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The synthesis of new bimetallic complex salts by halide/sulfur chelate cross transfer: X-ray crystal structures of the salts $[Ni(S_2CNEt_2)(dppe)]_2[HgBr_4]$, $[Pt(S_2CNEt_2)(dppe)]_2[CdCl_4]$, $[Co(S_2CNEt_2)_2(dppe)]_2[Cl_3ZnO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}OZnCl_3]$ and $[Pd(S_2CN^nBu_2)(bipy)]_2[CdCl_4]$

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Abstract

The nickel and platinum complexes $[MX_2(dppe)]$ ($X = Cl$, Br) react with bi- and tri-valent metal diethyldithiocarbamates $[M'(S_2CNEt_2)_n]$ ($M' = Pb$, Zn, Cd, Hg, Ni, MoO_2, VO, $n = 2$; $M' = Co$, Fe, Mn, $n = 3$) to afford salts $[M(S_2CNEt_2)(dppe)]_2[M'X_4]$; reactions involving $[Cu(S_2CNEt_2)_2]$ and $[Ag(S_2CNEt_2)]$ gave salts of the form $[M(S_2CNEt_2)(dppe)][M'X_2]$ ($M' = Cu$, Ag). The complexes *cis* $[RuCl_2(dppm)_2]$, $[CoCl_2(dppe)]$ and $[PdX_2(bipy)]$ likewise react with the same dithiocarbamates to form salts $[Ru(S_2CNEt_2)(dppe)_2]_2[M'Cl_4]$ $[Co(S_2CNEt_2)_2(dppe)]_2[M'Cl_4]$ and $[Pd(S_2CN^nBu_2)(bipy)]_2[M'X_4]$, respectively. Sample reactions involving other S-chelate ligands—S_2COEt^-, $S_2PPh_2^-$ and $S_2P(OEt)_2^-$—appear to follow the same general pattern. However, the *O*-ethyldithio carbonates (ethylxanthates) are partly converted to the corresponding dithiocarbonates. An anomalous reaction between $[CoCl_2(dppe)]$ and $[Zn(S_2CNEt_2)_2]$ in the presence of $(S_2CNEt_2)_2$ affords the novel complex $[Co(S_2CNEt_2)_2(dppe)]_2[Cl_3ZnO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}OZnCl_3]$. A selection of these salts have been fully characterised by elemental analysis and spectroscopic techniques, the remainder have been identified by spectroscopic methods alone. X-ray crystal structures are reported for the salts $[Ni(S_2CNEt_2)(dppe)]_2$ $[HgBr_4]$, $[Pt(S_2CNEt_2)(dppe)]_2[CdCl_4]$, $[Co(S_2CNEt_2)_2(dppe)]_2$-$[Cl_3ZnO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}OZnCl_3]$ and $[Pd(S_2CN^nBu_2)$ $(bipy)]_2[CdCl_4]$. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Bimetallic complex salts; Halide/sulfur chelate cross transfer; Crystal structures

1. Introduction

In the course of attempts to synthesise bimetallic dithiocarbamato complexes we observed facile reactions between palladium complexes $[PdX_2\{Ph_2P(CH_2)_nPPh_2\}]$ ($n = 1$–4) and bi- or tri-valent metal dithiocarbamato complexes leading to the formation of salts containing $[Pd(S_2CNEt_2)\{Ph_2P(CH_2)_nPPh_2\}]^+$ cations and a range of chloro- or bromo-metallate anions [1,2]. A feature of these reactions was the ease with which even soft metals, notably lead, mercury and silver, readily gave up dithiocarbamate ligands to form the halo-metallate salts of the $[Pd(S_2CNEt_2)\{Ph_2P(CH_2)_nPPh_2\}]^+$ cations in essentially quantitative yield. In this paper we describe similar reactions involving the corresponding nickel and platinum complexes. $[MX_2(dppe)]$, and related complexes of ruthenium *cis*-$[RuCl_2(dppm)_2]$, cobalt $[CoCl_2(dppe)]$ and palladium $[PdX_2(bipy)]$. Finally, in order to investigate the generality of these reactions the dithiocarbamate complex precursors were replaced by xanthate S_2COEt^-, dithiophosphinate $S_2PPh_2^-$ and dithiophosphate $S_2P(OEt)_2^-$ complexes.

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2. Experimental

2.1. General procedures

Hydrated cobalt and nickel halides were purchased from Aldrich and ruthenium, palladium and platinum halides were obtained from Johnson Matthey. Metal dithiocarbamates, ethyldithiocarbonates, dithiophosphinates and dithiophosphates were prepared by mixing aqueous solutions of the sodium salts of the sulfur ligands and the appropriate metal halides, and were crystallised from dichloromethane. All other reagents conditions and instrumentation were as described in a previous paper [1].

2.1.1. (N,N-Diethyldithiocarbamato)[1,2-bis(diphenylphosphino)ethane]nickel(II) tetrachlorozincate

Dichloro[1,2-bis(diphenylphosphosphino)ethane]nickel (0.211 g, 0.40 mmol) and bis(*N*,*N*-diethyldithiocarbamato)zinc (0.072 g, 0.20 mmol) were heated under reflux in acetonitrile (60 cm^3) for 1 h. The solution thereby obtained was filtered and evaporated to dryness under reduced pressure. The oily residue was dissolved in dichloromethane (10 cm^3) and the complex re-precipitated by the addition of diethyl ether (75 cm^3). The fine yellow–orange powder obtained was filtered off, washed with diethyl ether and dried in vacuo. Yield 0.265 g, 93%; m.p. 133–135 °C. *Anal*. Found: C, 52.05; H, 4.85; N, 1.85. Calc. for $C_{62}H_{68}Cl_4N_2Ni_2P_4S_4Zn$: C, 52.5; H, 4.85; N, 2.0%.

The following complexes were obtained on a similar scale by the same general method.

(*N*,*N*-Diethyldithiocarbamato)[1,2-bis(diphenylphosphino)ethane]nickel(II) tetrachlorocadmate 0.5 dichloromethane as a fine yellow–orange powder. Yield 93%; m.p. 131–133 °C. *Anal*. Found: C, 50.15; H, 4.75; N, 1.80. Calc. for $C_{62}H_{68}CdCl_4N_2Ni_2P_4S_4{\cdot}0.5CH_2Cl_2$: C, 49.8; H, 4.6; N, 1.85%.

(*N*,*N*-Diethyldithiocarbamato)[1,2-bis(diphenylphosphino)ethane]nickel(II) tetrabromomercurate as a fine yellow–orange powder. Yield 93%; m.p. 136–138 °C. *Anal*. Found: C, 42.8; H, 3.85; N, 1.5. Calc. for $C_{62}H_{68}Br_4HgN_2Ni_2P_4S_4$: C, 43.0; H, 3.95; N, 1.6%.

2.1.2. (N,N-Diethyldithiocarbamato)[1,2-bis(diphenylphosphino)ethane]nickel(II) ‘dichloroargentate(I)’

Dichloro[1,2-bis(diphenylphosphino)ethane]nickel (0.211 g, 0.40 mmol) and (*N*,*N*,-diethyldithiocarbamato)silver(I) (0.102 g, 0.40 mmol) were stirred and heated under reflux in acetonitrile (60 cm^3) for 1 h. The solution obtained was filtered through celite to remove the fine grey–white precipitate of silver chloride and then evaporated to dryness under reduced pressure. The oily residue remaining was dissolved in dichloromethane (10 cm^3) and the complex re-precipitated by the addition of diethyl ether (75 cm^3). The fine yellow–ochre powder obtained was filtered off, washed with diethyl ether and dried in vacuo. Yield 0.262 g, 92%; m.p. 179–181 °C. *Anal*. Found: C, 48.6; H, 4.3; N, 1.7. Calc. for $C_{31}H_{34}AgCl_2NNiP_2S_2$; C, 47.5; H, 4.4; N, 1.8%. Calc. for $C_{62}H_{68}AgCl_3N_2Ni_2P_4S_4$; C, 52.25; H, 4.8; N, 1.85%.

2.1.3. (N,N-Diethyldithiocarbamato)[1,2-bis(diphenylphosphino)ethane]nickel(II) tetrachloromanganate(II)·1.0 dichloromethane

Dichloro[1,2-bis(diphenylphosphino)ethane]nickel (0.211 g, 0.40 mmol) and tris(*N*,*N*-diethyldithiocarbamato)manganese (0.100 g, 0.20 mmol) were heated under reflux in acetonitrile (70 cm^3) for 1 h. The solution thus obtained was filtered and evaporated to dryness under reduced pressure. The oily residue remaining was dissolved in dichloromethane (10 cm^3) and the complex re-precipitated by addition of diethyl ether (75 cm^3). The fine yellow–ochre powder obtained was washed repeatedly with diethyl ether to remove all the tetraethylthiuram disulfide by-product, and dried in vacuo. Yield 0.265 g, 89%; m.p. 127–130 °C. *Anal*. Found: C, 50.0; H, 4.7; N, 1.95. Calc. for $C_{62}H_{68}Cl_4MnN_2Ni_2P_4S_4{\cdot}1.0CH_2Cl_2$: C, 50.7; H, 4.75; N, 1.9%.

