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Stereospecific reactions of the "$M(C_6F_5)_2$" (M = Pd or Pt) synthons towards *cis*-dithiolato complexes

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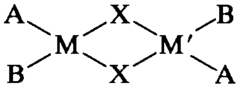
Abstract

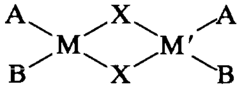
Complexes of the general formula *cis*-$[M(SC_6F_5)_2L_2]$ (M = Ni, Pd, or Pt; L_2 = dppm [bis(diphenylphosphino)methane], dppe [1,2-bis(diphenylphosphino)ethane], or $2PPh_3$) were synthesized by the reaction (1:2) between the corresponding *cis*-$[MCl_2L_2]$ and $Tl(SC_6F_5)$. When treated with *cis*-$[M(C_6F_5)_2(THF)_2]$ (M = Pd or Pt; THF = OC_4H_8) they yield geminal homo- or hetero-binuclear compounds, which were characterized by IR, NMR and mass spectroscopy.

1. Introduction

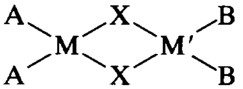
Binuclear complexes of palladium(II) or platinum(II) with a double halide or pseudohalide bridge are well known. Most of them exhibit a trans structure of type **A**, the cis geometry **B** being very rare [1,2].



A



B



C

Only recently [3,4] have species with the geminal structure been described, since even in reactions aiming at their synthesis, ligand rearrangement usually takes place.

As has repeatedly been shown [5], the tetrahydrofuran in the complexes *cis*-$[M(C_6F_5)_2(THF)_2]$ (M = Pd or Pt; THF = OC_4H_8), can readily be displaced and the reaction proceeds with stereoretention, which makes these complexes especially valuable as a reagent for the synthesis of the gem isomers, provided that a compound with two potentially bridging ligands, preferably in a cis geometry, is available.

In this paper we describe the isolation of compounds of the type *cis*-$[M(SC_6F_5)_2L_2]$ (M = Ni, Pd, or Pt; L_2 = dppm, dppe, or $2PPh_3$) and their reactions towards the "*cis*-$M(C_6F_5)_2$" moieties.

2. Experimental details

Unless otherwise stated, all reactions were carried out at room temperature in solvents purified by standard procedures. The compounds $Tl(SC_6F_5)$ [6], *cis*-$[M(C_6F_5)_2(THF)_2]$ (M = Pd or Pt) [7], $[MCl_2dppe]$ (M = Ni [8], Pd [9], or Pt [10]), $[MCl_2dppm]$ (M = Pd [9] or Pt [10]), *cis*-$[PtCl_2(PPh_3)_2]$ [11] and *trans*-$[Pd(O_3ClO)(C_6F_5)(PPh_3)_2]$ [12] were prepared by previously published procedures.

C and H analyses were performed with a Perkin–Elmer 240B 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 [13]. The ^{19}F and ^{31}P spectra of $CDCl_3$ solutions of the compounds were run on Varian XL-200 or Unity 300 spectrometers; chemical shifts are relative to $CFCl_3$ or, respectively, external 85% H_3PO_4.

The conductivity of an acetone solution of compound **19** was measured with a Philips PW9509 apparatus, using a PW9550/60 cell. Melting points were mea-

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sured on a Reichert "Thermopan" microscope, and are uncorrected.

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.

EPR data were taken in a Varian E-112 spectrometer working in the X-band. Measurements at liquid nitrogen temperature were taken using a quartz immersion Dewar.

Elemental analyses, melting points and yields are given in Table 1; IR and NMR data are given in Tables 2 and 3 respectively.

2.1. *General procedure for the synthesis of compounds of the type* $[M(SC_6F_5)_2(L\text{–}L)]$ *(L–L = dppm, M = Pd or Pt; L–L = dppe, M = Ni, Pd, or Pt)*

The corresponding dichloro(diphosphino)metal(II) complex was allowed to react (1:2) with $Tl(SC_6F_5)$, and the TlCl formed was removed by filtration. The solution was evaporated to dryness and the residue was repeatedly washed with diethylether. A typical preparation was as follows.

To a suspension of 0.3322 g (0.5 mmol) of $[PtCl_2dppe]$ in acetone (15 cm^3) was added 0.4035 g (1.0 mmol) of $Tl(SC_6F_5)$. The solution immediately turned yellow and a fine white precipitate was observed.

