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# Nickel complexes of 1,2-bis(diisopropylphosphino)ethane with sulfur-containing ligands

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The complex $[NiBr_2(dippe)]$ **1** [dippe = 1,2-bis(diisopropylphosphino)ethane] reacted with benzene- and polyfluorobenzene-thiolates furnishing square-planar complexes $[Ni(SR)_2(dippe)]$ (R = $C_6F_5$ **2a**, $C_6F_4H$ **2b**, $C_6H_4F$ **2c** or Ph **2d**). These compounds reacted with $CNBu^t$ and $Na[BPh_4]$ in EtOH to yield the derivatives *cis*-$[Ni(SR)(CNBu^t)(dippe)][BPh_4]$ (R = $C_6F_5$ **3a**, $C_6F_4H$ **3b**, $C_6H_4F$ **3c** or Ph **3d**). No reaction takes place with CO under similar conditions. These compounds exhibit fluxional behaviour in solution. Compound **1** also reacted with sodium dialkyldithiocarbamates affording $[Ni(S_2CNR_2)(dippe)]Br$ (R = Et **4a** or Me **4b**), which contain one bidentate dithiocarbamate ligand. However, the reaction with alkyl dithiocarbonates occurs with degradation, and the ultimate metal-containing product is the dithiocarbonate complex $[Ni(S_2CO)(dippe)]$ **5**, the crystal structure of which has been determined. All the compounds have been characterized by IR and NMR spectroscopy and microanalysis.

There has been increasing interest in the synthesis and reactivity of mononuclear complexes with sulfur-containing ligands,[1] in part because of the reactivity they display towards organic substrates[2] and also because of their relevance as models of biologically redox-active metalloproteins.[3] In this context, nickel complexes with S-donor ligands are present in many hydrogenases.[4] Despite the great amount of work devoted to the study of metal–thiolate complexes,[1a,5] fundamental knowledge of the structures of mononuclear species is relatively sparse. Some discrete nickel(II) homoleptic thiolate complexes have been reported, *e.g.* tetrahedral $[Ni(SPh)_4]^{2-}$.[6] When simple nickel(II) salts are treated with thiols different products are obtained depending on the basicity and the bulkiness of the thiol. In most cases stable thiolate-bridged polymers are formed.[1b] Further treatment of these polymers with either tertiary phosphines or isocyanides yields in some instances to mononuclear mixed-ligand complexes of the type $[Ni(SR)_2L_2]$.[7] These are often accessible by metathetical exchange of halide X by SR in halogeno-complexes of the type $[NiX_2L_2]$.[8,9] Mixed thiolate–phosphine complexes of nickel with known structure are limited, as far as we are aware, to $[Ni(SC_6F_5)_2(dppe)]$[9] (dppe = $Ph_2PCH_2CH_2PPh_2$) and trinuclear $[\{Ni(S_2C_{10}Cl_6)(PPh_3)\}_3]$.[10] Considering related complexes with other sulfur-containing ligands, mononuclear derivatives such as $[Ni(S_2CNEt_2)(PPh_3)_2]^+$,[11] $[Ni(S_2COEt)_2(PPh_3)]$[12] and $[Ni(CS_3)(dmpe)]$ [dmpe = 1,2-bis(dimethylphosphino)ethane][2] have also been studied.

In this work we report the synthesis and properties of several nickel complexes with the bulky diphosphine dippe ($Pr^i{}_2PCH_2CH_2PPr^i{}_2$) and sulfur-containing ligands, namely benzene- and polyfluorobenzene-thiolates, dithiocarbamates and dithiocarbonate. The crystal structure of the dithiocarbonate complex $[Ni(S_2CO)(dippe)]$ is also reported.

## Experimental

All synthetic operations were routinely performed under a dry dinitrogen atmosphere following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether and light petroleum (b.p. 40-60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane[13] and $[NiBr_2(dippe)]$[14] were prepared according to the literature. Lead polyfluorobenzenethiolates were gifts from Dr. Juventino García, Universidad Nacional Autónoma de México (UNAM), who prepared them following published procedures.[15] Benzenethiol, *tert*-butyl isocyanide and hydrated sodium dialkyldithiocarbamates were supplied by Aldrich. Potassium alkyl thiocarbonates were prepared by reaction of $CS_2$ with KOH in the corresponding alcohol. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer 881 spectrophotometer, NMR spectra on Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in ppm from $SiMe_4$ ($^1H$ and $^{13}C-\{^1H\}$), 85% $H_3PO_4$ ($^{31}P-\{^1H\}$) or $C_6F_6$ ($^{19}F$). The phosphine protons for all the compounds appeared in the corresponding $^1H$ NMR spectra as a series of overlapping multiplets in the range δ 1–3 and were not assigned. Microanalyses were by Dr. Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía.