2.1.4. (N,N-Diethyldithiocarbamato)[1,2-bis(diphenylphosphino)ethane]platinum(II) tetrachlorozincate

Dichloro[1,2-bis(diphenylphosphino)ethane]platinum (0.133 g, 0.20 mmol) and bis(*N*,*N*-diethyldithiocarbamato)zinc (0.036 g, 0.10 mmol) were heated under reflux in acetonitrile (60 cm^3) for 1 h. The solution obtained was filtered and evaporated to dryness under reduced pressure. The oily residue remaining was dissolved in dichloromethane (7 cm^3) and the complex re-precipitated by addition of diethyl ether (60 cm^3). The fine white powder obtained was filtered off, washed with diethyl ether and dried in vacuo. Yield 0.151 g, 89%; m.p. 142–145 °C. *Anal*. Found: C, 44.15; H, 4.05; N, 1.7. Calc. for $C_{62}H_{68}Cl_4N_2P_4Pt_2S_4Zn$: C, 44.05; H, 4.05; N, 1.65%.

(*N*,*N*-Diethyldithiocarbamato)[1,2-bis(diphenylphosphino)ethane]platinum(II) tetrachlorocadmate was similarly prepared as a fine white powder. Yield 92%; m.p. 134–136 °C. *Anal*. Found: C, 42.8; H, 3.9; N, 1.5. Calc. for $C_{62}H_{68}CdCl_4N_2P_4Pt_2S_4$: C, 42.85; H, 3.95; N, 1.6%.

2.1.5. (N,N-Diethyldithiocarbamato)[1,2-bis(diphenylphosphino)ethane]platinum(II) ‘dichloroargentate(I)’

Dichloro[1,2-bis(diphenylphosphino)ethane]platinum (0.133 g, 0.20 mmol) and (*N*,*N*-diethyldithiocarbamato)silver (0.051 g, 0.20 mmol) were heated under reflux in acetonitrile (60 cm^3) for 1 h. The solution obtained was filtered through celite to remove a fine grey–white precipitate of silver chloride and evaporated to dryness under reduced pressure. The oily residue thus obtained was dissolved in dichloromethane (7 cm^3) and the complex precipitated by addition of diethyl ether (60 cm^3). The fine white powder obtained was filtered off, washed with diethyl ether and dried in vacuo. Yield 0.142 g, 91%; m.p. 160–162 °C. *Anal.* Found: C, 41.15; H, 3.55; N, 1.55. Calc. for $C_{31}H_{34}AgCl_2NP_2PtS_2$; C, 40.45; H, 3.7; N, 1.5%. Calc. for $C_{62}H_{68}AgCl_3N_2P_4Pt_2S_4$: C, 43.85; H, 4.05; N, 1.65%.

2.1.6. (N,N-Diethyldithiocarbamato)[1,2-bis(diphenylphosphine)ethane]platinum(II) dichlorocuprate(I)·0.5 dichloromethane

Dichloro[1,2-bis(diphenylphosphino)ethane]platinum (0.133 g, 0.20 mmol) and bis(*N*,*N*-diethyldithiocarbamato)copper (0.036 g, 0.10 mmol) were heated under reflux in acetonitrile for 1 h. The solution was then filtered and evaporated to dryness under reduced pressure. The oily residue was dissolved in dichloromethane (7 cm^3) and the complex re-precipitated by the addition of diethyl ether (60 cm^3). The fine green powder obtained was filtered off, washed with diethyl ether several times to remove the tetraethylthiuram disulfide byproduct and dried in vacuo. Yield 0.166 g, 90%; m.p. 163–165 °C. *Anal.* Found: C, 41.75; H, 4.0; N, 2.05. Calc. for $C_{31}H_{34}Cl_2CuNP_2PtS_2{\cdot}0.5CH_2Cl_2$: C, 41.2; H, 3.85, N, 1.5%.

2.1.7. (N,N-Diethyldithiocarbamato)[1,2-bis(diphenylphosphino)ethane]platinum(II) tetrachloroferrate(II)·1.0 chloroform

Dichloro[1,2-bis(diphenylphosphino)ethane]platinum (0.133 g, 0.20 mmol) and tris(*N*,*N*-diethyldithiocarbamato)iron (0.050 g, 0.10 mmol) were heated under reflux in acetonitrile (60 cm^3) with stirring for 1 h under a dinitrogen atmosphere. The solution obtained was filtered and evaporated to dryness under reduced pressure. The residue was dissolved in chloroform (8 cm^3) and the complex re-precipitated by the addition of diethyl ether (60 cm^3). The slightly air-sensitive olive green powder was filtered off, washed several times with diethyl ether to remove all traces of tetraethylthiuram disulfide byproduct and dried in vacuo. Yield 0.166 g, 92%; m.p. 123–125 °C. *Anal.* Found: C, 41.9; H, 3.95; N, 1.75. Calc. for $C_{62}H_{68}Cl_4FeN_2P_4Pt_2S_4{\cdot}1.0CHCl_3$: C, 42.0; H, 3.85; N, 1.55%.

In addition to salts described above a further series of examples were prepared in approximately 85–95% yields by similar methods, but were not submitted for elemental analysis. Identification was achieved by spectroscopic methods (infrared and ^1H and ^{31}P NMR) and by comparison with the corresponding salts of the palladium complex cation $[Pd(S_2CNEt_2)(Ph_2PCH_2CH_2PPh_2)]^+$. A full listing, together with colour and selected infrared data, is given in Table 1. Spectroscopic data are also described in Section 3.

2.1.8. (N,N-Diethyldithiocarbamato)di[bis(diphenylphosphino)methane]ruthenium(II) tetrachlorocadmate

cis-Dichlorodi[bis(diphenylphosphino)methane]ruthenium (0.188 g, 0.20 mmol) and bis(*N*,*N*-diethyldithiocarbamato)cadmium (0.041 g, 0.10 mmol) were heated under reflux in acetonitrile (60 cm^3) for 3 h. The solution thus obtained was filtered and evaporated to dryness under reduced pressure. The oily residue was dissolved in dichloromethane (10 cm^3) and then diluted with diethyl ether (75 cm^3). The resulting precipitate was filtered off, washed with diethyl ether (3 × 10 cm^3) and dried in vacuo to yield a yellowish white powder. Yield 0.213 g, 93%. Crystallisation from chloroform–toluene gave pale yellow needles. *Anal.* Found: C, 55.00; H, 4.60; N, 1.20. Calc. for $C_{60}H_{64}CdCl_4N_2P_8Ru_2S_4$: C, 57.70; H, 4.75; N, 1.20%. Calc. for $CHCl_3$ mono-solvate C, 55.35; H, 4.55; N, 1.15%.

A range of tetrachlorometallate salts containing the same cation were synthesised by similar procedures, and characterised by spectroscopic methods. Details are given in Table 2 and in Section 3.

2.1.9. (N,N-Di-n-butyldithiocarbamato)(2,2′-dipyridyl)palladium(II) tetrachlorocadmate

Dichloro(2,2′-dipyridyl)palladium (0.133 g, 0.40 mmol) and bis(*N*,*N*-di-*n*-butyldithiocarbam-ato)cadmium (0.104 g, 0.20 mmol) were heated under reflux in acetonitrile (70 cm^3) for 2 h. The solution thus obtained was filtered hot, evaporated to approximately 25 cm^3 under reduced pressure, and then cooled in an ice/water bath for 30 min. The product which precipitated was filtered off, washed with ethanol (3 × 10 cm^3) and diethyl ether (3 × 10 cm^3), and then dried in vacuo as bright yellow feathery plates. Yield 0.213 g, 90%. *Anal.* Found: C, 38.30; H, 4.25; N, 6.85. Calc. for $C_{38}H_{52}CdCl_4N_6Pd_2S_4$: C, 38.65; H, 3.75; N, 7.10%.

A range of tetrahalometallate salts containing the same cation were synthesised by similar procedures and characterised by spectroscopic methods. Details are given in Table 2 and in Section 3.

2.1.10. Di(N,N-diethyldithiocarbamato)[1,2-bis(diphenylphosphino)ethane]cobalt(III) tetrachlorocadmate

A solution of bis(*N*,*N*-diethyldithiocarbamato)cadmium (0.082 g, 0.20 mmol) and tetraethylthiuram disulfide (0.059 g, 0.20 mmol) in dichloromethane (40 cm^3) was added to a solution of dichloro[1,2-bis(diphenylphosphino)ethane]cobalt(II) (0.211 g, 0.40 mmol) in dichloromethane (30 cm^3). The mixture was stirred at room temperature for 30 min, filtered and concentrated under reduced pressure to small volume (ca. 5 cm^3). Diethyl ether (75 cm^3) was added to the concentrate and the precipitate obtained was filtered off, washed with ethanol (2 × 10 cm^3) and diethylether (5 × 10 cm^3) then dried in vacuo to yield a fine brick-red powder. Yield 0.313 g, 89%. Recrystallisation from chloroform solution gave dark red plates. *Anal*. Found: C, 46.40; H, 4.65; N, 2.90. Calc. for $C_{72}H_{88}CdCl_4Co_2N_4P_4S_8$: C, 49.10; H, 5.05; N, 3.20%. Calc. for $CHCl_3$ mono solvate: C, 46.60; H, 4.75; N, 3.0%.

A range of tetrahalometallate salts containing the same cation were synthesised by similar procedures and characterised by spectroscopic methods. Details are given in Table 2 and in Section 3.