After 22 h stirring, the TlCl formed was filtered off and the solution was evaporated *in vacuo*. Diethyl ether (1 cm^3) was added and the resulting yellow solid was filtered off, washed with ether (3 × 0.5 cm^3) and suction dried.

2.2. *Synthesis of cis-*$[Pt(SC_6F_5)_2(PPh_3)_2]$

A suspension of 0.3619 g (0.46 mmol) of *cis*-$[PtCl_2(PPh_3)_2]$ in 20 cm^3 of cold acetone (NaCl/ice bath) was treated with 0.3694 g (0.92 mmol) of $Tl(SC_6F_5)$.

After 8 h stirring, the TlCl precipitate was filtered off and the solvent was removed under reduced pressure. The yellow residue was treated with diethyl ether (1 cm^3), filtered, washed with ether (2 × 1 cm^3) and dried *in vacuo* over P_2O_5.

2.3. *General procedure for the synthesis of compounds of the type* $[(L\text{–}L)M(\mu\text{-}SC_6F_5)_2M'(C_6F_5)_2]$ *(M = Ni, L–L = dppe, M' = Pd or Pt; M = Pd, Pt, L–L = dppm or dppe, M' = Pd or Pt)*

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

The addition of 0.0673 g (0.1 mmol) of *cis*-$[Pt(C_6F_5)_2(THF)_2]$ to a solution of 0.0992 g of $[Pt(SC_6F_5)_2dppm]$ in dichloromethane (6 cm^3) causes an immediate colour intensification.

After 2 h stirring, the solution was evaporated to

TABLE 1. Elemental analyses, melting points and yields of complexes **1–19**, calculated values are given in parentheses

Compound	C (%)	H (%)	M.p. (°C) [a]	Yield (%)
$[Ni(SC_6F_5)_2dppe]$ (**1**)	53.6 (53.4)	2.7 (2.8)	216 [b]	84
$[Pd(SC_6F_5)_2dppm]$ (**2**)	50.0 (50.0)	2.3 (2.5)	177	84
$[Pd(SC_6F_5)_2dppe]$ (**3**)	50.7 (50.5)	2.7 (2.7)	231	74
$[Pt(SC_6F_5)_2dppm]$ (**4**)	45.4 (45.5)	2.1 (2.3)	222	94
$[Pt(SC_6F_5)_2dppe]$ (**5**)	46.3 (46.0)	2.3 (2.4)	238	85
cis-$[Pt(SC_6F_5)_2(PPh_3)_2]$ (**6**)	52.3 (51.6)	2.9 (2.7)	202	75
$[dppeNi(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$ (**7**)	46.8 (46.3)	1.9 (1.9)	194	81
$[dppeNi(\mu\text{-}SC_6F_5)_2Pt(C_6F_5)_2]$ (**8**)	42.9 (43.4)	1.4 (1.7)	183	57
$[dppmPd(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$ (**9**)	44.5 (44.3)	1.5 (1.7)	204 [c]	89
$[dppmPd(\mu\text{-}SC_6F_5)_2Pt(C_6F_5)_2]$ (**10**)	41.8 (41.5)	1.3 (1.6)	204	72
$[dppePd(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$ (**11**)	45.0 (44.7)	1.7 (1.8)	199	88
$[dppePd(\mu\text{-}SC_6F_5)_2Pt(C_6F_5)_2]$ (**12**)	42.4 (41.9)	1.5 (1.7)	251	87
$[dppmPt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$ (**13**)	42.0 (41.5)	1.5 (1.6)	190	73
$[dppmPt(\mu\text{-}SC_6F_5)_2Pt(C_6F_5)_2]$ (**14**)	39.6 (39.1)	1.4 (1.5)	217	64
$[dppePt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$ (**15**)	42.6 (41.9)	1.7 (1.7)	232	68
$[dppePt(\mu\text{-}SC_6F_5)_2Pt(C_6F_5)_2]$ (**16**)	39.8 (39.5)	1.5 (1.6)	267	81
$[(PPh_3)_2Pt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$ (**17**)	46.8 (46.2)	2.0 (1.9)	199	74
$[(PPh_3)_2Pt(\mu\text{-}SC_6F_5)_2Pt(C_6F_5)_2]$ (**18**)	43.2 (43.8)	1.7 (1.8)	268	62
$[dppePt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)(PPh_3)]ClO_4$(**19**)	46.0 (45.8)	2.2 (2.4)	139	90

[a] Small colour changes are observed during the heating process for all the compounds. [b] Decomposes. [c] Decomposes on melting.

