

JOM 23506

Synthesis and characterization of cyclopentadienylnickel(II) thiolates. Crystal structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{SC}_6\text{H}_5)(\text{PPh}_3)]$

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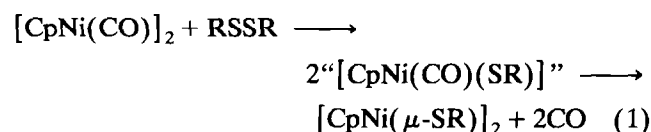
(Received November 12, 1992)

Abstract

The thiolate complexes $\text{CpNi}(\text{SR})(\text{PPh}_3)$ (**1**), ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{R} = \text{C}_6\text{H}_5$ and $\text{C}_6\text{H}_4\text{Me-4}$) were prepared by the reaction of $\text{CpNiX}(\text{PPh}_3)$ ($\text{X} = \text{Cl, Br, or I}$) with HSC_6H_5 and $\text{HSC}_6\text{H}_4\text{Me-4}$ respectively, in the presence of Et_3N . The structure of $\text{CpNi}(\text{SC}_6\text{H}_5)(\text{PPh}_3)$ (**1a**) was determined by X-ray crystallography. The reaction of $\text{CpNiX}(\text{PPh}_3)$ with the dithiols, toluene-dithiol and $\text{HS}(\text{CH}_2)_x\text{SH}$ ($x = 2, 3$) resulted in the loss of PPh_3 and the formation of complexes of general formula $\text{CpNi}(\text{HS}_2\text{R}')$ ($\text{R}' = \text{C}_6\text{H}_3\text{Me-4}$) (**2a**) or $\text{R}' = (\text{CH}_2)_x$ where $x = 2, 3$ (**2b** and **2c**). However, when butanedithiol was used in the same reaction the product was $\text{CpNi}(\text{S}(\text{CH}_2)_4\text{SH})(\text{PPh}_3)$ (**1c**).

1. Introduction

Cyclopentadienylnickel thiolates are usually synthesized from nickelocene and the appropriate thiol [1,2]. The reaction proceeds with loss of a cyclopentadienyl ligand from the nickelocene, and the products are usually dimers containing bridging thiolate ligands. The presence of only one cyclopentadienyl ligand per nickel in these products suggested that monocyclopentadienylnickel complexes could be used as starting materials for the synthesis of these thiolate compounds, as exemplified by the photolysis of $[\text{CpNi}(\text{CO})]_2$ in the presence of organic disulfides (RSSR) to give $[\text{CpNi}(\mu\text{-SR})]_2$, accompanied by the loss of CO as in eqn. (1) [3].



The use of monocyclopentadienylnickel complexes as an entry into cyclopentadienyl chemistry was employed previously by F. Sato *et al.*, the reaction of

$[\text{CpNi}(\text{PBU}_3)_2]^+[\text{Cl}]^-$ and sulfur-containing salts yielding compounds of the type $\text{CpNi}(\text{PBU}_3)(\text{SC}(\text{S})\text{X})$ ($\text{X} = \text{R, OR and NRH}$) [4]. However, this approach is limited to thiolate salts that are soluble in an aqueous medium.

Using non-aqueous solvents, Rauchfuss [5] and Shaver [6a] independently demonstrated the use of the monocyclopentadienylruthenium complex $\text{CpRuCl}(\text{PPh}_3)_2$ as a starting material for the synthesis of organoruthenium polysulfides and thiolate complexes. In these reactions, one of the triphenylphosphine ligands is retained in the product and the other is lost. The versatility of $\text{CpRuCl}(\text{PPh}_3)_2$ in the reactions of Rauchfuss and Shaver, and also as described in a recent review [6b], coupled with the work of Fenske *et al.* [7] on the iso-electronic $\text{CpNiCl}(\text{PPh}_3)$, prompted us to investigate the potential of $\text{CpNiX}(\text{PPh}_3)$ as a starting material for cyclopentadienylnickel polysulfides and thiolates. As part of the investigation we studied the reactions of $\text{CpNiX}(\text{PPh}_3)$ with thiols in the presence of an organic base. One of the products of our reactions, $\text{CpNi}(\text{SC}_6\text{H}_5)(\text{PPh}_3)$, has been described previously [8], but all three methods of synthesis gave low yields. We describe below a simple and high yield

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synthesis of this complex, its crystal structure, and extension of the method to other thiols.