### Preparations

**$[Ni(SR)_2(dippe)]$ (R = $C_6F_5$ 2a, $C_6F_4H$ 2b or $C_6H_4F$ 2c).** To a suspension of $[NiBr_2(dippe)]$ **1** in acetone was added an equimolar amount of the corresponding solid lead thiolate $Pb(SR)_2$ (R = $C_6F_5$, $C_6F_4H$ or $C_6H_4F$). The mixture was stirred at room temperature for 15 min. A red solution and a white–yellow precipitate of $PbBr_2$ was obtained. The mixture was centrifuged, and the red solution taken to dryness upon decantation. The residue was extracted with diethyl ether, and the solution filtered. Concentration and cooling to −20 °C afforded red crystals in good yields (*ca.* 80–90%). Complex **2a** (Found: C, 43.2; H, 4.40. $C_{26}H_{32}F_{10}NiP_2S_2$ requires C, 43.4; H, 4.45%): NMR ($CDCl_3$) $^{31}P-\{^1H\}$, δ 82.46 (s); $^{13}C-\{^1H\}$, δ 18.25, 19.77 {s, $P[CH(CH_3)_2]$}, 21.36 (t, $J_{CP}$ = 19.1, $PCH_2$), 25.78 {t, $J_{CP}$ = 12.2, $P[CH(CH_3)_2]$}, 137.1 (d, br, $J_{CF}$ = 245, $C_6F_5$) and 147.2 (d, br, $J_{CF}$ = 239, $C_6F_5$); $^{19}F$, δ −0.223 (m), 1.879 (t, $J_{FF}$ = 20.7) and 31.89 (dd, $J_{FF}$ = 20.3, 6.8 Hz). Complex **2b** (Found: C, 45.7; H, 5.05. $C_{26}H_{34}F_8NiP_2S_2$ requires C, 45.7; H, 5.00%): NMR ($CDCl_3$) $^1H$, δ 6.610 (t of t, $J_{HF}$ = 7.26, $J_{HF'}$ = 10.0, $C_6F_4H$); $^{31}P-\{^1H\}$ δ 82.75 (s); $^{13}C-\{^1H\}$, δ 18.29, 19.85 {s, $P[CH(CH_3)_2]$}, 21.43 (t, $J_{CP}$ = 19.8, $PCH_2$), 25.77 {t, $J_{CP}$ = 12.2, $P[CH(CH_3)_2]$}, 99.68 (t, $J_{CF}$ = 23.5, $HC_6F_4$), 145.1 (d, br, $J_{CF}$ = 158, $C_6F_4H$) and 147.0 (d, br, $J_{CF}$ = 175 Hz, $C_6F_4H$); $^{19}F$, δ 17.37 (m) and 26.47 (m). Complex **2c** (Found: C, 53.9; H, 6.85. $C_{26}H_{40}F_2NiP_2S_2$ requires C, 54.2; H, 6.95%): NMR ($CDCl_3$) $^1H$, δ 6.477, 7.069

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(m, $C_6H_4F$); $^{31}$P-{$^1$H}, δ 81.67 (s); $^{13}$C-{$^1$H}, δ 18.67, 20.37 {s, P[CH(*C*H$_3$)$_2$]}, 21.14 (t, $J_{CP}$ = 19.1, PCH$_2$), 25.61 {t, $J_{CP}$ = 9.8, P[*C*H(CH$_3$)$_2$]}, 113.13 (d, $J_{CF}$ = 21.1, $C_6H_4F$), 134.64 (d, $J_{CF}$ = 9.8, $C_6H_4F$) and 159.8 (d, br, $J_{CF}$ = 239 Hz, $C_6H_4F$); $^{19}$F, δ 42.33 (m).

**[Ni(SPh)$_2$(dippe)] 2d.** A suspension of complex **1** (0.24 g, 0.5 mmol) in tetrahydrofuran (thf) was treated with an excess of PhSH (0.5 cm$^3$, 4.5 mmol). Then LiBu$^n$ was added (0.7 cm$^3$ of a 1.6 mol dm$^{-3}$ solution in hexanes, 1.1 mmol). A dark red solution was immediately obtained. The solvent was removed *in vacuo*, and the residue extracted with toluene. Centrifugation, concentration and cooling to −20 °C afforded well formed red crystals. Yield: 77% (Found: C, 57.6; H, 7.65. $C_{26}H_{42}NiP_2S_2$ requires C, 57.9; H, 7.80%). NMR (CDCl$_3$): $^1$H, δ 6.760, 7.190 (m, $C_6H_5$); $^{31}$P-{$^1$H}, δ 81.15 (s); $^{13}$C-{$^1$H}, δ 18.69, 20.47 {s, P[CH(*C*H$_3$)$_2$]}, 21.18 (t, $J_{CP}$ = 19.1, PCH$_2$), 25.64 {t, $J_{CP}$ = 12.2 Hz, P[*C*H(CH$_3$)$_2$]}, 121.61, 126.34, 134.02 and 143.95 (s, $C_6H_5$).