TABLE 2. Characteristic IR absorptions

Compound	ν(C–S)	X-sensitive	C_6F_5	Phosphine
1	858vs		1310m, 1126w, 1078vs 1059m, 1014m, 972vs	1441vs, 1192m, 1164m, 1104vs, 1029m, 999s 828vs, 752s, 740vs, 704vs, 687vs, 534vs, 484vs
2	859vs		1505vs, 1306w, 1273w, 1079s 1129w, 1009m, 969vs	1438vs, 1191w, 1160w, 1098s, 1027w 998m, 754m, 695s, 687s, 540m, 505m, 477m
3	860vs		1506vs, 1309m, 1268w, 1125w 1076vs, 1062w, 1013m, 972vs	1440vs, 1184w, 1163m, 1105vs, 1029w, 998m 828vs, 751s, 740s, 706vs, 687vs, 535vs, 482s
4	855vs		1505vs, 1308m, 1280m 1083vs, 1015m, 975vs	1440vs, 1190m, 1164w, 1106vs, 1029m 999s, 754m, 735vs, 699vs, 691vs, 674m, 629w 549s, 504vs, 482s, 466w, 451m, 404w
5	859vs		1502vs, 1310w, 1078vs 1063m, 1013w, 972vs	1440vs, 1163w, 1106vs, 999m, 831s, 752m 741m, 707vs, 688vs, 538vs, 487s, 476w
6	857vs		1511vs, 1314m, 1269m, 1129m 1076vs, 1008m, 970vs	1435vs, 1188s, 1161m, 1095vs, 1028m 1001s, 748vs, 739vs, 703vs, 691vs 543w, 526vs, 517vs, 499vs
7	856vs	776s, 786m	1510vs, 1311m, 1279w, 1250w, 1081vs 1055vs, 1014m, 973vs, 950vs	1142w, 1107s, 1027w, 999m, 882m, 821s 749s, 704s, 690s, 680m, 534vs, 485m
8	853vs	789s, 800m	1310m, 1082s, 1057s, 1016w 972s, 956vs	1194w, 1106m, 1027s, 999w 882m, 822s, 749m, 704m
9	859vs	778m, 790m	1513vs, 1307w, 1085vs, 1054vs 1013w, 977vs, 954vs	1440vs, 1099vs, 999m, 750m 742vs, 689m, 545m, 502m
10	857vs	792s, 801m	1513vs, 1306w, 1270w, 1086vs 1058vs, 1014w, 977vs, 957vs	1441vs, 1100vs, 999w, 750m, 743vs 689m, 545m, 502m
11	856vs	776s, 786m	1510vs, 1311m, 1279w, 1250w, 1156vw 1081vs, 1054vs, 1013m, 973vs, 954vs	1109vs, 1027w, 999m, 882m, 822s 749s, 706vs, 689s, 681m, 534vs, 484m
12	854vs	789s, 800m	1510vs, 1310m, 1275w, 1253w, 1082s 1057s, 1015w, 973vs, 956vs	1109s, 1027w, 999w, 749s 882m, 822s, 707vs
13	857vs	777m, 787s	1512vs, 1308m, 1276w, 1084s 1056vs, 1009w, 978vs, 956vs	1106vs, 1093vs, 1040w, 1025w, 999m, 749vs 739s, 712vs, 689s, 554m, 507s, 484m, 476w
14	854vs	791s, 801s	1308vs, 1059vs, 978vs, 958vs	1186m, 1167m, 1092vs, 1025m, 998s, 749vs 739vs, 689s, 554s, 507s, 484m, 475m, 464m, 438w
15	854s	777m, 787m	1510vs, 1310m, 1279w, 1251w, 1082s 1055m, 1012w, 975s, 954vs	1189w, 1109m, 1027w, 999w, 883w, 825m, 750m 707m, 690m, 537m, 487w, 466w, 451m, 404w
16	852vs	790vs, 801vs	1511vs, 1311m, 1291m, 1275m, 1255m 1083vs, 1059vs, 1015m, 976vs, 956vs	1189w, 1109vs, 1027m, 998m 883m, 825s, 751vs, 707vs
17	848vs	780m, 791w	1515vs, 1315w, 1282w, 1083vs 1056s, 976vs, 954vs	1441vs, 1098s, 1046m, 1002m, 755m, 745m, 702s 693m, 688m, 543m, 526s, 520m, 495w,487w
18	846vs	794s, 805s	1514vs, 1315vs, 1282m, 1265m 1084vs, 1059vs, 977vs, 957vs	1098vs, 1044w, 1002m, 745s, 739s, 702vs 687vs, 543s, 525vs, 512m, 495m, 487m
19	855vs	788m	1310m, 1085vs, 1014m 978vs, 956vs	1193m, 1163m, 1028m, 998s, 884w, 824m 693s, 531s, 511m, 486s, 438w

dryness; methanol (1 cm^3) was added and the beige solid was filtered off, washed with methanol (2 × 0.5 cm^3) and dried *in vacuo* over P_2O_5.