2.1.11. Di(N,N-diethyldithiocarbamato)[1,2-bis(diphenylphosphino)ethane]cobalt(III) bis-trichlorozincate)[μ-O,O′-1,2-bis(diphenyl phosphinoyl)ethane]

A solution of bis(*N*,*N*-diethyldithiocarbamato)zinc (0.072 g, 0.02 mmol) and tetraethylthiuram disulfide (0.059 g, 0.20 mmol) in dichloromethane (40 cm^3) was added to a solution of dichloro[2-bis(diphenylphosphino)ethane]cobalt (0.211 g, 0.40 mmol) in di-

Table 1
Colour and metal halide infrared vibrations for halometallate salts of $[M(S_2CNEt_2)(dppe)]^+$ cations

Anions	M = Ni		M = Pt	
	Colour	ν(M–X) (cm^{-1})	Colour	ν(M–X) (cm^{-1})
$[PbCl_4]^{2-}$	yellow–orange	201vw [a]	white	205vw [a]
$[ZnCl_4]^{2-}$	yellow–orange	278s	white	278s
$[CdCl_4]^{2-}$	yellow–orange	247m	white	243m
$[HgCl_4]^{2-}$	yellow–orange	221m	white	222m
$[CuCl_2]^{-}$	brown–green	409w	green	411w
$[AgCl_2]^{-}/Cl^{-}$	yellow–ochre	295vw [a]	white	293vw[a]
$[NiCl_4]^{2-}$	brown–green	288m	pale green	290m
$[CoCl_4]^{2-}$	brown–green	296m	green	297m
$[FeCl_4]^{2-}$	olive-green	285m	olive-green	285m
$[MnCl_4]^{2-}$	yellow–ochre	282m	pale yellow	283m
$[MoO_2Cl_4]^{2-}$ [b]	yellow–orange	325m, 263m	pale yellow	321m, 268m
$[VOCl_4]^{2-}$ [c]	pale green	310m, 282m	pale green	312m, 281m
$[PbBr_4]^{2-}$	yellow–ochre	144vw [a]	white	146vw [a]
$[ZnBr_4]^{2-}$	yellow–brown	211m	white	213m
$[CdBr_4]^{2-}$	yellow–orange	183m	white	186m
$[HgBr_4]^{2-}$	yellow–orange	155w	white	157w
$[CuBr_2]^{-}$	brown–green	325w	brown–green	323w
$[AgBr_2]^{-}/Br^{-}$	yellow–ochre	247vw [a]	white	244vw [a]
$[NiBr_4]^{2-}$	brown–green	224w	pale green	219w
$[CoBr_4]^{2-}$	brown–green	226m	green	227m
$[FeBr_4]^{2-}$	brown–green	218m	dark olive green	218m
$[MnBr_4]^{2-}$	yellow–orange	222m	pale yellow	222m
$[MoO_2Br_4]^{2-}$ [b]	yellow–orange	244w, 218w	pale yellow	243w, 219w
$[VOBr_4]^{2-}$	pale green	243w, 217w	pale green	242w, 220w

[a] Tentative assignments.
[b] ν(Mo=O) 912 and 877 cm^{-1} (X = Cl and Br).
[c] ν(V=O) 952 cm^{-1} (X = Cl); 955 cm^{-1} (X = Br).

Table 2
Infrared data ν_3(M–X) for halometallate anions $[MX_4]^{2-}$

Anion	Cation					
	A	B	C	D	E	F
$[ZnCl_4]^{2-}$	278 (s)		276 (s)	279 (m)	277 (m)	276 (m)
$[CdCl_4]^{2-}$	245 (m)	247 (m)	245 (m)	249 (m)	246 (m)	244 (m)
$[HgCl_4]^{2-}$	219 (m)	223 (m)	220 (m)	224 (m)	218 (m)	220 (m)
$[PdCl_4]^{2-}$	207 (vw)		202 (vw)	206 (vw)	203 (vw)	206 (vw)
$[FeCl_4]^{2-}$				283 (m)		286 (m)
$[CoCl_4]^{2-}$					291 (m)	
$[NiCl_4]^{2-}$				287	287 (m)	288 (m)
$[ZnBr_4]^{2-}$			218 (m)	219 (m)	220 (m)	222 (m)
$[CdBr_4]^{2-}$		185 (m)	179 (m)	186 (m)	183 (m)	186 (m)
$[HgBr_4]^{2-}$		157 (w)	156 (w)	158 (w)	155 (w)	157 (w)
$[PbBr_4]^{2-}$					147 (vw)	151 (vw)

A = $[Ru(S_2CNEt_2)(dppm)_2]^+$; B = $[Co(S_2CNEt_2)_2(dppe)]^+$; C = $[Pd(S_2CN^{n}Bu_2)(bipy)]^+$; D = $[Pd(S_2COEt)(dppe)]^+$; E = $[Pd(S_2PPh_2)(dppe)]^+$; F = $[Pd\{S_2P(OEt)_2\}(dppe)]^+$.

chloromethane (30 cm^3). The mixture was stirred at room temperature for 30 min, filtered and concentrated under reduced pressure to small volume (ca. 5 cm^3). Diethyl ether (75 cm^3) was added to the concentrate and the precipitate obtained was filtered off, washed with ethanol (2 × 10 cm^3) and diethyl ether (5 × 10 cm^3) then dried in vacuo to yield a fine bright red powder. Yield 0.201 g. Recrystallisation from chloroform gave dark red prisms. *Anal.* Found: C, 50.3; H, 4.95; N, 2.4. Calc. for $C_{98}H_{112}Cl_6Co_2N_4O_2P_6S_8Zn_2$: C, 51.6; H, 4.95; N, 2.45%. Calc. for $CHCl_3$ hemi-solvate: C, 50.8; H, 4.85; N, 2.4%.

Attempted synthesis of *O*-ethyldithiocarbonato-[1,2-bis(diphenylphosphino)ethane]palladium(II) tetrachlorozincate

Dichloro[1,2-bis(diphenylphosphino)ethane]palladium (0.230 g, 0.40 mmol) and bis(*O*-ethyldithiocarbonato)zinc (0.062 g, 0.20 mmol) were stirred with dichloromethane (60 cm^3) for 1 h. The solution thus obtained was filtered and concentrated under reduced pressure to small volume (ca. 5 cm^3) then diluted with diethyl ether (75 cm^3). The resulting precipitate was filtered off, washed with diethyl ether (3 × 10 cm^3) and dried in vacuo to yield a fine yellow powder (yield 0.272 g). Spectroscopic examination revealed that the major product was the dithiocarbonato complex $[Pd(S_2CO)(dppe)]$. Reactions involving a range of these *O*-ethyldithiocarbonato complexes also gave mixtures of *O*-ethyldithiocarbonato and dithiocarbonato products. Further details are given in Section 3.

2.1.12. Diphenyldithiophosphinato[1,2-bis(diphenylphosphino)ethane]palladium(II) tetrachlorocadmate·1.0 dichloromethane

Dichloro[1,2-bis(diphenylphosphino)ethane]palladium (0.230 g, 0.40 mmol) and bis(diphenyldithiophosphinato)cadmium (0.12 g, 0.20 mmol) were stirred in dichloromethane (60 cm^3) for 1 h. The solution obtained was filtered and concentrated under reduced pressure to small volume (ca. 5 cm^3), then diluted with diethyl ether (75 cm^3). The resulting precipitate was filtered off, washed with diethyl ether (3 × 10 cm^3) and dried in vacuo for 3 h to yield a fine yellowish white powder. Yield 0.33 g, 94%. *Anal.* Found: C, 50.35; H, 3.80. Calc. for $C_{76}H_{68}CdCl_4P_6Pd_2S_4\cdot 1.0\ CH_2Cl_2$: C,50.05; H, 3.85%.

A range of tetrahalometallate salts containing the same cation was synthesised by similar procedures and characterised by spectroscopic methods. Details are given in Table 2 and in Section 3.

2.1.13. Diethyldithiophosphato[1,2-bis(diphenylphosphino)ethane]palladium(II) tetrachlorozincate

Dichloro[1,2-bis(diphenylphosphino)ethane]palladium (0.230 g, 0.40 mmol) and bis(*O*,*O*-diethyldithiophosphato)zinc (0.086 g, 0.20 mmol) were stirred together in dichloromethane (60 cm^3) for 1 h. The solution was then filtered, concentrated to small volume (ca. 5 cm^3) and diluted with diethyl ether. The precipitate which formed was filtered off, washed with diethyl ether (3 × 10 cm^3) and dried in vacuo for 3 h to leave a fine yellow powder (yield 0.288 g, 91%); m.p. 144–146 °C.

A range of tetrahalometallate salts containing the same cation were synthesised by similar procedures and characterised by spectroscopic methods. Details are given in Table 2 and in Section 3.

2.2. Crystallography

X-ray crystal structures have been determined for the complexes $[Ni(S_2CNEt_2)(dppe)]_2[HgBr_4]$ (**1**), $[Pt(S_2CNEt_2)(dppe)]_2[CdCl_4]\cdot 0.5CH_2Cl_2\cdot H_2O$ (**2**), $[Co(S_2CNEt_2)_2(dppe)]_2[Cl_3ZnO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}OZnCl_3]\cdot 6CHCl_3$ (**3**) and $[Pd(S_2CN^nBu_2)(bipy)]_2[CdCl_4]\cdot 2.0MeCN$ (**4**). Crystals suitable for X-ray diffraction study were grown from CH_2Cl_2–C_6H_5Me solution ((**1**) and (**2**)), $CHCl_3$ solution (**3**) and MeCN–$C_6H_5CH_3$ solution (**4**). Dark orange needles of **1**, colourless needles of **2**, thin yellow plates of **3** and dark red prisms of **4** were mounted on thin glass fibres using fast setting resin. A total of 180 oscillation frames of 90 s exposure time with 1° in θ were recorded using a Nonius Kappa CCD diffractometer, with a detector to crystal distance of 35 mm. The crystals were indexed from the first 10 frames using the DENZO package [3] and positional data were refined along with diffractometer constants to give the final unit cell parameters. Data were corrected for Lorentz and polarisation effects. The structures were solved using the direct methods option of SHELXS-86 [4] and developed via alternating least-squares cycles and difference Fourier synthesis SHELXL-93 [5] with the aid of the program RES2INS [6]. All non-hydrogen atoms were modelled anisotropically, while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times (1.5 times for CH_3 groups) that of the parent atom and allowed to ride. Crystal data and structure refinement details for all four complex salts are given in Table 3.