**[Ni(SR)(CNBu$^t$)(dippe)][BPh$_4$] (R = $C_6F_5$ 3a, $C_6F_4H$ 3b, $C_6H_4F$ 3c or Ph 3d).** To a solution of the corresponding dithiolate **2a–2d** in ethanol was added CNBu$^t$ (excess). Addition of an excess of solid Na[BPh$_4$] produced a yellow or yellow-orange crystalline precipitate. It was filtered off, washed with ethanol and light petroleum, and dried *in vacuo*. All the products were recrystallized from acetone–ethanol. Yield: 70–85%. Complex **3a** (Found: C, 64.0; H, 6.55; N, 1.4. $C_{49}H_{61}BF_5NNiP_2S$ requires C, 63.8; H, 6.60; N, 1.5%): IR ν(C≡N) 2193 cm$^{-1}$; NMR (CDCl$_3$) $^1$H (−30 °C), δ 1.144 [s, CNC(CH$_3$)$_3$]; $^{31}$P-{$^1$H} (+20 °C), δ 98.83 (s, br), 88.69 (s, br); (−30 °C), δ 99.33 (d), 89.15 (d, $J_{PP}$ = 36.7); $^{19}$F (+20 °C), δ 2.974 (t, $J_{FF}$ = 23.3), 7.068 (t, $J_{FF}$ = 20.7) and 34.13 (dd, $J_{FF}$ = 18.8, $J_{FF'}$ = 7.14 Hz). Complex **3b** (Found: C, 65.0; H, 6.80; N, 1.4. $C_{49}H_{62}BF_4NNiP_2S$ requires C, 65.1; H, 6.85; N, 1.55%): IR ν(C≡N) 2190 cm$^{-1}$; NMR (CDCl$_3$) $^1$H, δ 1.121 [s, CNC(CH$_3$)$_3$] and 6.910 (m, $C_6F_4H$); $^{31}$P-{$^1$H}, δ 98.36 (d), 88.20 (d, $J_{PP}$ = 36.7); $^{13}$C-{$^1$H}, δ 18.35, 18.64, 19.32 {d, $J_{CP}$ = 1.8, P[CH(*C*H$_3$)$_2$]}, 20.94 (t, $J_{CP}$ = 13, PCH$_2$), 21.49 (t, $J_{CP}$ = 12.8, PCH$_2$), 25.99 {d, $J_{CP}$ = 25.6, P[*C*H(CH$_3$)$_2$]}, 26.93 {d, $J_{CP}$ = 23.8, P[*C*H(CH$_3$)$_2$]}, 29.25 [s, CNC(*C*H$_3$)$_3$], 59.73 [s, CN*C*(CH$_3$)$_3$] and 102.1 (t, $J_{CF}$ = 23.1 Hz, $C_6HF_4$); $^{19}$F, δ 25.70 (m) and 33.29 (m). Complex **3c** (Found: C, 69.0; H, 7.50; N, 1.6. $C_{49}H_{65}BFNNiP_2S$ requires C, 69.2; H, 7.65; N, 1.65%): IR ν(C≡N) 2191 cm$^{-1}$; NMR (CDCl$_3$) $^1$H, δ 1.046 [s, CNC(CH$_3$)$_3$], 6.879, 7.355 (m, $C_6H_4F$); $^{31}$P-{$^1$H}, δ 94.99 (d), 85.861 (d) ($J_{PP}$ = 36.6); $^{13}$C-{$^1$H}, δ 18.44, 18.71, 19.48 {d, $J_{CP}$ = 1.8, P[CH(*C*H$_3$)$_2$]}, 21.03 (d, $J_{CP}$ = 26.8, PCH$_2$), 21.26 (dd, $J_{CP}$ = 24, $J_{CP'}$ = 2.5, PCH$_2$), 25.78 {d, $J_{CP}$ = 25.6, P[*C*H(CH$_3$)$_2$]}, 26.58 {d, $J_{CP}$ = 24, P[*C*H(CH$_3$)$_2$]}, 29.18 [s, CNC(*C*H$_3$)$_3$], 52.20 [s, CN*C*(CH$_3$)$_3$], 115.19 (d, $J_{CF}$ = 21.3, $C_6H_4F$) and 135.35 (d, $J_{CF}$ = 7.7 Hz, $C_6H_4F$), $^{19}$F, δ −18.6 (m, br). Complex **3d** (Found: C, 70.8; H, 7.80; N, 1.6. $C_{49}H_{66}BNNiP_2S$ requires C, 70.7; H, 7.95; N, 1.7%): IR ν(C≡N) 2191 cm$^{-1}$; NMR (CDCl$_3$) $^1$H, δ 0.985 [s, CNC(CH$_3$)$_3$], 7.127, 7.400 (m, $C_6H_5$); $^{31}$P-{$^1$H}, δ 97.54 (d), 88.46 (d) ($J_{PP}$ = 36.7); $^{13}$C-{$^1$H}, δ 18.44, 18.76, 19.53 {s, P[CH(*C*H$_3$)$_2$]}, 21.41 (m, PCH$_2$), 20.83 (m, PCH$_2$), 25.86 {d, $J_{CP}$ = 26.5, P[*C*H(CH$_3$)$_2$]}, 26.59 {d, $J_{CP}$ = 24.8 Hz, P[*C*H(CH$_3$)$_2$]}, 29.13 [s, CNC(*C*H$_3$)$_3$], 52.70 [s, CN*C*(CH$_3$)$_3$], 125.26, 128.30 and 134.07 (s, $C_6H_5$).