2.4. Synthesis of $[(PPh_3)_2Pt(\mu\text{-}SC_6F_5)_2M'(C_6F_5)_2]$ (M = Pd or Pt)

To a solution of 0.1118 g (0.1 mmol) of *cis*-$[Pt(SC_6F_5)_2(PPh_3)_2]$ in dichloromethane (5 cm^3) was added 0.1 mmol of the corresponding *cis*-$[M'(C_6F_5)_2(THF)_2]$.

A white precipitate was slowly formed and, after 2 h stirring, the solid was filtered off, washed with CH_2Cl_2 (1 cm^3) and suction dried.

2.5. Synthesis of $[dppePt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)(PPh_3)]ClO_4$

When a white toluene suspension of 0.1608 g (0.16 mmol) of $[Pt(SC_6F_5)_2dppe]$ was treated with 0.1445 g (0.16 mmol) of $[O_3ClOPd(C_6F_5)(PPh_3)_2]$, it slowly turned yellow.

After 24 h stirring, the solvent was evaporated to *ca.* 10 cm^3, hexane (15 cm^3) was added and the solid was filtered off, washed with diethyl ether (2×0.5 cm^3) and suction dried.

2.6. Mass spectral data

2.6.1. [dppeNi(μ-SC_6F_5)$_2$Pd(C_6F_5)$_2$ (7)]. FAB$^+$: $M-(C_6H_5+C_6F_5)$, 1052, 6%; $M-(2C_6F_5)$, 962, 5%; $M-(2C_6F_5+SC_6F_5)$, 763, 32%; $M-(2C_6F_5+SC_6F_5+Ni)$, 704, 16%; $M-(2C_6F_5+SC_6F_5+Pd)$ 656, 100%. FAB$^-$: $M-(dppe+Ni+SC_6F_5)$, 640, 100%; $M-(dppe+2SC_6F_5+Ni)$, 441, 27%.

2.6.2. [dppmPd(μ-SC_6F_5)$_2$Pd(C_6F_5)$_2$] (9). FAB$^+$: $M-(C_6F_5)$, 1162, 7%; $M-(2C_6F_5)$, 995, 19%; $M-(2C_6F_5+SC_6F_5)$, 796, 100%; $M-(2C_6F_5+SC_6F_5+C_5H_5)$, 720, 18%; $M-(2C_6F_5+SC_6F_5+Pd)$, 690, 71%. FAB$^-$: $M+(SC_6F_5+2C_6F_5+Pd)$, 1969, 7%; $M-(C_6H_5+H)$ 1251, 6%; $M-(dppm+C_6F_5)$, 778, 10%; $M-(dppm+SC_6F_5+Pd)$, 640, 100%; $M-(dppm+2SC_6F_5+Pd)$, 441, 40%.

2.6.3. [dppmPd(μ-SC_6F_5)$_2$Pt(C_6F_5)$_2$] (10). FAB +: M, 1418, 15%; $M-(C_6F_5)$, 1251, 29%; $M-(C_6F_5+SC_6F_5)$, 1052, 51%; $M-(2C_6F_5+SC_6F_5)$, 885, 63%; $M-(2C_6F_5+SC_6F_5+Pt)$, 690, 100%. FAB$^-$: $M+(2C_6F_5+SC_6F_5+Pt)$, 2147, 15%; M, 1418, 9%; $M-(dppm+SC_6F_5+Pd)$, 728, 100%.

2.6.4. [dppePd(μ-SC_6F_5)$_2$Pd(C_6F_5)$_2$] (11). FAB$^+$: $M-(2C_6F_5+SC_6F_5)$, 810, 96%; $M-(2C_6F_5+SC_6F_5+Pd)$, 704, 100%. FAB$^-$: $M-(dppe+SC_6F_5+Pd)$, 640, 100%; $M-(dppe+2SC_6F_5+Pd)$, 441, 23%.