2. Results and discussion

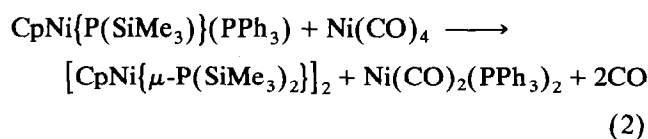
2.1. Reactions of $CpNiX(PPh_3)$ with monothiols

Addition of Et_3N to a solution of $CpNiX(PPh_3)$ and a thiol in CH_2Cl_2 results in the rapid formation of $CpNi(SR)(PPh_3)$ ($R = C_6H_5$ (**1a**) and C_6H_4Me-4 (**1b**)). The complexes are similar to $[CpNi(SC_6H_5)(PPh_3)]$, which was obtained from the reaction of $[CpNi(P-Bu_3)_2]^+[Cl]^-$ with the sodium salt of thiophenol [9]. There was no reaction when the appropriate thiol was added to a solution of $CpNiX(PPh_3)$ in the absence of the base.

Solutions of **1a** and **1b** are dark brown, but the crystals are dark green. The structures of the two compounds are the same in solution and in the solid state as is evident from the solution NMR spectrum and the crystal structure of **1a**. For example the 1H NMR spectrum of a solution of **1a** consists of a singlet at 5.11 ppm from Cp, a multiplet at 6.88 ppm from the thiolate ligand, and two sets of multiplets at 7.35 ppm and 7.68 ppm from PPh_3 . The $^{31}P\{^1H\}$ NMR spectrum shows only one peak at 33.4 ppm. The $^{13}C\{^1H\}$ NMR spectrum consists of peaks at 93.9 ppm from the Cp ligand, 122.1, 127.1, 130.1 and 145.0 ppm from the thiolate ligand, and a doublet at 128.13 and 128.27 [$J(C-P) = 10.1$ Hz], a doublet at 132.58 and 133.21 [$J(C-P) = 47.0$ Hz], a third doublet at 133.48 and 133.58 [$J(C-P) = 5.0$ Hz], and a singlet at 133.69 ppm from PPh_3 . The above NMR data and the diamagnetism of **1a** indicate that the structure in solution is the same as in the solid state as determined by X-ray crystallography (*vide infra*). The analytical data for **1b** are consistent with a composition similar to that established for **1a**.

Electron impact mass spectra of **1a** and **1b** showed no molecular ions. For **1a** the single crystals that were used for the X-ray study gave the ions: m/z 262 (100%, PPh_3^+), 185 (20%, PPh_2^+), 109 (3%, $SC_6H_5^+$), 108 (17%, PPh^+), 77 (9%, Ph^+) and 65 (4%, Cp^+). The higher relative intensities of the PPh_3 fragments compared to the others, might be a measure of the ease