**[Ni(S$_2$CNR$_2$)(dippe)]Br (R = Et 4a or Me 4b).** Complex **1** in acetone was treated with the stoichiometric amount of solid NaS$_2$CNR$_2$·H$_2$O (R = Et or Me). The mixture was stirred for 1 h at room temperature. During this time the starting material dissolved gradually to give an orange solution and a white precipitate of NaBr. The solution was filtered through Celite and concentrated. Large orange crystals were obtained upon cooling to −20 °C. Yield: 80–85%. Complex **4a** (Found: C, 41.6; H, 7.60; N, 2.4. $C_{19}H_{42}BrNNiP_2S_2$ requires C, 41.6; H, 7.65; N, 2.55%): IR ν(C=N) 1519 cm$^{-1}$; NMR (CDCl$_3$) $^1$H, δ 1.30 [t, $J_{HH}$ = 7.2, S$_2$CN(CH$_2$C*H*$_3$)$_2$] and 3.86 [q, $J_{HH}$ = 7.2, S$_2$CN(C*H*$_2$CH$_3$)$_2$]; $^{31}$P-{$^1$H}, δ 96.2 (s); $^{13}$C-{$^1$H}, δ 12.38 [s, S$_2$CN(CH$_2$*C*H$_3$)$_2$], 44.03 [s, S$_2$CN(*C*H$_2$CH$_3$)$_2$], 200.75 [s, S$_2$*C*N(CH$_2$CH$_3$)$_2$], 18.49, 19.17 {s, P[CH(*C*H$_3$)$_2$]}, 21.37 (t, $J_{CP}$ = 20.1, PCH$_2$) and 25.79 {t, $J_{CP}$ = 11.9 Hz, P[*C*H(CH$_3$)$_2$]}. Complex **4b** (Found: C, 39.3; H, 7.25; N, 2.6. $C_{17}H_{38}BrNNiP_2S_2$ requires C, 39.2; H, 7.30; N, 2.7%): IR ν(C=N) 1555 cm$^{-1}$; NMR (CDCl$_3$) $^1$H, δ 3.394 [s, S$_2$CN(C*H*$_3$)$_2$]; $^{31}$P-{$^1$H}, δ 96.76 (s); $^{13}$C-{$^1$H}, δ 38.57 [s, S$_2$CN(*C*H$_3$)$_2$], 202.16 [s, S$_2$*C*N(CH$_3$)$_2$], 18.66, 19.32 {s, P[CH(*C*H$_3$)$_2$]}, 21.57 (t, $J_{CP}$ = 20.1, PCH$_2$) and 25.94 {t, $J_{CP}$ = 11.9 Hz, P[*C*H(CH$_3$)$_2$]}.

**Table 1** Summary of data for the crystal structure analysis of compound **5**

| | |
|---|---|
| Formula | $C_{15}H_{32}NiOP_2S_2$ |
| $M$ | 413.18 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ (no. 14) |
| $a$/Å | 10.246(1) |
| $b$/Å | 13.981(2) |
| $c$/Å | 15.016(2) |
| β/° | 102.758(9) |
| $U$/Å$^3$ | 2098.0(8) |
| $Z$ | 4 |
| $D_c$/g cm$^{-3}$ | 1.308 |
| μ/cm$^{-1}$ | 46.01 |
| $F$(000) | 880 |
| Transmision factors | 0.56–1.00 |
| Scan speed (ω)/° min$^{-1}$ | 8 |
| 2θ Interval/° | 5–120 |
| Measured reflections | 3484 |
| Unique reflections | 3281 ($R_{int}$ = 0.168) |
| Observed reflections ($I > 3\sigma_I$) | 2632 |
| Number of parameters | 190 |
| Reflection: parameter ratio | 13.06:1 |
| $R^a$ | 0.056 |
| $R'$ ($w = \sigma_F^{-2}$)$^b$ | 0.075 |
| Maximum Δ/σ in final cycle | 0.05 |
| Goodness of fit | 3.38 |

$^a$ $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b$ $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