2.6.5. [(PPh_3)$_2$Pt(μ-SC_6F_5)$_2$Pd(C_6F_5)$_2$] (17). FAB$^+$: $M-(2C_6F_5+SC_6F_5)$, 1025, 79%; $M-(2C_6F_5+SC_6F_5+Pd)$, 919, 15%; $M-(2C_6F_5+2SC_6F_5+Pd)$, 720, 100%; $M-(2C_6F_5+2SC_6F_5+Pd+PPh_3)$, 457, 28%. FAB$^-$: $M-(PPh_3+SC_6F_5+Pt)$, 640, 100%.

TABLE 3. NMR data for complexes **1–19**

Compound	δ_o	J_{o-m}	J_{Pt-Fo}	δ_m	δ_p	J_{m-p}	δ_P	J_{Pt-P}
1	−132.9	27	–	−166.0	−163.1	21	56.9	–
2	−132.2	26	–	−165.6	−162.6	21	−39.4	–
3	−132.2	22	–	−166.6	−165.3	21	57.9	–
4	−131.3	30	–	−164.7	−161.1	20	−49.8	2578
5	−132.4	28	–	−165.8	−162.7	20	46.0	3016
6	−135.0	22	–	−166.2	−163.3	21	18.7	3114
7	−117.3	23	–	−165.5	−157.6	21	55.0	–
	−130.3	21			−162.5 [a]			
8	−120.1	25	444	−162.2	−156.1	21	55.6	–
	−129.4	23	–	−166.0	−164.0	20		
9	−116.5	33	–	−161.9	−156.8	21	−40.9	–
	−128.9	24	–	−164.8	−162.5	21		
10	−119.1	28	442	−164.5	−159.2	21	−43.0	–
	−130.2	– [b]	–	−166.0	−167.8	20		
11	−117.9	23	–	−163.6	−158.5	21	59.5	–
	−131.4	22	–	−164.6	−163.2	21		
12	−120.4	28	445	−162.8	−157.0	21	58.9	–
	−130.8	23	–	−166.0	−164.0	20		
13	−116.9	26	–	−161.7	−155.8	21	−52.0	2645
	−128.4	22	–	−162.3	−164.8	21		
14	−120.4	29	447	−161.7	−155.2	21	−51.7	2605
	−129.1	20	–	−165.8	−163.6	20		
15	−118.3	28	–	−163.6	−157.7	21	44.7	3054
	−131.0	26	–	−165.5	−163.0	20		
16	−120.8	27	445	−162.8	−156.3	21	46.3	3008
	−130.7	22	–	−165.9	−163.8	20		
17	−117.3	30	–	−163.5	−157.7	20	13.4	3129
	−130.6	26	–	−164.8	−162.5	19		
18	−121.0	30	444	−164.0	−157.6	20	14.5	3098
	−131.3	25	–	−166.5	−164.6	20		
19	−120.3	25	–	−161.8 [a]	−154.2	21	46.3	3081
	−127.9	22	–		−155.1	21	45.7	3111
	−130.0	23	–		−158.8	20	29.7	

[a] Superimposed signals. [b] Unresolved in $(CD_3)_2CO$ (broad signal, see text).

2.6.6. [dppePt(μ-SC_6F_5)$_2$Pd(C_6F_5)(PPh_3)]ClO_4 (19). FAB$^+$: M, 1528, 70%; M − (PPh_3 + C_6F_5 + SC_6F_5), 899, 10%; M − (PPh_3 + C_6F_5 + SC_6F_5 + Pd), 793, 100%; M − (dppe + $2SC_6F_5$ + Pd + Pt), 429, 69%.

3. Results and discussion

Addition (2 : 1) of thallium pentafluorobenzenethiolate to an acetone solution of [MCl_2L_2] leads to the formation of the corresponding bis(pentafluorothiophenolato)-complex:

$$cis\text{-}[MCl_2L_2] + 2Tl(SC_6F_5) \rightarrow cis\text{-}M(SC_6F_5)_2L_2 + 2TlCl\downarrow \quad (1)$$

$M = Ni, L_2 = dppe$ (**1**)

$M = Pd, L_2 = dppm$ (**2**); $M = Pd, L_2 = dppe$ (**3**)

$M = Pt, L_2 = dppm$ (**4**); $M = Pt, L_2 = dppe$ (**5**);

$M = Pt, L_2 = 2PPh_3$ (**6**)

The reaction is driven by the low solubility of thallium chloride. This fine precipitate must be carefully filtered off. Compound **6** was synthesized at low temperature (NaCl/ice bath) to prevent partial isomerization to the trans configuration.