with which the PPh_3 dissociates from the nickel centre in the complex. To investigate this further we treated **1a** and **1b** with elemental sulfur. When **1a** was treated with sulfur, the PPh_3 was removed as $SPPH_3$ and $[CpNi(\mu-SC_6H_5)]_2$ was formed (Scheme 1). The reaction of **1b** gave the corresponding complex and $SPPH_3$. The identity of $[CpNi(\mu-SC_6H_5)]_2$ was established by comparing its spectra with those of an authentic sample prepared by a published procedure [2]. The 1H NMR signals from $[CpNi(\mu-SC_6H_5)]_2$ at 4.46 ppm and 7.10 ppm for Cp and thiolate respectively, agree well with the literature values of 4.50 ppm and 7.09 ppm [10]. The $SPPH_3$ by-product was identified by its characteristic infrared spectrum [11]. We suggest that the formation of $[CpNi(\mu-SC_6H_5)]_2$ proceeds in a similar manner to that of $[CpNi(\mu-P(SiMe_3)_2)]_2$, in which $Ni(CO)_4$ abstracts PPh_3 from $CpNi(P(SiMe_3))(PPh_3)$ [12], as in eqn. (2).

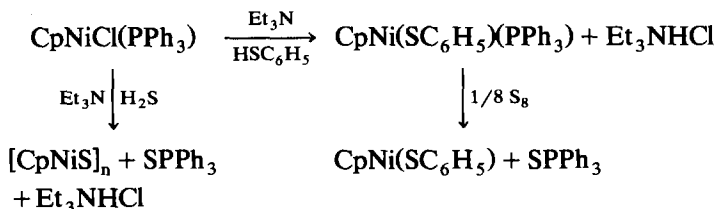


Complexes **1a** and **1b** also react with H_2S to form an insoluble black solid. The same product is obtained when H_2S is passed through a solution of $CpNiX(PPh_3)$ in the presence of Et_3N (Scheme 1).

We have been unable to characterise the black solid fully because of its insoluble nature. We are currently working on the reactions of the methylcyclopentadienyl analog, which appears to be more soluble, in order to establish the identity of this solid. The reactions nevertheless indicate the tendency of **1a**, **1b** and $CpNiX(PPh_3)$ to lose PPh_3 , which we have exploited in the reactions described below.

2.2. Structure of $CpNi(SC_6H_5)(PPh_3)$

The molecular structure of **1a** is shown in Fig. 1. It contains a pentahapto C_5H_5 ring. If the centroid of the C_5H_5 is assumed to occupy one coordination site, then the nickel has a distorted trigonal geometry, the bond angles being Cp-Ni-S 133.0° , Cp-Ni-P 136.4° , and S-Ni-P 90.5° . The distance from the centroid of the C_5H_5 ring to the nickel atom is 1.748 \AA , shorter than that in the nickel(I) complex $CpNi(bipy)$ ($bipy =$



Scheme 1.

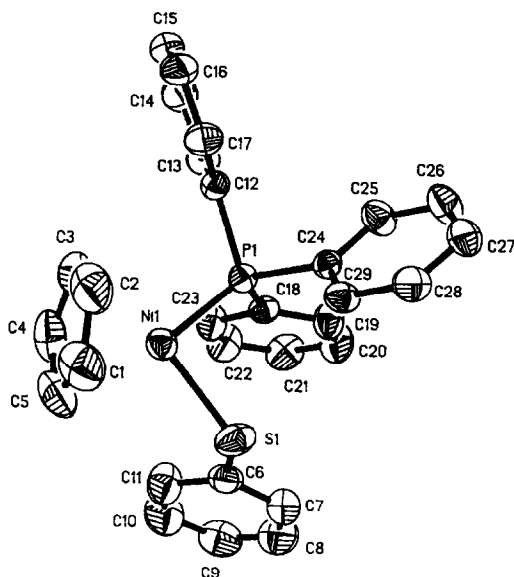
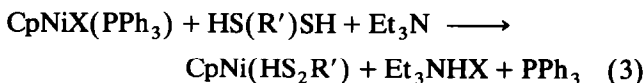


Fig. 1. The structure of $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{SC}_6\text{H}_5)(\text{PPh}_3)$.