**[Ni(S$_2$CO)(dippe)] 5.** This compound was obtained following a procedure analogous to that used for the preparation of **4a**, **4b**, starting from **1** and 2 equivalents of any alkyl dithiocarbonate KS$_2$COR (R = Me, Et or Pr$^i$) in acetone. In the course of the reaction the concomitant formation of ROCS$_2$R was detected by NMR spectroscopy. The resulting orange solution was filtered through Celite in order to remove KBr. Concentration and cooling to −20 °C afforded orange crystals, which can be recrystallized from acetone. Yield: 68% (Found: C, 43.3; H, 7.80. $C_{15}H_{32}NiOP_2S_2$ requires C, 43.55; H, 7.75%). IR: ν(C=O) 1675 and 1593 cm$^{-1}$. NMR (CDCl$_3$): $^{31}$P-{$^1$H}, δ 92.2 (s); $^{13}$C-{$^1$H}, δ 18.48, 19.32 {s, P[CH(*C*H$_3$)$_2$]}, 21.37 (t, $J_{CP}$ = 19.8, PCH$_2$), 25.89 {t, $J_{CP}$ = 12.2, P[*C*H(CH$_3$)$_2$]} and 194.85 (t, $J_{CP}$ = 4.5 Hz, S$_2$CO).

## Crystallography

A summary of crystallographic data for compound **5** is given in Table 1. X-Ray measurements were made on a plate-shaped crystal of dimensions 0.30 × 0.45 × 0.15 mm, which was mounted on a glass fibre and transferred to an AFC6S-Rigaku automatic diffractometer, using Cu-Kα graphite-monochromated radiation (λ 1.541 78 Å). Cell parameters were determined from the settings of 25 high-angle reflections. Data were collected at 290 K by the ω–2θ scan method. Lorentz-polarization and absorption (ψ-scan method) corrections were applied. Three standard reflections were intensity controlled, in order to establish a decay correction (overall −2.40%).

**Table 2** Selected bond distances (Å) and angles (°) for [Ni(S$_2$CO)(dippe)]

| | | | |
|---|---|---|---|
| Ni–S(31) | 2.197(1) | S(31)–C(3) | 1.769(5) |
| Ni–S(32) | 2.207(1) | S(32)–C(3) | 1.759(6) |
| Ni–P(1) | 2.165(1) | O(3)–C(3) | 1.235(6) |
| Ni–P(2) | 2.162(2) | | |
| S(31)–Ni–S(32) | 79.72(6) | P(1)–Ni–P(2) | 89.21(5) |
| S(31)–Ni–P(1) | 94.73(5) | S(31)–C(3)–S(32) | 106.3(3) |
| S(31)–Ni–P(2) | 174.94(6) | S(31)–C(3)–O(3) | 126.1(5) |
| S(32)–Ni–P(1) | 172.30(6) | S(32)–C(3)–O(3) | 127.7(5) |
| S(32)–Ni–P(2) | 96.06(6) | | |

Reflections having $I > 3\sigma(I)$ were used for structure resolution. All calculations for data reduction, structure solution and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[16] software system and ORTEP[17] for plotting. The structure was solved by the Patterson method, and anisotropically refined on $F$ by full-matrix least-squares methods for all non-hydrogen atoms. Approximately one-half of the H atoms were located in Fourier-difference maps and not refined. All other hydrogen atoms were included at idealized positions and not refined. Some disorder was observed for C(222) showing large thermal parameters. This effect was not modelled, and final refinement concluded with $R = 0.056$ and $R' = 0.075$. Maximum and minimum peaks in the final Fourier-difference maps were +0.83 and −0.59 e Å$^{-3}$. Selected bond lengths and angles are listed in Table 2.

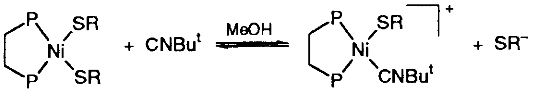
Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for the material should quote the full literature citation and the reference number 186/6.

## Results and Discussion

The bis(thiolate) derivatives [Ni(SR)$_2$(dippe)] (R = C$_6$F$_5$ **2a**, C$_6$F$_4$H **2b** or C$_6$H$_4$F **2c**) were prepared by reaction of [NiBr$_2$(dippe)] **1** with the corresponding lead thiolate Pb(SR)$_2$ in acetone. The complex [Ni(SPh)$_2$(dippe)] **2d** was obtained directly using HSPh and LiBu$^n$ in thf, in order to generate LiSPh *in situ*. These complexes are red, crystalline, diamagnetic materials, soluble in non-polar solvents except **2d** which is rather insoluble in light petroleum and diethyl ether so it is better to recrystallize it from toluene. The $^{31}$P-{$^1$H} NMR spectra consist of one sharp singlet in all cases. The $^1$H NMR spectra display signals corresponding to the protons of the phosphine ligand, plus those of the R group of the thiolate ligands. The $^{13}$C-{$^1$H} NMR spectra are rather simple, corresponding to highly symmetrical species, and need no further comment. These spectral data suggest a monomeric *cis*-square-planar structure for these complexes, as has been found by X-ray crystallography for the related complex [Ni(SC$_6$F$_5$)$_2$(dppe)].[9]