3. Results and discussion

3.1. Nickel and platinum dithiocarbamato complexes

The reactions of nickel and platinum complexes $[MX_2(dppe)]$ with metal dithiocarbamato complexes $[M'(S_2CNEt_2)_n]$ ($M' = Co$, Fe, Mn, $n = 3$; $M' = Pb$, Zn, Cd, Hg, Ni, Cu, MoO_2, VO, $n = 2$; $M' = Ag$, $n = 1$) in boiling acetonitrile followed a similar pattern to that

Table 3
Crystal data and structure refinement parameters for the complex salts $[Ni(S_2CNEt_2)(dppe)]_2[HgBr_4]$ (**1**), $Pt(S_2CNEt_2)(dppe)]_2[CdCl_4]\cdot 0.5CH_2Cl_2\cdot H_2O$(**2**), $[Co(S_2CNEt_2)_2(dppe)]_2[Cl_3ZnO(Ph)_2PCH_2CH_2P(Ph)_2OZnCl_3]\cdot 6CHCl_3$ (**3**) and $[Pd(S_2CN^{n}Bu_2)(bipy)]_2[CdCl_4]\cdot 2MeCN$ (**4**)

	1	**2**	**3**	**4**
Empirical formula	$C_{62}H_{68}Br_4HgN_2Ni_2P_4S_4$	$C_{125}H_{142}Cd_2Cl_{10}N_4O_2P_8Pt_4S_8$	$C_{52}H_{59}Cl_{12}CoN_2OP_3S_4Zn$	$C_{42}H_{58}CdCl_4N_8Pd_2S_4$
Formula weight	1730.95	3594.31	1498.86	1270.20
Temperature (K)	293(2)	173(2)	173(2)	100(2)
Wavelength (Å)	0.71070	0.71070	0.71070	0.71070
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic Fd2d
Space group	$P2_1/c$	$P2_1/a$	$P\bar{1}$	
Unit cell dimensions				
a (Å)	10.9720(2)	21.7506(6)	11.7318(10)	18.6817(5)
b (Å)	39.3870(8)	14.3867(4)	16.5257(13)	20.3727(11)
c (Å)	15.4790(3)	21.9300(3)	18.8520 (13)	57.560 (3)
α (°)			64.965(1)	
β (°)	90.953(1)	94.269(1)	80.620(1)	
γ (°)			86.457(1)	
V (Å^3)	6688.4(2)	6843.3(3)	3267.2(4)	21907.3(17)
Z	4	2	2	16
D_{calc} (Mg m^{-3})	1.719	1.744	1.524	1.540
Absorption coefficient (mm^{-1})	5.496	4.838	1.351	1.418
F(000)	3416	3520	1526	10208
Crystal size (mm)	$0.50\times0.10\times0.10$	$0.20\times0.20\times0.05$	$0.20\times0.20\times0.10$	$0.40\times0.40\times0.40$
θ Range for data collection (°)	2.42–21.24	3.39–26.00	3.29–25.00	3.04–25.00
Index ranges	$0\leq h\leq 11$, $0\leq k\leq 40$, $-15\leq l\leq 15$	$-26\leq h\leq 26$, $-17\leq k\leq 17$, $-26\leq l\leq 26$	$-13\leq h\leq 13$, $-18\leq k\leq 19$, $-21\leq l\leq 22$	$-21\leq h\leq 20$, $-24\leq k\leq 24$, $-68\leq l\leq 67$
Reflections collected	7326	24 816	24 513	9215
Independent reflections	7326 [$R_{int}=0.0000$]	12 920 [$R_{int}=0.0616$]	10 540 [$R_{int}=0.1017$]	9215 [$R_{int}=0.0000$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7326/0/713	12 920/0/748	10 540/0/713	9215/19/559
Final R indices	$R_1=0.0347$, $wR_2=0.0806$	$R_1=0.0410$, $wR_2=0.1000$	$R_1=0.0806$, $wR_2=0.1452$	$R_1=0.0533$, $wR_2=0.1271$
R indices (all data)	$R_1=0.0436$, $wR_2=0.0868$	$R_1=0.0506$, $wR_2=0.1070$	$R_1=0.1250$, $wR_2=0.1586$	$R_1=0.0625$, $wR_2=0.1327$
Goodness-of-fit on F^2	1.048	1.036	1.092	1.088
Largest difference peak and hole (e Å^{-3})	0.747 and −0.656	1.794 and −4.278	0.706 and −0.520	0.881 and −0.795

previously observed [1] with the corresponding palladium complexes, $[PdX_2(dppe)]$. In all cases halometallic salts of the complex cations $[M(S_2CNEt_2)(dppe)]^+$ are obtained in virtually quantitative yield. All the salts prepared were characterised by spectroscopic means and by comparison with their palladium analogues, however, only those fully described in Section 2 were submitted for elemental analysis. The cations present in each complex, were identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Typically the $[Ni(S_2CNEt_2)(dppe)]^+$ cations display proton resonances at δ 1.23 (t), CH_3CH_2N; 3.70 (q), CH_3CH_2N; 3.00 (d, $^2J_{HP}=19.1$ Hz), PCH_2CH_2P; 7.46 (m) and 7.81 (m), C_6H_5, and a ^{31}P resonance at δ 62.3 (s). Variations associated with changes in the nature of the anion present were ± 0.1 and ± 0.5 ppm for the ^1H and $^{31}P\{^1H\}$ resonances, respectively. The corresponding platinum cations $[Pt(S_2CNEt_2)(dppe)]^+$ typically display proton resonances at δ 1.34 (t), CH_3CH_2N; 3.72 (q), CH_3CH_2N; 2.90 (d, $^2J_{HP}=18.8$ Hz), PCH_2CH_2P; 7.53 (m) and 7.75 (m), C_6H_5 and a ^{31}P resonance at δ 43.25 (s) with platinum-195 satellites ($^1J_{PPt}=3120$ Hz). Variations associated changes in the nature of the counter-anion were similar in magnitude to those observed for the nickel complex cation. The NMR data for the platinum complex cation are in good agreement with a previously published spectrum [7]. In those instances where analytical data indicated the presence of solvent of crystallisation confirmation was provided by detection of the appropriate ^1H NMR resonance (δ CH_2Cl_2, 5.3 ppm; δ $CHCl_3$, 7.27 ppm). The complex cations were further characterised by infrared spectroscopy. All salts of the $[Ni(S_2CNEt_2)(dppe)]^+$ cation displayed absorptions (cm^{-1}) at 1528(s), ν(C–N); approximately 998(s) and

910(m), ν(C–S); approximately 394(w), ν(Ni–P); and approximately 355(m), ν(Ni–S). Those containing the $[Pt(S_2CNEt_2)(dppe)]^+$ cation displayed absorptions (cm^{-1}) at approximately 1533(s), ν(C–N); approximately 998(s) and 910(m), ν(C–S); approximately 399 (w), ν(Pt–P); approximately 376 (m), ν(Pt–S). Variations associated with changes in the nature of the counter-anions at ± 1 cm^{-1} were well within experimental error limits. The halometallate counter-anions were also characterised by infrared spectroscopy (Table 1). With the exception of the $[PbX_4]^{2-}$ anions, for which no reliable data could be found, and the $[HgX_4]^{2-}$ anions where the literature data display serious inconsistencies [8–10], the absorptions attributed to the halometallate anions agree well with those reported by previous authors [9,10]. Our data for the mercury anions are at variance with those given in some recent data compilations [9,10] which assign almost identical values to ν_3(Zn–Cl) and ν_3(Hg–Cl)! However, our results are well supported by the earlier work of Adams et al. [8]. Finally, the structures of two salts, $[Ni(S_2CNEt_2)(dppe)]_2[HgBr_4]$ and $[Pt(S_2CNEt_2)(dppe)]_2[CdCl_4]$, were confirmed by X-ray diffraction methods (see below).

As noted above the salts of the nickel and platinum complex cations are essentially similar to those of their palladium analogues. The relative inertness of platinum(II) species and the relative hardness of nickel(II) centres do not appear to materially alter the rate or outcome of the ligand exchange processes. In particular the nickel(II) centres, presumably softened by the presence of the ancillary diphosphine ligand, were able to abstract dithiocarbamate ligands from their complexes with even the 'softest' metals, notably Pb(II), Hg(II) and Ag(I).