Evaporation of the clear solution to dryness and addition of diethyl ether affords the desired complex. Yields, melting points and elemental analyses are given in Table 1.

The IR spectra (see Table 2) of the solids show a strong, slightly broad band at 855–860 cm^{-1} assignable [14] to the ν(C–S) vibrations of the thiolato-groups, along with typical absorptions of the pentafluorophenyl ring [14,15] and those due to the neutral ligands.

Complexes **2** and **4** show a strong band at 540 and 549 cm^{-1}, respectively, characteristic [16] of chelating dppm.

Complex **6** shows four absorptions in the 550–490 cm^{-1} region, which demonstrate [17] that the cis geometry of the PPh_3 ligands is maintained.

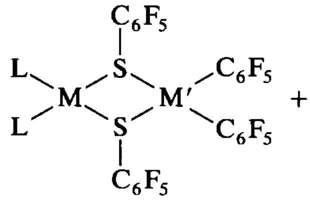
The ^{31}P NMR spectra (see Table 3) of complexes **1–6** show a single signal (along with the expected platinum satellites in the case of compounds **4–6**), indicating that in solution all phosphorus nuclei are equivalent. The negative value (from 85% H_3PO_4, as the reference) of the chemical shift in complexes **2** and **4** is taken as proof [16] of the chelate character of the dppm.

The ^{19}F NMR spectra of complexes **1–6** show a doublet, as expected, in the region assigned [18] to the *ortho*-fluorine nuclei of pentafluorothiophenolato-groups, −125 to −135 ppm. No coupling to ^{31}P or ^{195}Pt is observed (*i.e.* ^5J(P–F) and ^4J(Pt–F) ≈ 0).

All these data support a mononuclear nature for complexes **1–6** and a cis configuration, as proposed in eqn. (1). This geometry, together with the ability of thiolato-groups to act as bridging ligands [19], makes them especially suitable for the synthesis of geminal homo- or hetero-binuclear compounds.

Thus, when a dichloromethane solution of *cis*-[$M(SC_6F_5)_2L_2$] is treated with an equivalent amount of *cis*-[$M'(C_6F_5)_2(THF)_2$] the two labile tetrahydrofuran groups are displaced and the desired dinuclear compound is formed, according to eqn. (2):

$$cis\text{-}[M(SC_6F_5)_2L_2] + cis\text{-}[M'(C_6F_5)_2(THF)_2] \longrightarrow$$



+ 2THF (2)

$M = Ni, L_2 = dppe, M' = Pd$(**7**) or Pt(**8**)

$M = Pd, L_2 = dppm, M' = Pd$(**9**) or Pt(**10**)

$M = Pd, L_2 = dppe, M' = Pd$(**11**) or Pt(**12**)

$M = Pt, L_2 = dppm, M' = Pd$(**13**) or Pt(**14**)

$M = Pt, L_2 = dppe, M' = Pd$(**15**) or Pt(**16**)

$M = Pt, L = PPh_3, M' = Pd$(**17**) or Pt(**18**)

For compounds **7–16**, the solvent was evaporated and the residue was washed with diethyl ether or methanol; compounds **17** and **18** precipitate in dichloromethane and were simply filtered and washed; prolonged vacuum drying of most of them was necessary, since they tend to occlude solvent.

The IR spectra of these binuclear complexes show (besides other absorptions, which arise from the C_6F_5 ring of both the pentafluorobenzenethiolato [14] and the pentafluorophenyl [15] ligands) two bands in the 805–760 cm^{-1} region (X-sensitive vibration [15,20]) indicative of a *cis* geometry of the pentafluorophenyl groups, and a somewhat broad peak assignable to ν(C–S) of the thiolato moieties.

Amongst the bands due to the neutral ligands, a strong one around 550 cm^{-1}, indicative [16] of chelating dppm, can be observed for compounds **9**, **10**, **13** and **14**; four bands in the 550–490 cm^{-1} region, characteristic [17] of two mutually *cis* triphenylphosphines are found for compounds **17** and **18**.

The $^{31}P\{^1H\}$ NMR spectra consist of a single peak (with platinum satellites in the case of compounds **13–18**) the phosphorus nuclei being, therefore, magnetically equivalent. Again, the high field position of the resonance (relative to 85% H_3PO_4) in compounds

9, **10**, **13** and **14** proves [16] the chelating role of the dppm.