Mononuclear bis(thiolate) complexes owe most of their reactivity to the presence of terminal thiolates which possess lone pairs at sulfur. For this reason, these compounds may act as S-donor chelating agents towards certain transition-metal complexes, furnishing polynuclear compounds such as [(dppe)Ni(μ-SPh)$_2$Ni(μ-SPh)$_2$Ni(dppe)]$^{2+}$[18] and [(C$_5$H$_5$)$_2$Mo(μ-SMe)$_2$Ni(μ-SMe)$_2$Mo(C$_5$H$_5$)$_2$]$^{2+}$.[19] The presence of lone pairs at sulfur is also responsible for the reactivity these complexes display in the presence of protons. Protonation of a thiolate complex at sulfur leads initially to the formation of a co-ordinated thiol. This ligand is very substitution labile in most cases and is released, although there are some examples of stable thiol complexes.[20] This means that a thiolate ligand becomes a relatively good leaving group in the presence of protons, enabling its substitution by good anionic or neutral donors. Thus, **2a**–**2c** react with aqueous HBr in acetone yielding in all cases an orange, crystalline precipitate of **1**. The formation of free thiol in the reaction mixture was detected in each case by $^{19}$F NMR spectroscopy. The same reaction occurs for **2d**, both thiolate ligands being replaced by Br$^-$ in all cases. The lability of the thiolate ligands in these complexes under protic conditions has been exploited for synthetic purposes.

Complexes **2a**–**2d** dissolve in MeOH or EtOH yielding red solutions. Addition of an excess of CNBu$^t$ does not produce any appreciable change in the solutions. However, addition of NaBPh$_4$ at this stage produced a yellow or yellow-orange, crystalline precipitate, which exhibits one strong ν(CN) band near 2200 cm$^{-1}$ in the respective IR spectra. Microanalyses are consistent with the general formula [Ni(SR)(CNBu$^t$)(dippe)][BPh$_4$] (R = C$_6$F$_5$ **3a**, C$_6$F$_4$H **3b**, C$_6$H$_4$F **3c** or Ph **3d**) for these materials. These data are consistent with the occurrence in solution of the equilibrium (1). The equilibrium



(1)

shifts to the right when the corresponding cationic complex [Ni(SR)(CNBu$^t$)(dippe)]$^+$ is removed by precipitation as its [BPh$_4$]$^-$ salt. No reaction is observed with CO under these conditions, possibly due to the strong π-acceptor character of this molecule, at variance with the isoelectronic CNBu$^t$ ligand[21] which acts mainly as a good σ donor. The high ν(C≡N) value observed for these complexes indicates that the nickel site is not strongly electron releasing, and the poor σ-donor capacity of CO is hence not compensated by any appreciable back bonding from the nickel site.