As in the case of the corresponding salts of the palladium complex cation [1], the infrared data are consistent with the presence of square pyramidal $[VOX_4]^{2-}$, octahedral *cis*-dioxo $[MoO_2X_4]^{2-}$ and tetrahedral $[M'X_4]^{2-}$ anions (M′ = Pb, Zn, Cd, Hg, Ni, Co, Fe, Mn) in the respective complexes. Reactions involving the tris(dithiocarbamato) complexes $[M'(S_2CNEt_2)_3]$ (M′ = Co, Fe, Mn) are again accompanied by reduction of these metals to the divalent state and the concomitant formation of tetraethylthiuram disulfide. In the case of the relatively inert Co(III) precursor a reaction time of 10 h was allowed to ensure complete conversion. Likewise reactions involving copper(II) diethyldithiocarbamate were accompanied by reduction of that metal to the mono-valent state, and yielded salts containing the linear $[CuX_2]^-$ anions, similar to those previously characterised in salts of the palladium complex cation $[Pd(S_2CNEt_2)(dppe)]^+$ [1]. Finally reactions involving $Ag(S_2CNEt_2)$ were accompanied by the deposition of silver halide. The amounts recorded are less than anticipated for reaction (1) alone, however they are consistent with a combination of reactions (1)–(3)

$$2[MX_2(dppe)] + 2[Ag(S_2CNEt_2)] \rightarrow [M(S_2CNEt_2)(dppe)]_2[AgX_3] + AgX \quad (1)$$

$$[M(S_2CNEt_2)(dppe)]_2[AgX_3] \rightarrow [M(S_2CNEt_2)(dppe)]\ [AgX_2] + [M(S_2CNEt_2)(dppe)]X \quad (2)$$

$$[MX_2(dppe)] + [Ag(S_2CNEt_2)] \rightarrow [M(S_2CNEt_2)(dppe)][AgX_2] \quad (3)$$

Analytical data support this conclusion and suggest that salts of the dihalo anions $[AgX_2]^-$ are the major products present. Rather similar behaviour was previously noted [1] for chloroargentate salts of the corresponding palladium cation.

The crystal structures of the salts $[Ni(S_2CNEt_2)(dppe)]_2[HgBr_4]$ (**1**) and $[Pt\ (S_2CNEt_2)(dppe)]_2[CdCl_4]\cdot 0.5CH_2Cl_2\cdot H_2O$ (**2**) are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles for the two complexes are collated in Table 4. Both complexes

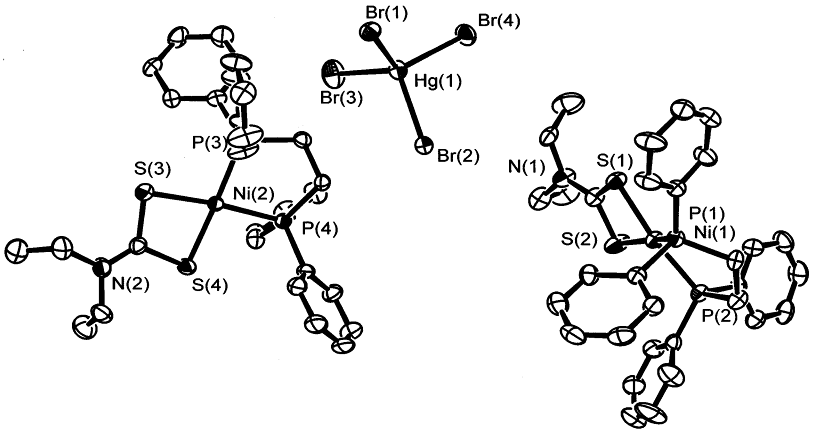

Fig. 1. Molecular structure of $[Ni(S_2CNEt_2)(dppe)]_2[HgBr_4]$ (**1**) showing atom labelling scheme.

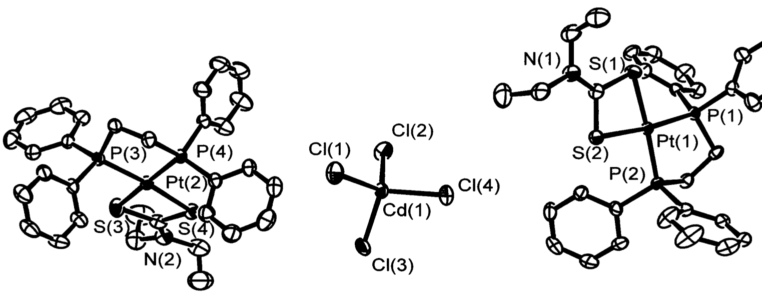

Fig. 2. Molecular structure of [Pt(S$_2$CNEt$_2$)(dppe)]$_2$[CdCl$_4$] (**2**) showing atom labelling scheme.

feature essentially square planar cations and tetrahedral anions. Comparison of structural data recorded here for the nickel and platinum complex cations with those previously reported for the corresponding palladium complex cation [1] reveals the expected trends in metal–ligand bond lengths and chelate angles. Generally increases in the former and decreases in the latter accompany increases in metal ion size Ni < Pd < Pt. As expected differences between the nickel and palladium complex cations are much more pronounced than those between the palladium and platinum species. Thus average M–P distances are 2.165, 2.265 and 2.256 Å and average M–S distances are 2.202, 2.333 and 2.360 Å for Ni, Pd and Pt, respectively. Increases in metal–ligand bond lengths lead to decreases in chelate angles, and as anticipated, these are more pronounced for the very acute S–M–S angles of the dithiocarbamate ligands which display values of 79.59, 75.73 and 74.97° for the nickel, palladium and platinum complexes respectively. Structural data for the nickel complex cation are essentially similar to those previously reported [11] for the closely related cation [Ni(S$_2$CN^{i}Pr$_2$)(dppe)]$^+$ save for a slight asymmetry in the Ni–S and Ni–P bond lengths, possibly due to packing forces, apparent in the former. A similar asymmetry observed for the cation [Ni(S$_2$CNEt$_2$)(PPh$_3$)$_2$]$^+$ has been attributed to steric interaction between the bulky PPh$_3$ ligands [12]. The platinum cation [Pt(S$_2$CNEt$_2$)(dppe)]$^+$ also displays asymmetric coordination about the platinum centre, notably in the Pt–S bond lengths. The [HgBr$_4$]$^{2-}$ anions are essentially tetrahedral with only minor distortions and display bond lengths and bond angles in good agreement with data previously recorded [13,14]. Likewise the [CdCl$_4$]$^{2-}$ anions deviate little from tetrahedral symmetry and have bond length and bond angle data similar to those previously reported for this anion [2,15,16].

3.2. Ruthenium dithiocarbamato complexes

The ruthenium complex *cis*-[RuCl$_2$(dppm)$_2$] reacts with dithiocarbamates of zinc, cadmium, mercury and lead, [M′(S$_2$CNEt$_2$)$_2$] in boiling acetonitrile to afford salts of the general form [Ru(S$_2$CNEt$_2$)(dppm)$_2$]$_2$[M′Cl$_4$] in excellent yield. The salts, which were isolated as pale yellow, air stable crystals, were characterised by infrared and NMR data. The stoichiometry and structure of one example, [Ru(S$_2$CNEt$_2$)(dppm)$_2$]$_2$[CdCl$_4$] were confirmed by elemental analysis and a partial X-ray

Table 4
Selected bond lengths (Å) and bond angles (°) for the complex salts [Ni(S$_2$CNEt$_2$)(dppe)]$_2$[HgBr$_4$] (**1**) and [Pt(S$_2$CNEt$_2$)(dppe)]$_2$[CdCl$_4$]·0.5CH$_2$Cl$_2$·H$_2$O (**2**)

1		**2**	
Bond lengths			
Ni(1)–S(1)	2.1942(19)	Pt(1)–S(1)	2.3488(14)
Ni(1)–S(2)	2.211(2)	Pt(1)–S(2)	2.3723(13)
Ni(1)–P(1)	2.1480(18)	Pt(1)–P(1)	2.2587(13)
Ni(1)–P(2)	2.1810(19)	Pt(1)–P(2)	2.2533(14)
Ni(2)–S(3)	2.2117(19)	Pt(2)–S(3)	2.3464(17)
Ni(2)–S(4)	2.2074(18)	Pt(2)–S(4)	2.3613(15)
Ni(2)–P(3)	2.1847(18)	Pt(2)–P(3)	2.2458(15)
Ni(2)–P(4)	2.1651(18)	Pt(2)–P(4)	2.2484(15)
S(1)–C(1)	1.719(7)	S(1)–C(1)	1.737(6)
S(2)–C(1)	1.719(7)	S(2)–C(1)	1.741(6)
S(3)–C(32)	1.720(7)	S(3)–C(32)	1.728(7)
S(4)–C(32)	1.719(7)	S(4)–C(32)	1.733(7)
N(1)–C(1)	1.310(8)	N(1)–C(1)	1.296(8)
N(1)–C(2)	1.472(9)	N(1)–C(2)	1.481(8)
N(1)–C(4)	1.542(10)	N(1)–C(4)	1.469(8)
N(2)–C(32)	1.311(8)	N(2)–C(32)	1.307(8)
N(2)–C(33)	1.465(9)	N(2)–C(33)	1.471(10)
N(2)–C(35)	1.497(10)	N(2)–C(35)	1.475(10)
Hg(1)–Br(1)	2.6515(8)	Cd(1)–Cl(1)	2.4369(17)
Hg(1)–Br(2)	2.6284(9)	Cd(1)–Cl(2)	2.4721(17)
Hg(1)–Br(3)	2.5659(9)	Cd(1)–Cl(3)	2.4678(18)
Hg(1)–Br(4)	2.5986(9)	Cd(1)–Cl(4)	2.4642(16)
Bond angles			
P(1)–Ni(1)–P(2)	86.47(7)	P(1)–Pt(1)–P(2)	85.84(5)
P(1)–Ni(1)–S(1)	96.07(7)	P(1)–Pt(1)–S(1)	98.24(5)
P(2)–Ni(1)–S(2)	99.79(7)	P(2)–Pt(1)–S(2)	100.92(5)
S(1)–Ni(1)–S(2)	79.57(7)	S(1)–Pt(1)–S(2)	75.00(5)
P(3)–Ni(2)–P(4)	87.16(7)	P(3)–Pt(2)–P(4)	85.66(5)
P(3)–Ni(2)–S(3)	97.48(7)	P(3)–Pt(2)–S(3)	98.35(6)
P(4)–Ni(2)–S(4)	96.07(7)	P(4)–Pt(2)–S(4)	101.28(5)
S(3)–Ni(2)–S(4)	79.18(7)	S(3)–Pt(2)–S(4)	74.85(6)
Br(1)–Hg(1)–Br(2)	110.64(3)	Cl(1)–Cd(1)–Cl(2)	112.27(7)
Br(1)–Hg(1)–Br(3)	108.06(3)	Cl(1)–Cd(1)–Cl(3)	107.12(7)
Br(1)–Hg(1)–Br(4)	110.09(3)	Cl(1)–Cd(1)–Cl(4)	113.45(7)
Br(2)–Hg(1)–Br(3)	108.29(4)	Cl(2)–Cd(1)–Cl(3)	108.79(8)
Br(3)–Hg(1)–Br(4)	114.79(3)	Cl(3)–Cd(1)–Cl(4)	108.02(7)