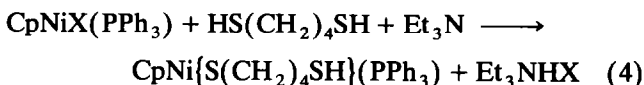
bipyridyl), viz. 1.844 Å [13]. This may be because of the fact that the formal oxidation state is +2 in **1a** compared with +1 in CpNi(bipy). The Ni–S distance of 2.192(1) Å in **1a** is also less than the Ni–S distance of 2.281 Å in $[\text{Et}_4\text{N}]_2[\text{Ni}(\text{SC}_6\text{H}_4\text{Cl})_4]$ [14] and 2.444(2) Å in $[\text{Ni}(\text{bipy})(\text{SC}_6\text{H}_5)_2] \cdot 2\text{D}_2\text{O}$ [15]. However, the Ni–P distance in **1a** is similar to that of 2.145(2) Å in $\text{Cp}_4\text{Ni}_4\text{Te}_2(\text{PPh}_3)_2$ [7], and even comparable with the distances, of 2.150(1) Å and 2.147(2) Å, in CpNi(CH₂SO₂Ph)(PPh₃) and CpNi(CH{CH=C(CH₃)₂}SO₂Ph)(PPh₃), respectively [16]. The Ni–S and Ni–P distances are indications that the nickel–sulfur bond is affected more than the nickel–phosphorus bond by the formal oxidation state of +2 of the nickel in **1a**.

2.3. Reactions of CpNiX(PPh₃) with dithiols

The reaction of dithiols with CpNiX(PPh₃) in the presence of Et₃N proceeded according to eqn. (3), except in the case of HS(CH₂)₄SH.

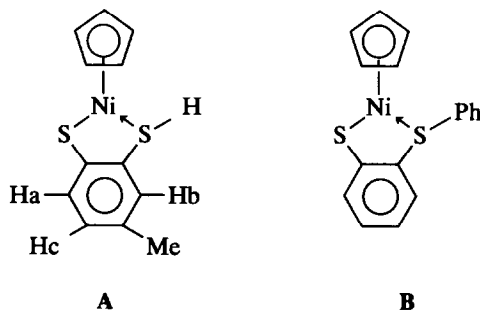


When the dithiol was HS(CH₂)₄SH, the product was CpNi{S(CH₂)₄SH}(PPh₃) (**1c**) eqn. (4).



Loss of PPh₃ in eqn. (3) resulted in the dithiolate functioning as a bidentate ligand. The ¹H NMR spectrum of **2a** consists of a multiplet at 6.81–6.95 ppm for Ha and Hc, a doublet at 6.30 ppm and 6.35 ppm for Hb (see labelling for **2a**), a doublet at 2.35 ppm and 2.38

ppm for SH, and a singlet at 1.70 ppm for Me of the thiolate. The elemental analysis is consistent with the formula CpNi(HS₂C₆H₃Me-4) containing 0.5 mol of toluene. On the basis of the analytical data, we propose the structure A for **2a**, similar to that of CpNi(PhS₂C₆H₄) (**B**) [17]. Compounds **2b** and **2c** are likely to have similar structures in view of the similarities in their ¹H NMR spectra. The outcome of the reactions of the alkyldithiolate complexes depends on the (CH₂)_x chain length. When x = 2 or 3, the reaction gives bidentate dithiolate compounds, whereas when x = 4 a product similar to that from the monothiols was obtained.



3. Experimental details

3.1. Materials and instrumentation

All compounds described are air-stable, but all reactions were performed under nitrogen in order to avoid oxidation of electron-deficient intermediates. Work-up in all cases was performed in air. Reagent grade hexane and toluene were distilled from sodium, and dichloromethane was distilled from P₂O₅. Triethylamine was distilled from, and stored over, NaOH. CpNiX(PPh₃) was prepared by the published procedure [18]. Infrared spectra were recorded on a Pye Unicam SP3-300S as a Nujol mull between KBr plates. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker AC 300 instrument and chemical shifts are reported in δ units (ppm), referenced to CHCl₃ at δ 7.26 ppm. The ³¹P{¹H} NMR spectrum was recorded on a Joel FX 90Q with H₃PO₄ as internal reference. Electron impact mass spectra were obtained with a Kratos MS50 mass spectrometer. Elemental analyses were performed by C H N Analysis Limited, Leicester, England, and by the University of Natal, Pietermaritzburg, South Africa.