The $^1$H NMR spectra of complexes **3b**–**3d** in CDCl$_3$ are dominated by the resonance of the *tert*-butyl protons of the isocyanide ligand, which appears as one singlet. The $^{31}$P-{$^1$H} NMR spectra display a pattern consisting of two doublets, corresponding to an AB spin system. These data are consistent with a square-planar structure having thiolate and isocyanide ligands in mutually *cis* positions. The $^{13}$C-{$^1$H} and $^{19}$F NMR data also support this structural assignment. Whereas these spectra are typical of stereochemically rigid species at room temperature, those of **3a** suggest that this compound is fluxional. The $^1$H NMR spectrum in CDCl$_3$ at room temperature consists of broad features, although the isocyanide signal is still distinguishable. The $^{31}$P-{$^1$H} NMR spectrum displays two broad signals, which resolve into two doublets at −20 °C. The low-temperature NMR data are consistent with the *cis*-square-planar structure proposed for compounds **3b**–**3c**. In order to clarify the apparently anomalous behaviour of **3a** compared, we attempted to determine its crystal structure. Unfortunately, the crystals were of poor quality and the reliability of the results was not satisfactory, despite the fact that several data collections were obtained on crystals from different samples independently prepared. Attempts to obtain good-quality crystals of the related compounds **3b**–**3d**, or salts of **3a** with a different counter ion, proved to be unsuccessful. The results of the many attempts to determine the structures of **3a**–**3d** by diffraction methods, were not of publishable quality, but the structures proposed for these complexes based upon NMR spectroscopy are consistent with the crude molecular skeletons derived from the diffraction experiments. The lack of stereochemical rigidity observed in solution could simply be due to the thermal motion of the atoms in the ligands. We have rationalized such motion in terms of a 'spanning' movement of the phosphorus atoms of the phosphine ligand combined with free rotation of the pentafluorophenyl ring of the thiolate group. The rotation of the C$_6$F$_5$ ring forces the phosphine ligand to rearrange, in order to minimize steric repulsions with the bulky isopropyl substituents. However, it seems rather surprising that this sort of dynamic behaviour affects only **3a**, and is not observed for **3b** and **3c**. At least for **3b**, which bears four fluorine atoms in the $C_6$ ring, something similar would be expected. One possible reason for this is the existence of a rotation barrier across the S–C bond, attributable to an interaction between the $\pi$ electrons of the ring and empty d orbitals at sulfur. This interaction confers a partial multiple character upon the S–C bond, but the presence of increasing number of electronegative fluorine atoms on the ring would reduce the effect of the $\pi$ interaction. This would explain why the process is easily observable for **3a** at room temperature, but it also suggests that by heating samples of **3b** and **3c** the process should also be observable at increasingly high temperatures as the number of fluorine atoms decreases. In order to heat the samples we chose a high-boiling-point NMR solvent such as $(CD_3)_2SO$. However, the $^{31}P-\{^1H\}$ NMR spectra recorded in this solvent at room temperature were rather different to those recorded in $CDCl_3$. In fact the solution behaviour of complexes containing polyfluorobenzenethiolate ligands has been found to be strongly solvent dependent.[22] Whereas the spectra of **3c** [Fig. 1(*a*)] and **3d** consist of two broadened doublets, that of **3b** [Fig. 1(*b*)] is almost featureless, and that of **3a** displays a single broad resonance. It seems that in this solvent all the compounds behave as stereochemically non-rigid, particularly **3a** and **3b**. When **3c** and **3d** are heated to 100° C the spectra become featureless, these changes being fully reversible [Fig. 1(*a*)]. In the case of **3b**, a very broad signal arises as the temperature increases [Fig. 1(*b*)], whereas the spectrum of **3a** changes only slightly when the temperature is raised to 105 °C. At higher temperatures these signals disappear, and two doublets appear in the spectra of **3a** and **3b**, suggesting that these species become stereochemically rigid at this temperature. However, the original spectrum is not restored when the samples are cooled to room temperature. Therefore some chemical transformation seems to take place at temperatures of 120–140 °C in $(CD_3)_2SO$. The $^1H$ NMR spectra of **3a** and **3b** cooled to room temperature indicate that the isocyanide ligand is lost from the starting complexes, so this behaviour has been interpreted in terms of substitution at high temperatures of the co-ordinated isocyanide in **3a** and **3b** by one solvent molecule, which is itself a good donor, yielding $[Ni(SR)\{(CD_3)_2SO\}(dippe)]^+$ (R = $C_6F_5$ or $C_6F_4H$). No attempts were made to isolate or characterize in full such species. It is interesting that no fluxional behaviour has been detected for the bis(thiolate) complexes **2a**–**2d**. As inferred from the crystal structure of the related derivative $[Ni(SC_6F_5)_2(dppe)]$,[9] this kind of complex adopts a square-planar structure, in which the planes of the two $C_6R_5$ (R = H or F) rings are kept almost parallel with each other, in order to minimize steric repulsions. In this fashion, free rotation is possibly hindered.

