophenylthiolate complex in hexadeuteroacetone solution, for which it was found to be solvent dependent.

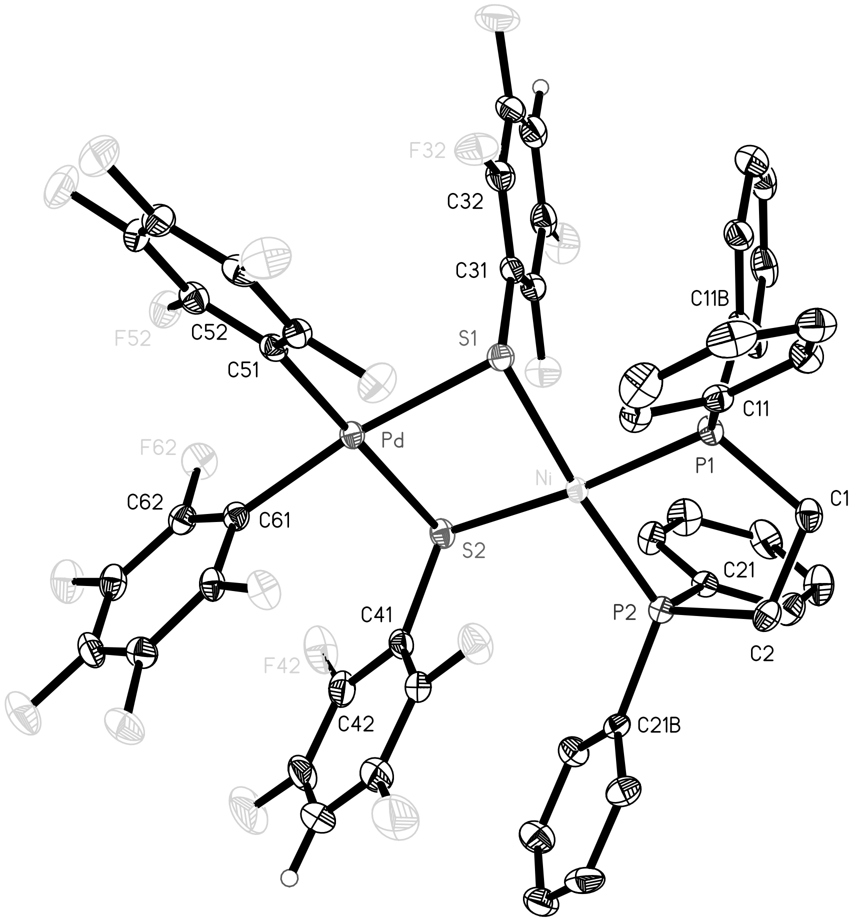
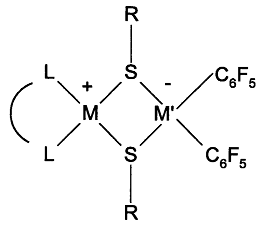


Fig. 2. Molecular structure and numbering scheme for $[(dppe)Ni(\mu-SC_6HF_4)_2Pd(C_6F_5)_2]$ (**6**); ellipsoids at 30% probability.



Scheme 1.

3.4. Mass spectroscopical results

Mass spectra in the FAB^+, as well as in the FAB^- techniques were recorded for the [(L–L)M(μ-$SC_6HF_4)_2M'(C_6F_5)_2$] complexes. Noteworthy general features are as follows.

While in the FAB^+ spectra the $L_2M(SC_6HF_4)$ and (L–L)M(SC_6HF_4)M′ fragments are invariably present, in FAB^- the most important peak is due to the (C_6HF_4S)M′$(C_6F_5)_2$ fragment (this agrees with the formal charge distribution, positive on M and negative on M′) (Scheme 1).

In those compounds containing dppm as the ancillary ligand, a peak above the molecular mass is always observed. It can be attributed as the addition fragment (L–L)M(μ-$SC_6HF_4)_2M'(C_6F_5)_2$ + (C_6HF_4S)M′$(C_6F_5)_2$; the low tendency of bis(diphenylphosphine)methane to act as a chelate ligand may be the reason why this fragment is formed, since it is not observed when L–L is dppe.

3.5. Molecular structures of [(dppe)Ni(μ-$SC_6HF_4)_2Pd(C_6F_5)_2$] (**6**) and [(dppe)Ni(μ-$SC_6F_5)_2Pd(C_6F_5)_2$]

As expected, coordination around the nickel and palladium centres in compound **6** (see Fig. 2) is square-planar (the sum of the bond angles are 360.1 and 359.7°, the mean deviations from the least-squares planes are 0.0636 and 0.0592 Å, respectively). The two coordination planes form a dihedral angle of 30.32(5)°, and the thiolato ligands adopt an *anti* comformation.

The chelate ring is puckered [25] (41% twist with axis through P1 and C1, and 59% envelope with flap at C2).