3.2. Reactions of CpNiX(PPh₃) (X = Cl, Br, I) with HSC₆H₃: formation of CpNi(SC₆H₃)(PPh₃)

In a typical procedure neat Et₃N (0.20 mL) was added to a solution of CpNiCl(PPh₃) (0.58 g, 1.18 mmol) and HSC₆H₃ (0.12 mL, 1.17 mmol) in CH₂Cl₂

(30 mL). The purple solution turned brown immediately. The mixture was stirred at room temperature for 2 h, and the solvent removed under reduced pressure. The residue was extracted with toluene (50 mL), and the extract filtered and concentrated to 20 mL. An equal volume of hexane was added, to give dark-green crystals of $\text{CpNi}(\text{SC}_6\text{H}_5)(\text{PPh}_3)$. Recrystallization from a minimum volume of CH_2Cl_2 layered with an equal volume of hexane gave an analytically pure product. Yield = 0.36 g, 61%. Anal. Found: C, 70.52; H, 5.17. $\text{C}_{29}\text{H}_{25}\text{PSNi}$ calc.: C, 70.33; H, 5.09%. ^1H NMR (CDCl_3): δ 7.68–7.35 (m, 15H, PPh_3); 6.88 (m, 5H, SPh); 5.11 (Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 136.69 (s, PPh_3); 133.58, 133.48 (d, PPh_3); 133.21, 132.58 (d, PPh_3); 128.27, 128.13 (d, PPh_3); 145.0, 130.1, 127.1, 122.1 (SPh); 93.9 (Cp). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 33.4 (s, 1P, PPh_3).

3.3. Reactions of $\text{CpNiX}(\text{PPh}_3)$ ($X = \text{Cl}, \text{Br}, \text{I}$) with $\text{HSC}_6\text{H}_4\text{Me-4}$: formation of $\text{CpNi}(\text{SC}_6\text{H}_4\text{Me-4})(\text{PPh}_3)$

Et_3N (0.20 mL) was added to a solution of $\text{CpNiCl}(\text{PPh}_3)$ (0.50 g, 1.18 mmol) and $\text{HSC}_6\text{H}_4\text{Me-4}$ (0.15 g, 1.20 mmol) in CH_2Cl_2 (30 mL). The subsequent procedure was as described for the reaction of HSC_6H_5 . Yield = 0.40 g, 66%. Anal. Found: C, 71.02; H, 5.41. $\text{C}_{30}\text{H}_{27}\text{PSNi}$ calc.: C, 70.75; H, 5.33%. ^1H NMR (CDCl_3): δ 7.60–7.29 (m, 15H, PPh_3); 6.80 (m, 5H, SPhMe); 5.06 (s, 5H, Cp); 2.15 (s, 3H, PhMe).

3.4. Reaction of $\text{CpNi}(\text{SC}_6\text{H}_5)(\text{PPh}_3)$ with sulfur: formation of $[\text{CpNi}(\mu\text{-SC}_6\text{H}_5)]_2$

A mixture of $\text{CpNi}(\text{SC}_6\text{H}_5)(\text{PPh}_3)$ (0.10 g, 0.20 mmol) and sulfur (0.052 g, 0.20 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 16 h. The dark-brown solution gradually turned reddish brown. The solvent was removed *in vacuo* and the residue extracted with toluene (20 mL), and the extract filtered and concentrated to 10 mL. An equal volume of hexane was added and the mixture kept at -15°C to give needle-like crystals of SPPH_3 and a brown powder of $[\text{CpNi}(\mu\text{-SC}_6\text{H}_5)]_2$. The crystals of SPPH_3 were physically separated from the $[\text{CpNi}(\mu\text{-SC}_6\text{H}_5)]_2$.