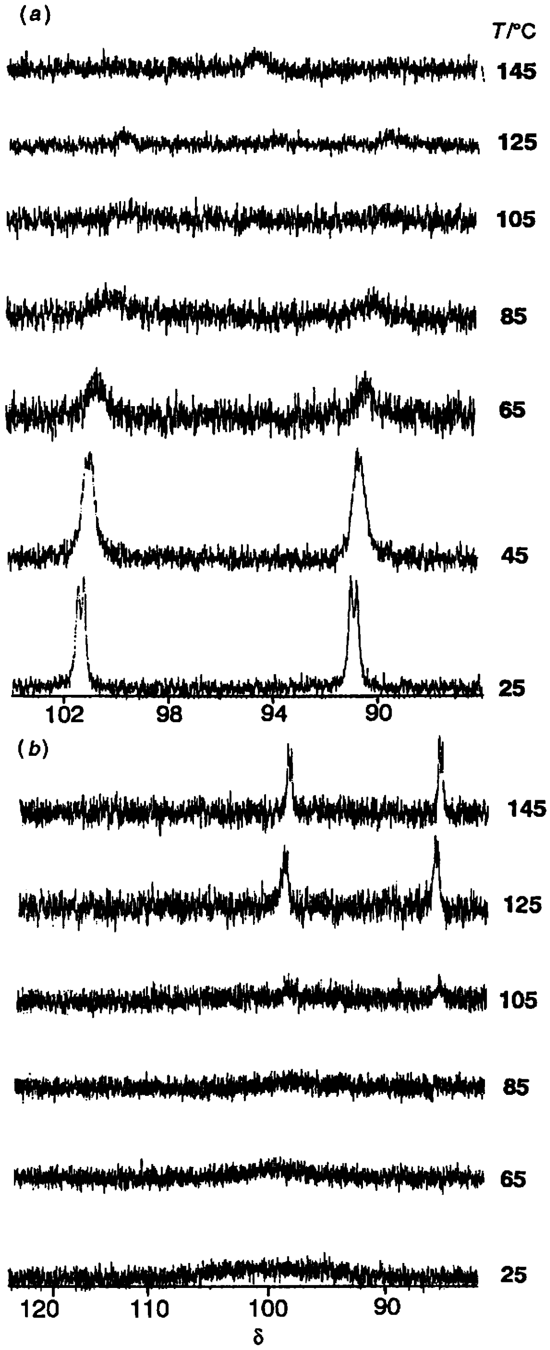


**Fig. 1** Variable-temperature $^{31}P-\{^1H\}$ NMR spectra of (*a*) **3c** and (*b*) **3b** in $(CD_3)_2SO$

The reaction of complex **1** with sodium salts of dialkyldithiocarbamates in acetone is straightforward, and complexes $[Ni(S_2CNR_2)(dippe)]Br$ (R = Me **4a** or Et **4b**) are obtained. Compounds of general formula $[Ni(S_2CNR_2)(L–L)]X$ (L–L = diphosphine) have previously been reported.[23] These complexes are square planar, and contain one bidentate dithiocarbamate ligand, as inferred from NMR spectral data. The frequency of the ν(C=N) band in the IR spectra is also consistent with a bidentate chelating co-ordination mode for the dithiocarbamate ligand.[24] Whereas sodium dialkyldithiocarbamates react with **1** to yield the corresponding complexes, the reaction with potassium alkyl dithiocarbonates $KS_2COR$ (R = Me, Et or $Pr^i$) always yields the same complex, irrespective of the carbonate used and the ratio $KS_2COR:[NiBr_2(dippe)]$. This material does not show any resonance in the $^1H$ NMR spectrum apart from those due to the phosphine protons. The $^{31}P-\{^1H\}$ NMR spectrum consists of one singlet, and the IR spectrum displays two strong absorption bands at 1675 and 1593 $cm^{-1}$. These data together with microanalysis suggest that the alkyl dithiocarbonates are degraded during their reaction with **1**, and the ultimate product of this reaction is the dithiocarbonate-*S*,*S′* complex $[Ni(S_2CO)(dippe)]$ **5**, which has been structurally characterized by X-ray crystallography. (Fig. 2, selected bond lengths and angles in Table 2). The co-ordination around nickel is very distorted square planar, with the mean deviation from the $NiS_2P_2$ least-squares plane of 0.041 Å. The dithiocarbonate ligand is considerably more planar, with a mean deviation from the $S_2CO$ plane of 0.001 Å. The bond angles around C(3) can be reasonably explained in terms of a $sp^2$ hybridization for this carbon atom. The bond lengths Ni–P(1) and Ni–P(2) are in the normal range of Ni–P distances. The same can be said for the Ni–S bond lengths, all these parameters comparing well with those found for the related trithiocarbonate complex $[Ni(CS_3)(dmpe)]$.[2] Transition-metal dithiocarbonate complexes

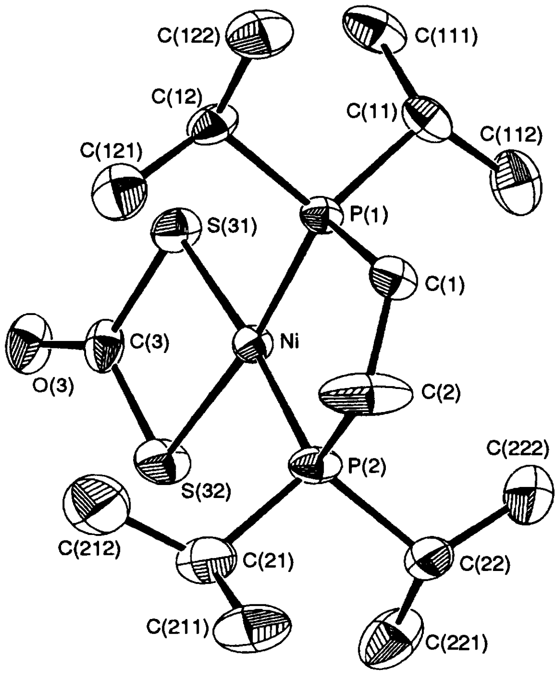


**Fig. 2** An ORTEP drawing of the complex [Ni($S_2CO$)(dippe)] with 50% probability thermal ellipsoids. Hydrogen atoms are omitted

have been known for some time. Complexes of the type [M($S_2CO$)($PPh_3$)$_2$] (M = Ni, Pd or Pt) have been prepared by reaction of the bis(alkyl dithiocarbonate) complexes [M($S_2COR$)$_2$] with $PPh_3$.[25,26] In the course of these reactions one alkyl dithiocarbonate is transformed into a dithiocarbonate. One mechanism proposed involves the formation of *S*-alkyl *O*-alkyl dithiocarbonate, according to equation (2) (M = Ni,

$$[M(S_2COR)_2] + 2\,PPh_3 \longrightarrow [M(S_2CO)(PPh_3)_2] + ROCS_2R \quad (2)$$

Pd or Pt).[26] We also have detected the formation of *S*-alkyl *O*-alkyl dithiocarbonate in our reaction mixture by $^1H$ NMR spectroscopy, suggesting that probably the complex [Ni($S_2COR$)(dippe)]$^+$ is formed first, and this then reacts with free dithiocarbonate yielding the final product **5** plus the corresponding *S*-alkyl *O*-alkyl dithiocarbonate.

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