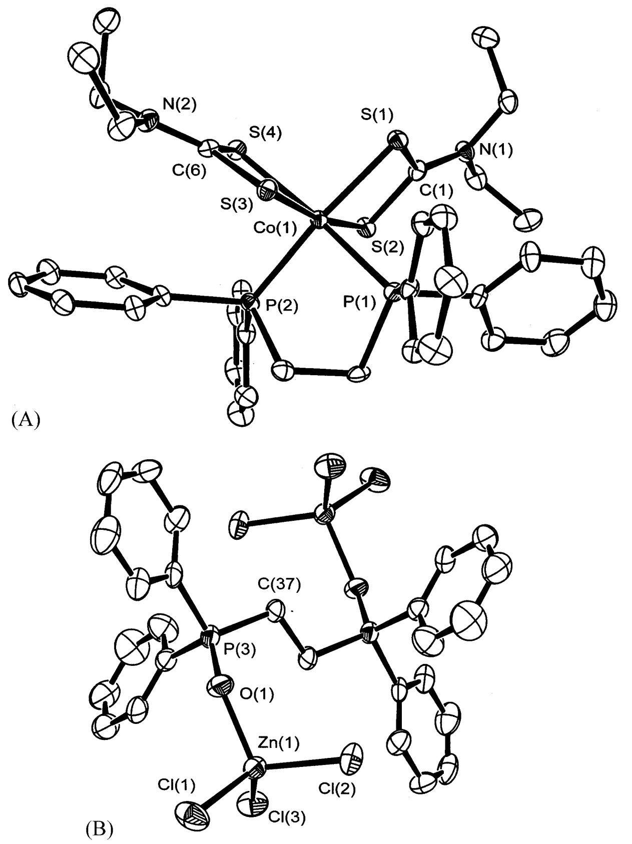

Fig. 3. (A) Molecular structure of cation $[Co(S_2CNEt_2)_2(dppe)]^+$ from salt (**3**) showing atom labelling scheme. (B) Molecular structure of anion $[Cl_3ZnO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}OZnCl_3]^{2-}$ from salt (**3**) showing atom labelling scheme.

crystal structure determination. The infrared data (Table 2) are in each case consistent with the presence of coordinated diothiocarbamate ligands (ν(C–N) ca. 1500 cm^{-1}; ν(C–S) ca. 1000 and 915 cm^{-1}; ν(Ru–S) ca. 380 cm^{-1}) and discrete tetrahedral $[M'Cl_4]^{2-}$ anions. All the salts displayed essentially identical ^1H and $^{31}P\{^1H\}$ NMR data consistent with the presence of $[Ru(S_2CNEt_2)(dppm)_2]^+$ cations. A typical data set is as follows: ^1H NMR: δ 1.06 (t, CH_3CH_2N), 3.50 (m, CH_3CH_2N), 4.60 and 4.91 (m, PCH_2P); 6.45 (m), 7.0 (m), 7.25 (m) and 7.64 (m, C_6H_5). $^{31}P\{^1H\}$ NMR: δ −4.8 and −17.5 (t, PCH_2P). Anion dependent variations do not exceed ±0.1 ppm (^1H) and ±0.3 ppm $^{31}P\{^1H\}$. An X-ray crystallographic study of $[Ru(S_2CNEt_2)(dppm)_2]_2[CdCl_4]$ was undertaken, unfortunately the molecules were severely disordered and the crystals contained large amounts of chloroform which was readily lost when they were removed from the mother liquor. A complete structure determination was not possible however, the partial data set obtained was sufficient to provide unit cell parameters ($a = 15.2087$ Å, $b = 15.3479$ Å, $c = 17.1224$ Å, $\alpha = 73.218°$, $\beta = 83.073°$, $\gamma = 19.732°$) and confirm the proposed stoichiometry and stereochemistry.

3.3. Cobalt dithiocarbamato complexes

The cobalt(II) halides $[CoX_2(dppe)]$ react with dithiocarbamates $[M'(S_2CNEt_2)_2]$ ($M' = Cd$, Hg) undergoing oxidation to afford cobalt(III) salts $[Co(S_2CNEt_2)_2(dppe)]_2\ [M'X_4]$ in moderate yield as dark red powders. Addition of the appropriate amount of the corresponding thiouram disulfide $(Et_2NCS_2)_2$ as an oxidising agent and source of extra dithiocarbamate anions gave the products in essentially quantitative yield (Eq. (4)).

$$2[CoCl_2(dppe)] + [M'(S_2CNEt_2)_2] + (S_2CNEt_2)_2 \rightarrow 2[Co(S_2CNEt_2)_2(dppe)]2[M'Cl_4] \quad (4)$$

The cobalt(III) complex salts were characterised by their infrared (Table 2) and NMR spectra; the stoichiometry and stereochemistry of the tetrachlorocadmate salt were confirmed by elemental analysis and X-ray diffraction methods. The $[Co(S_2CNEt_2)_2(dppe)]^+$ cation has previously been characterised as its $[BF_4]^-$ salt. Our infrared and NMR data are in good agreement with those presented by the previous authors [17] and clearly establish the presence of the $[Co(S_2CNEt_2)_2(dppe)]^+$ cation in each case. A typical data set is as follows: ^1H NMR: δ 0.75 and 0.87 (t, CH_3CH_2N), 3.06 and 3.32 (m, CH_3CH_2N), 2.72 (br d, PCH_2CH_2P), 7.10 (m), 7.26 (m), 7.55 (m) and 7.85 (m) C_6H_5. $^{31}P\{^1H\}$NMR: δ 60.3 (s). Changes associated with variations in the identity of the counter anion present are ±0.1 and ±0.5 ppm for ^1H and $^{31}P\{^1H\}$ resonances, respectively. All the NMR resonances show broadening attributable to coupling with the ^{59}Co quadrupole moment. An attempted X-ray crystal structure determination for the complex $[Co(S_2CNEt_2)_2(dppe)]_2[CdCl_4]$ revealed severe disordering and variable amounts of chloroform of crystallisation, consequently only unit cell parameters could be determined ($a = 23.6388(10)$ Å, $b = 11.4468(4)$ Å, $c = 47.2679(2)$ Å, $\beta = 104.0990°$).

The reaction of $[CoCl_2(dppe)]$ with $[Zn(S_2CNEt_2)_2]/(S_2CNEt_2)_2$ afforded as the only isolated product a dark red crystalline solid, which on the basis of elemental analysis and spectroscopic evidence was not the expected salt $[Co(S_2CNEt_2)_2(dppe)]_2[ZnCl_4]$. In addition to the ^1H and $^{31}P\{^1H\}$ NMR resonances typical of the $[Co(S_2CNEt_2)_2(dppe)]^+$ cation the spectra displayed a ^1H NMR signal at δ 2.20 (broadened doublet) and a $^{31}P\{^1H\}$ signal at δ 42.4 (s). An X-ray crystal structure determination revealed a 2:1 salt containing the expected cation $[Co(S_2CNEt_2)_2(dppe)]^+$ and the novel anion $[Cl_3ZnO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}O\ ZnCl_3]^{2-}$ (Fig. 3(A) and (B)). Bond length and angle data are given in Table 5.

The cation $[Co(S_2CNEt_2)_2(dppe)]^+$ has not previously been structurally characterised, however a crystal structure determination has been reported for the

$[BPh_4]^-$ salt of the closely related cation $[Co(S_2CNMe_2)_2(dmpf)]^+$ [dmpf = 1,1′-bis(dimethylphosphino)ferrocene] [18]. The two cations have very similar Co–S and Co–P bond lengths with Co–S *trans* to P approximately 0.03 Å longer than Co–S *trans* to S in each case. The difference no doubt reflecting the greater *trans* influence of the P-donor. The Co–S distances *trans* to S are very similar to those previously reported for $[Co(S_2CNEt_2)_3]$ [19]. The angle subtended at cobalt by the dmpf ligand (102.3(1)°) is substantially larger than that subtended by the dppe ligand (87.01(2)°). However, this difference is not reflected in the angles subtended at cobalt by the dithiocarbamate ligands which remain essentially constant at approximately 76° for the two complexes.