3.5. Reaction of $\text{CpNiX}(\text{PPh}_3)$ with dithiols

Et_3N (0.5 mL) was added to a solution of $\text{CpNiX}(\text{PPh}_3)$ (0.50 g, 1.18 mmol) and $(\text{HS})_2\text{C}_6\text{H}_3\text{Me-4}$ (0.15 mL, 1.13 mmol) in CH_2Cl_2 (40 mL). The purple solution turned dark green within 15 min and was stirred at room temperature for 2 h, then evaporated to dryness. The residue was extracted with toluene until the extract was colourless. The filtrate was concentrated and hexane added to precipitate a dark-green solid. This was recrystallized twice from toluene/hexane (1:2) to give dark-green crystals of $\text{CpNi}(\text{HS}_2\text{-}$

$\text{C}_6\text{H}_3\text{Me-4}$). Yield = 0.25 g, 76%. Anal. Found (for three different samples): C, 58.01; H, 4.70; C, 57.93; H, 4.23; C, 58.59; H, 4.36. $\text{C}_{15.5}\text{H}_{16}\text{S}_2\text{Ni}$: Calc.: C, 57.26; H, 4.96. ^1H NMR (CDCl_3): δ 6.95, 6.81 (m, 2H, $\text{C}_6\text{H}_3\text{Me}$); 6.35, 6.30 (d, 1H, $\text{C}_6\text{H}_3\text{Me}$); 5.82 (s, 5H, Cp); 2.38, 2.35 (d, 1H, SH); 1.70 (s, 3H, $\text{C}_6\text{H}_3\text{Me}$). MS m/e 278 (M^+).

The other dithiol reactions were performed in an analogous manner and the work-up was the same, except in the case of **2b**. Because of the insoluble nature of this product the residue, after removal of CH_2Cl_2 , was washed with H_2O , followed by ethanol and diethyl ether.

$\text{CpNi}\{\text{S}(\text{CH}_2)_2\text{SH}\}$ Yield = 72%. Anal. Found: C, 37.49; H, 4.27. $\text{C}_7\text{H}_{10}\text{S}_2\text{Ni}$ calc.: C, 38.75; H, 4.65%.

$\text{CpNi}\{\text{S}(\text{CH}_2)_3\text{SH}\}$ Yield = 69%. Anal. Found: C, 41.85; H, 5.34. $\text{C}_8\text{H}_{12}\text{S}_2\text{Ni}$ calc.: C, 41.59; H, 5.23%. ^1H NMR (CDCl_3): δ 5.03 (s, 5H, Cp); 3.15 (s, br, 1H, $\text{S}(\text{CH}_2)_3\text{SH}$); 2.18–1.85 (m, 6H, $\text{S}(\text{CH}_2)_3\text{SH}$).

$\text{CpNi}\{\text{S}(\text{CH}_2)_4\text{SH}\}(\text{PPh}_3)$ Yield = 55%. Anal. Found: C, 63.31; H, 5.05. $\text{C}_{27}\text{H}_{29}\text{PS}_2\text{Ni}$ calc.: C, 63.92; H, 5.76%. ^1H NMR (CDCl_3): δ 7.72–7.33 (s, 15H, PPh_3); 5.08 (s, 5H, Cp); 3.12 (s, br, 1H, $\text{S}(\text{CH}_2)_4\text{SH}$); 1.82–1.65 (m, br, 8H, $\text{S}(\text{CH}_2)_4\text{SH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 133.53, 133.92 (d, PPh_3); 131.9–132.20 (m, PPh_3); 128.38, 128.62 (d, PPh_3); 90.47 (Cp); 32.66, 29.30 ($\text{S}(\text{CH}_2)_4\text{SH}$).