Complexes **7–18** show two doublets in the *ortho*-fluorine region: one in the −110 to −122 range (pentafluorophenyl) and another between −125 and −135 ppm (pentafluorobenzenethiolate); in the case of compounds **13–18**, the doublet at higher frequency shows ^{195}Pt satellites, as expected.

Owing to the very low solubility of compound **10** in chloroform, its ^{19}F NMR spectrum was at first recorded using hexadeuteroacetone as the solvent; in the *ortho*-fluorine region a doublet with ^{195}Pt satellites ($\delta = -117.5$ ppm, ^4J(Pt–F) = 441 Hz, C_6F_5) and a slightly broadened peak ($\delta = -128.7$ ppm, SC_6F_5) were observed at room temperature, the latter suggesting a dynamic process. Hence, a variable-temperature NMR study was undertaken (see Fig. 1).

At +55°C, the signal assigned to the *ortho*-fluorine of the pentafluorothiophenolato-groups is a sharp doublet which disappears into the baseline by −30°C, while the signal in the pentafluorophenyl region is observed as a broad hump.

At −60°C, two doublets with ^{195}Pt satellites (C_6F_5) plus a slightly broader signal and a doublet with no satellites (SC_6F_5) are observed.

The fluxional behaviour of this compound is tentatively ascribed to an exchange between the syn and anti-planar geometries, through inversion at the sulphur centres, as commonly encountered [21] in double thiolato-bridged binuclear compounds.

Since this was initially the only compound (among those described here) whose NMR was studied as an acetone solution, long-term (overnight) accumulation of transients of a saturated $CDCl_3$ solution was carried out at room temperature.

In the *ortho*-fluorine region [18] two sharp doublets were observed at −119.9 ppm (with platinum satellites, ^4J(Pt–P) = 448 Hz, C_6F_5) and −129.2 ppm (no satellites, SC_6F_5). Addition of a catalytic amount of acetone (0.025 ml to 0.6 ml of the deuterochloroform solution) did not change the spectral pattern. Thus coordination of acetone can be discarded as a necessary step in the exchange.

The ^{19}F NMR spectra of hexadeuteroacetone solutions of compounds **13** and **18** were recorded, and a slight broadening of the bands was observed at room temperature; a fluxional process is clearly distinguishable when the spectra are run at −30°C.

The absence of any signal in the EPR spectrum of compound **8** at 298 and 77 K is indicative of a square planar coordination around the d^8 nickel, excluding a tetrahedral geometry or a mixture of polytopes. It is noteworthy that the colour of this compound changes reversibly from brick-red to orange on cooling.

An attempt was made to synthesize trinuclear species by reaction (1 : 2) between a bis(pentafluoroben-