The anion, $[Cl_3ZnO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}OZnCl_3]^{2-}$ provides a rare example of the bridging 1,2-bis(diphenylphosphinoyl)ethane ligand. To the best of our knowledge the only previously reported examples are three cobalt(II) species—the cyclic dimer $[CoCl_2\{O{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}O\}]_2$ [20], the linear polymer $[CoCl_2\{O{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}O\}]_n$ [21] and the ionic salt $[Co(CO)(dppe)_2]_2[Cl_3CoO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}OCoCl_3]$ [22]. Since analogous Zn(II) and Co(II) complexes are often isostructural, it seems particularly appropriate to compare the zinc and cobalt complex anions $[Cl_3MO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}OMCl_3]^{2-}$. Both anions are centrosymmetric with a fully staggered arrangement of the diphosphine and the attached $OMCl_3$ groups. The P=O bond length (1.520(5) Å) and P–O–M bond angle (141.1(3)°) in the zinc anion are significantly greater than the corresponding parameters for the cobalt anion (1.477(5) Å and 133.8(3)°) [22]. Coordination geometry at the zinc and cobalt atoms is essentially tetrahedral with angles subtended at the metal by adjacent ligands ranging from 102.45(15) to 115.78(8)° in the case of zinc and from 101.0(1) to 117.86(8)° in the case of cobalt. The Zn–O and Zn–Cl bonds in the $(Cl_3ZnO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}OZnCl_3]^{2-}$ dianion are all significantly (ca. 0.05 and 0.04 Å) longer than the corresponding bonds in the neutral complex $[ZnCl_2(OPPh_3)_2]$ [23], the differences can probably be attributed to the presence of negative charges on the former species.

In the light of this structure it is possible to assign the additional ^1H and $^{31}P\{^1H\}$ NMR resonances reported above to the methylene protons and P (V) atoms of the complex anion.

Table 5
Selected bond lengths (Å) and bond angles (°) for the salt $[Co(S_2CNEt_2)_2(dppe)]_2[Cl_3ZnO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}OZnCl_3]$ (**3**)

Cation		Anion	
Bond lengths			
Co(1)–P(1)	2.2370(18)	Zn(1)–Cl(1)	2.229(2)
Co(1)–P(2)	2.2415(19)	Zn(1)–Cl(2)	2.238(2)
Co(1)–S(1)	2.2931(19)	Zn(1)–Cl(3)	2.2533(19)
Co(1)–S(2)	2.2703(18)	Zn(1)–O(1)	2.009(5)
Co(1)–S(3)	2.2653(19)	P(3)–O(1)	1.520(5)
Co(1)–S(4)	2.3044(18)	P(3)–C(37)	1.796(7)
S(1)–C(1)	1.727(6)	C(37)–C(37A)	1.531(12)
S(2)–C(1)	1.713(7)		
S(3)–C(6)	1.719(6)		
S(4)–C(6)	1.705(6)		
N(1)–C(1)	1.316(8)		
N(2)–C(6)	1.347(8)		
P(1)–C(12)	1.826(6)		
P(2)–C(11)	1.815(6)		
C(11)–C(12)	1.534(9)		
Bond angles			
P(1)–Co(1)–P(2)	87.01(7)	O(1)–Zn(1)–Cl(1)	102.45(15)
P(1)–Co(1)–S(1)	89.85(7)	O(1)–Zn(1)–Cl(2)	106.09(15)
P(1)–Co(1)–S(2)	90.54(7)	O(1)–Zn(1)–Cl(3)	109.44(14)
P(1)–Co(1)–S(3)	98.86(7)	Cl(1)–Zn(1)–Cl(2)	115.78(8)
P(1)–Co(1)–S(4)	172.19(7)	Cl(1)–Zn(1)–Cl(3)	112.50(8)
P(2)–Co(1)–S(1)	173.54(7)	Cl(2)–Zn(1)–Cl(3)	109.98(8)
P(2)–Co(1)–S(2)	98.28(7)		
P(2)–Co(1)–S(3)	89.50(7)		
P(2)–Co(1)–S(4)	89.87(7)		
S(1)–Co(1)–S(2)	76.10(7)		
S(1)–Co(1)–S(3)	96.48(7)		
S(1)–Co(1)–S(4)	93.94(7)		
S(2)–Co(1)–S(3)	169.44(7)		
S(2)–Co(1)–S(4)	96.99(7)		
S(3)–Co(1)–S(4)	75.97(6)		

3.4. Palladium dithiocarbamato complexes

In order to ascertain if the presence of a chelate diphosphine ligand was an essential prerequisite for ligand cross transfer to occur, reactions of the bipyridyl complexes $[PdX_2(bipy)]$ with a range of dithiocarbamates was investigated. The low solubility of the bipyridyl precursors necessitated the use of boiling acetonitrile as reaction medium. Furthermore, in order to facilitate crystallisation of the products it was found convenient to use di-*n*-butyldithiocarbamates which possess a suitable solubility profile. The ligand cross transfer reactions proceeded smoothly to afford tetrahalometallate salts $[Pd(S_2CN^nBu_2)(bipy)]_2$ $[M'X_4]$ (M′ = Zn, Cd, Hg; X = Cl, Br, M′ = Pb, X = Cl) in good yield. Changing the relatively soft diphosphine ligand for the somewhat harder bipyridyl does not, in the present instance at least, alter the course of the ligand transfer process. The tetrahalometallate salts formed are air-stable solids which are moderately soluble in boiling solvents of high polarity, and crystallise well therefrom. One representative example, $[Pd(S_2CN^nBu_2)(bipy)]_2[CdCl_4]$, was characterised by elemental analysis and X-ray crystal structure determination; the remainder were identified by spectroscopic methods. The recording of the ^1H NMR spectra was hampered by the relatively low solubility of the complex salts. However, ^1H data of acceptable quality were collected and these confirm the presence of dipyridyl

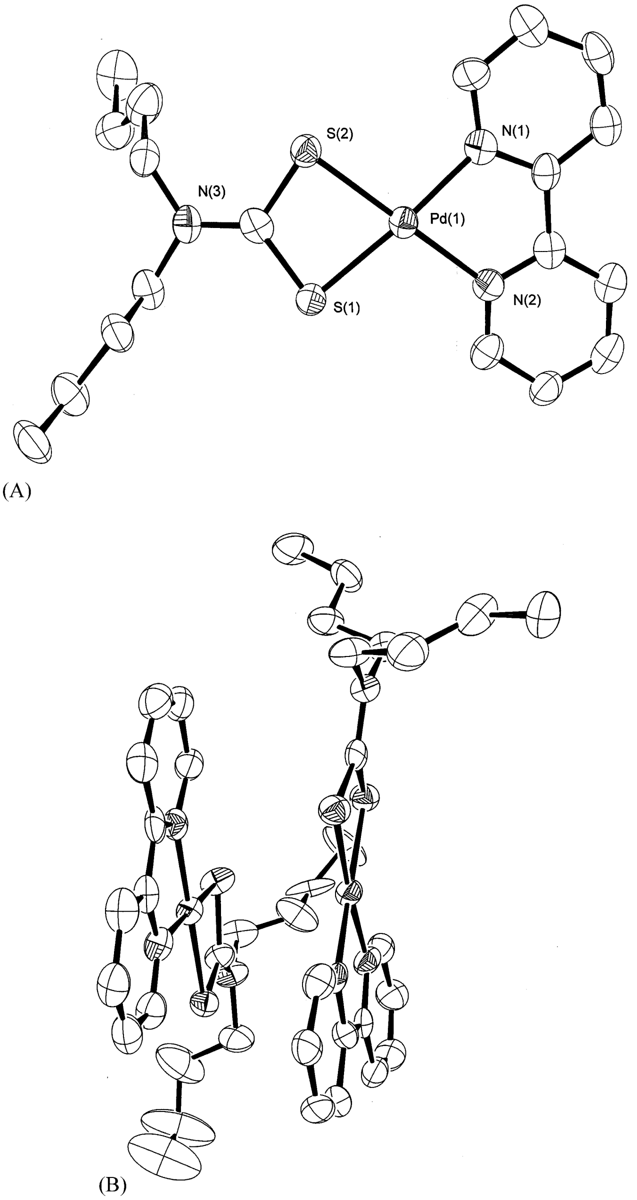

Fig. 4. (A) Molecular structure for cation $[Pd(S_2CN^nBu_2(bipy)]^+$ from salt (**4**) showing atom labelling scheme. (B) Arrangement of cation pairs in salt (**4**).

and dithiocarbamate ligands in the correct 1/1 ratio. A typical NMR data set is as follows: ^1H NMR: δ 0.90 (t, $CH_3CH_2CH_2CH_2N$), 1.30 (m, $CH_3CH_2CH_2CH_2N$), 1.61 (m, $CH_3CH_2CH_2CH_2N$), 3.68 (t, $CH_3CH_2CH_2CH_2N$), 7.70 (m), 8.24 (m) and 8.46 (m) $(C_5H_4N)_2$. Variations associated with changes in the nature of the counteranion were within the range ± 0.1 ppm. Infrared data are given in Table 2. The complex $[Pd(S_2CN^nBu_2)(bipy)]_2[CdCl_4]$ crystallises from $CH_3CN-C_6H_5CH_3$ with two molecules of CH_3CN per anion, these are lost on drying the crystals in vacuo prior to analysis. The X-ray crystal structure determination was performed on fully solvated crystals. The molecular structure of the cation showing the atom numbering scheme and the arrangement of cation pairs are shown in Fig. 4(A) and (B). Selected bond length and bond angle data are presented in Table 6.