On formation of the double thiolato bridge, the nickel–phosphorus (2.1849(9) and 2.1966(9) Å) and, most noteworthy, the nickel–sulfur (2.2640(9) and 2.2826(8) Å) distances increase only slightly.

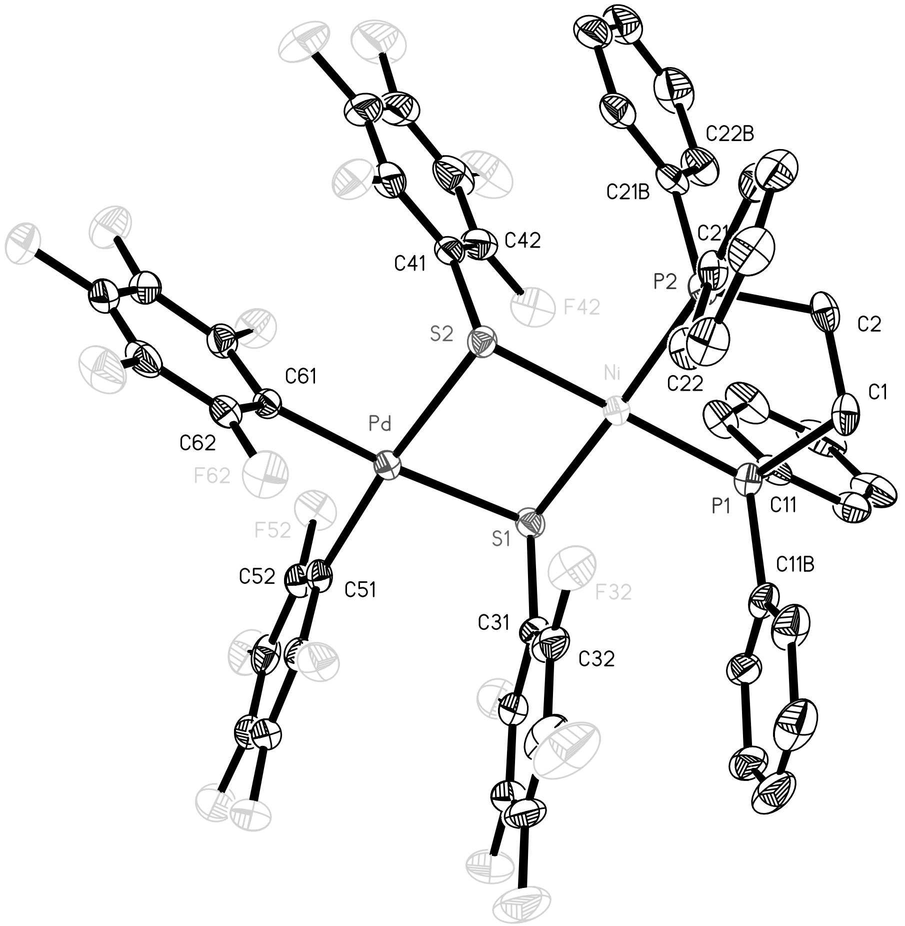


Fig. 3. Molecular structure and numbering scheme for [(dppe)Ni(μ-$SC_6F_5)_2Pd(C_6F_5)_2$]; ellipsoids at 30% probability.

One of the tetrafluorothiophenolato rings exhibits an interfacial interaction with one phenyl ring of the diphosphine: the planes are at an angle of 5.55(7)°, set off by 0.889 Å, and the mean separation is 3.348 Å.

In the homologous [(dppe)Ni(μ-SC$_6$F$_5$)$_2$Pd(C$_6$F$_5$)$_2$] the coordination around the nickel and palladium centres is ca. square-planar (the sum of the bonding angles are 361.3 and 360.2°, the mean deviations are 0.1479 and 0.0614 Å, respectively). The dihedral angle between the two coordination planes is 6.53(13)°, and the thiolato ligands are in an *anti* comformation. Fig. 3 shows the numbering scheme and the structure.

The chelate NiP$_2$C$_2$ ring is puckered [25] (64% twist, with axis through Ni and P1, and 36% envelope, with flap at C1).

The nickel–phosphorus (2.1817(14) and 2.1819(14) Å) distances almost do not vary, and nickel–sulfur (2.2592(14) and 2.2654(14) Å) bonds are only slightly longer than those of the parent mononuclear compound [23].

In this compound, both thiolato rings show interfacial interactions, each to one phenyl ring of the diphosphine. So, ring C31–C36 interacts with C11b–C16b (the angle is 5.93(28)°, the offset 0.972 and the mean distance is 3.264 Å) while ring C41–C46 interacts with C21b–C26b (angle 6.11(27)°, offset 1.140 and mean distance between planes of 3.286 Å).

The structure of a related compound with double thiophenol bridges between palladium and nickel, [(dppe)Pd(μ-SC$_6$H$_5$)$_2$Ni(C$_6$F$_5$)$_2$], has been recently published [29].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 185711–185713. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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