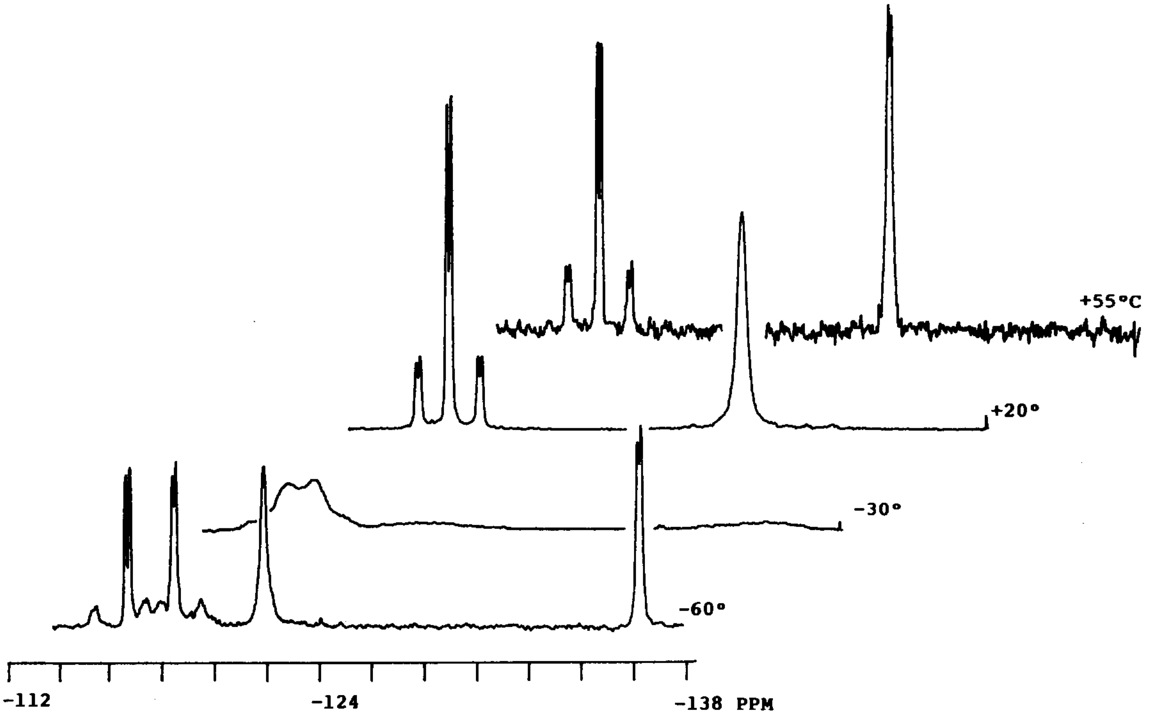


Fig. 1. ^{19}F NMR spectra (*ortho*-fluorine region) of compound **10** in hexadeuteroacetone, at various temperatures.

zenethiolato)-compound and pentafluorophenylperchloratobis(triphenylphosphino)palladium(II), where the covalent $OClO_3$ group is readily replaced. However, a mixture of compounds is obtained, as shown by ^{31}P NMR spectroscopy.

In contrast, when equimolecular amounts of the reactants are stirred together in toluene, and hexane is added, a pure solid is obtained.

Its IR spectrum demonstrates [21] that the ClO_4 group is ionic (T_d symmetry) since a very broad band centred at approximately 1095 cm^{-1} and a single sharp absorption at 624 cm^{-1} are observed. Whereas ν(C–S) appears as a single broad band at 855 cm^{-1}, only one sharp band is observed in the 800–760 cm^{-1} region (X-sensitive [20], arising from C_6F_5); other characteristic bands of the neutral and ionic ligands are given in Table 2.

The ^{31}P NMR spectrum consists of three peaks (two of them with ^{195}Pt satellites), whereas in the *ortho*-fluorine region of the ^{19}F spectrum three doublets which integrate 1:1:1 are observed. One, at −120.3 ppm, is assignable to a C_6F_5 group (see above) and the other two at −127.9 and −130.0 ppm are in the SC_6F_5 region.

These data support the following reaction scheme:

$$[Pt(SC_6F_5)_2dppe] + \textit{trans}\text{-}[Pd(OClO_3)(C_6F_5)(PPh_3)_2] \rightarrow [dppePt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)(PPh_3)]ClO_4 + PPh_3 \quad (3)$$

The elemental analysis and the molar conductivity [23] of an acetone solution of compound **19** ($c = 5.14 \times 10^{-4}$ M; $\Lambda_M = 122.9\ \Omega^{-1}\ cm^2\ mol^{-1}$) are in good agreement with this formulation.

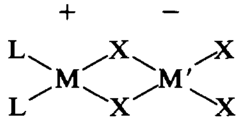
When the reaction is tried in a 2:1 ratio (see above) the ^{31}P spectrum of the isolated mixture comfirms that the displaced triphenylphosphine reacts with the excess perchlorato-complex to give $[Pd(C_6F_5)(PPh_3)_3]ClO_4$.

3.1. Mass spectroscopy results

3.1.1. Neutral compounds

Mass spectra (FAB^+ as well as FAB^-) were recorded for a selection of the $[L_2M(\mu\text{-}SC_6F_5)_2\text{-}M'(C_6F_5)_2]$ complexes. Noteworthy general features are as follows.

While in the FAB^+ spectra $L_2M(SC_6F_5)$ and $L_2M(SC_6F_5)M'$ fragments are invariably present, in the FAB^- the most important peak is assigned to $(C_6F_5S)M'(C_6F_5)_2$. This agrees with the formal charge distribution, positive on M and negative on M′:



In those compounds containing dppm as the ancillary ligand, a peak above the molecular mass is always observed. It can be attributed to the addition fragment $L_2M(\mu\text{-}SC_6F_5)_2M'(C_6F_5)_2 + (C_6F_5S)M'(C_6F_5)_2$; the low tendency of the dppm to chelate may be the reason why this fragment is not observed when L_2 is dppe or $2PPh_3$.

3.1.2. [dppePt(μ-$SC_6F_5)_2Pd(C_6F_5)(PPh_3)]ClO_4$

The FAB^+ spectrum of this complex shows the parent peak of the cation and the fragments $dppePt(SC_6F_5)$ and $dppePt(SC_6F_5)Pd$ associated with the formally positive metal centre.

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