The core of the palladium(II) cation is strictly planar with the Pd atom situated in the plane defined by the bipy ligand and the S_2CN skeleton of the dithiocarbamate ligand. Differences of ca. 0.02 and 0.03 Å in the length of the Pd–N and Pd–S bonds, respectively, bestow a slight asymmetry on the cation coordination sphere with the shortest Pd–N bond *trans* to the longest Pd–S bond. The Pd–S distances in the present complex are slightly shorter than those found for the complex $[Pd(S_2CN^nBu_2)_2]$ [24], the difference probably being attributable in part to the presence of a positive charge on the cation. The bipyridyl and dithiocarbamate ligands displaying typical narrow 'bite' angles of 80.1(3) and 75.66(8)°, respectively. The cations are stacked in mutually parallel pairs. However, the Pd–Pd distance of 3.376 Å is too great for significant Pd–Pd bonding interaction. Likewise, the closest intermolecular Pd–S distance (4.261 Å) clearly indicates the absence of any significant Pd–S interaction. To minimise steric interactions between $S_2CN^nBu_2$ groups within the cation pairs each cation is rotated through 117.4° relative to its partner. The $[CdCl_4]^{2-}$ anions have almost ideal tetrahedral symmetry with Cd–Cl bond lengths in the range 2.451(3)–2.485 (2) Å and Cl–Cd–Cl bond angles in the range 106.11(9)–110.01(10)°. Their values lie well

Table 6
Selected bond length (Å) and bond angle (°) data for the salt $[Pd(S_2CNBu^n_2)(bipy)]_2[CdCl_4].2MeCn$ (**4**)

Cation		Anion	
Bond lengths			
Pd(1)–N(1)	2.038(8)	Cd(1)–Cl(1)	2.454(3)
Pd(1)–N(2)	2.067(7)	Cd(1)–Cl(2)	2.456(3)
Pd(1)–S(1)	2.303(2)	Cd(1)–Cl(3)	2.450(3)
Pd(1)–S(2)	2.282(2)	Cd(1)–Cl(4)	2.484(2)
Pd(2)–N(4)	2.058(2)		
Pd(2)–N(5)	2.033(7)		
Pd(2)–S(3)	2.277(2)		
Pd(2)–S(4)	2.290(2)		
S(1)–C(11)	1.725(10)		
S(2)–C(11)	1.708(10)		
N(3)–C(11)	1.337(12)		
S(3)–C(30)	1.721(9)		
S(4)–C(30)	1.732(9)		
N(6)–C(30)	1.287(12)		
Bond angles			
N(1)–Pd(1)–N(2)	80.2(3)	Cl(1)–Cd(1)–Cl(2)	110.99(10)
N(1)–Pd(1)–S(1)	175.6(2)	Cl(1)–Cd(1)–Cl(3)	110.35(10)
N(1)–Pd(1)–S(2)	100.4(2)	Cl(1)–Cd(1)–Cl(4)	106.12(9)
S(1)–Pd(1)–S(2)	75.67(8)	Cl(2)–Cd(1)–Cl(3)	109.83(12)
N(4)–Pd(2)–N(5)	79.0(3)	Cl(2)–Cd(1)–Cl(4)	108.55(10)
N(4)–Pd(2)–S(3)	176.9(2)	Cl(3)–Cd(1)–Cl(4)	110.94(10)
N(4)–Pd(2)–S(4)	101.8(2)		
S(3)–Pd(2)–S(4)	75.91(9)		

within the range of values previously reported for this anion [2,15,16].

3.5. Palladium complexes of other S-donor chelate ligands

Finally, in order to further explore the generality of these halide/S chelate ligand cross transfers the reaction of the palladium complexes [PdX_2(dppe)] with a range of transition metal xanthates (*O*-ethyldithiocarbonates), diphenyldithiophosphinates and diethyldithiophosphates were examined.

3.5.1. Palladium O-ethyldithiocarbonate and dithiocarbonate complexes

Reaction between the palladium dihalide complexes [PdX_2(dppe)] and transition metal *O*-ethyldithiocarbonate [$M'(S_2COEt)_2$] (M' = Zn, Cd, Hg, Pb, Fe and Ni) in cold dichloromethane all afforded fine yellow or pale green (M' = Fe, Ni) powdery products in good yield. However, on examination by infrared and NMR spectroscopy it became apparent that each was a approximately 30/70 mixture of two components—the anticipated salt [$Pd(S_2COEt)$(dppe)]$_2$[$M'X_4$] and the neutral dithiocarbonate complex [$Pd(S_2CO)$(dppe)]. A typical set of NMR data comprised ^1H resonances at δ 1.52 (t) CH_3CH_2O; 2.56 (d, $^2J_{HP} = 19.8$ Hz) and 3.27 (d, $^2J_{HP} = 23.4$ Hz) PCH_2CH_2P; 4.74(q) CH_3CH_2O; 7.42 (m) and 7.73 (m) C_6H_5 and $^{31}P\{^1H\}$ resonances are δ 64.5 (s) and 53.0 (s). On the basis of integration data and by comparison with related complexes it is possible to assign the triplet at δ 1.51, the quartet at δ 4.74, the doublet at δ 3.27 and the $^{31}P\{^1H\}$ singlet at δ 53.0 to the *O*-ethyldithiocarbonate complex salt. The remaining doublet at δ 2.56 and the $^{31}P\{^1H\}$ singlet at δ 64.5 are attributed to the dithiocarbonate complex [$Pd(S_2CO)$(dppe)].

A further indication of the presence of the dithiocarbonate complex [$Pd(S_2CO)$(dppe)] was provided by the appearance of sharp bands at approximately 1675 and 1603 cm^{-1} in the infrared spectra of the product mixtures. A similar pair of bands (1681 and 1603 cm^{-1}) have been reported for the related palladium complex [$Pd(S_2CO)(PMePh_2)_2$] [25]. Attempts to complete the conversion of the product mixtures to the pure dithiocarbonato complex [$Pd(S_2CO)$(dppe)] in boiling acetonitrile were unsuccessful. At first sight this failure is unexpected given the very facile conversion of the *O*-alkyldithiocarbonates [$M'(S_2COR)_2$] (M' = Ni, Pt) to the corresponding dithiocarbonato complexes [$M(S_2CO)$(dppe)] accomplished by addition of the diphosphine to cold dichloromethane solutions of the former complexes [26,27]. However, it has previously been suggested that mechanisms of *O*-alkyldithiocarbonate → dithiocarbonate conversion in complexes of the nickel triad involve free *O*-alkyldithiocarbonate anions functioning as alkyl cation abstractors [28,29]. It therefore seems probable that in our systems the conversion proceeds so long as labile $EtOCS_2^-$ anions are present but it is inhibited once they are all bound in the palladium product. It is also possible that the presence of the chelating diphosphine on the palladium precursor may play a part in inhibiting the conversion.

3.5.2. Palladium dithiophosphinate complexes

Reactions of the palladium complexes [PdX_2(dppe)] with metal diphenyldithiophosphinates [$M'(S_2PPh_2)_2$] (M' = Zn, Cd, Hg, Pb, Co, Ni) in dichloromethane at room temperature gave fine pale yellow or light green (M' = Co, Ni) powdery products in good yield. These were characterised primarily by spectroscopic methods. Infrared data (Table 2) are consistent with the presence of [$M'X_4$]$^{2-}$ anions. NMR data for the complex cation—^1H NMR: δ 3.25 (d, $^2J_{HP} = 24.7$ Hz, PCH_2CH_2P), 7.48 and 7.75 (m, C_6H_5). $^{31}P\{^1H\}$ NMR: δ 66.6 (s, PCH_2CH_2P), 88.57 (s, Ph_2PS_2)—are consistent with the proposed stoichiometry and structure. Anion dependent variations are less that ± 0.1 and ± 0.5 ppm for ^1H and $^{31}P\{^1H\}$ spectra, respectively. Confirmation of stoichiometry was obtained for one complex, [$Pd(S_2PPh_2)$(dppe)]$_2$[$CdCl_4$], by elemental analysis.

3.5.3. Palladium dithiophosphato complexes

The palladium complex [PdX_2(dppe)] reacted in similar fashion with the dithiophosphate complex [$M'\{S_2P(OEt)_2\}_2$] (M' = Zn, Cd, Hg, Pb, Fe, Ni) to afford the salts [$Pd\{S_2P(OEt)_2\}$(dppe)]$_2$[$M'X_4$] in good yield as pale yellow or green (M' = Fe, Ni) air stable powders. Characterisation was by spectroscopic methods. Infrared data (Table 2) are consistent with the proposed structures of the complex cation [$Pd\{S_2P(OEt)_2\}$(dppe)]$^+$ and the various anions [MX_4]$^{2-}$. NMR data for the complex cation—^1H NMR: δ 1.35 (t, CH_3CH_2O), 3.35 (d, $^2J_{HP} = 24.4$ Hz, PCH_2CH_2P) 4.12 (q, CH_3CH_2O), 7.48 and 7.78 (m, C_6H_5). $^{31}P\{^1H\}$ NMR: δ 67.0 (s, PCH_2CH_2P), 100.1 (s, $S_2P(OEt)_2$). Anion dependent variations are less than ± 0.1 and ± 0.3 ppm for ^1H and $^{31}P(^1H)$ resonances, respectively. The NMR spectra revealed no evidence to suggest that significant conversion to Pd{S_2P(O)-OEt}(dppe)] had occurred in any of the syntheses. Since free $S_2P(OEt)_2^-$ anions have previously been implicated in these reactions as ethyl cation acceptors [30] it seems likely that their absence in the present systems inhibited the conversion.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC Nos. 141135, 141134, 158199 and 158200 for compounds **1**, **2**, **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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