3.6. Determination of the crystal structure of $\text{CpNi}(\text{SC}_6\text{H}_5)(\text{PPh}_3)$

Crystals were obtained by layering a toluene solution of $\text{CpNi}(\text{SC}_6\text{H}_5)(\text{PPh}_3)$ with hexane and keeping it at -15°C . The dark single crystal selected (0.75 mm \times 0.35 mm \times 0.35 mm) was mounted on fibre glass. All geometric and intensity data were collected on an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).

The lattice vectors were identified by applying the automatic indexing routine of the diffractometer to the positions of 30 reflections taken from a rotation photograph and centred by the diffractometer. The ω - 2θ technique was used to measure 5586 reflections (5254 unique) in the range $5^\circ \leq 2\theta \leq 55^\circ$. Three standard reflections (measured every 97 scans) showed no significant loss in intensity. The data were corrected for Lorentz effects, and empirically for absorption. The 3929 unique data with $I \geq 3.0\sigma(I)$ were used to solve and refine the structure in triclinic space group $P\bar{1}$.

The structure was solved by Patterson methods and developed by using alternating cycles of least-squares refinements and difference Fourier synthesis. The non-hydrogen atoms were refined anisotropically and hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal

TABLE 1. Crystallographic data for $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{SC}_6\text{H}_5)_3(\text{PC}_6\text{H}_5)_3]$

Formula	$\text{C}_{29}\text{H}_{25}\text{P}_1\text{S}_1\text{Ni}_1$
Space group	$P\bar{1}$
a (Å)	9.551(3)
b (Å)	11.438(4)
c (Å)	11.509(4)
α (°)	79.22(3)
β (°)	83.99(3)
γ (°)	74.45(3)
V (Å ³)	1188
Z	2
$F(000)$	516
d_{calc} (g cm ⁻³)	1.38
Cryst. size (mm)	$0.75 \times 0.35 \times 0.35$
μ (Mo-K α) (cm ⁻¹)	9.8
Data collection instrument	Nicolet R3m/V
Radiation	Mo-K α ($\lambda = 0.71073$ Å)
Orientation reflections: No.;	30
range (2θ)	$14^\circ \leq 2\theta \leq 29^\circ$
Temperature (K)	292
Data measured	5586
Unique data	5254
No. of unique with $I \geq 3.0\sigma(I)$	3929
No. of parameters	289
R^a	0.0470
R_w^b	0.0523
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.001825F^2$
Largest shift/esd, final cycle	0.005
Largest peak, e Å ⁻³	0.85

^a $R = \sum[|F_o| - |F_c|]/\sum|F_o|$; ^b $R_w = \sum w^{1/2} \cdot [|F_o| - |F_c|]/\sum w^{1/2} \cdot |F_o|$.

parameter ($U = 0.08$ Å²). The final cycle of least-square refinement included 289 parameters for 3929 variables and did not shift any parameter by more than 0.005 times its standard deviation. The final refinement gave R ($= \sum[|F_o| - |F_c|]/\sum|F_o|$) = 0.0470 and R_w ($= \sum w^{1/2} \cdot [|F_o| - |F_c|]/\sum w^{1/2} \cdot |F_o|$) = 0.0523. The final difference Fourier was featureless, with no peaks greater than 0.85 eÅ⁻³. Crystallographic calculations

TABLE 2. Selected bond distances (Å) and angles (°) in $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{SC}_6\text{H}_5)(\text{PPh}_3)]$

Ni-P	2.139(1)	Ni-S	2.192(1)
Ni-Cp ^a	1.748	P-C(12)	1.834(3)
P-C(18)	1.820(3)	P-C(24)	1.822(3)
S-C(6)	1.768(4)	Ni-S-C(6)	110.4(1)
Ni-P-C(12)	113.9(1)	Ni-P-C(18)	111.8(1)
Ni-P-C(24)	117.0(1)	S-Ni-P	90.5(1)
C(12)-P-C(24)	100.5(1)	C(12)-P-C(18)	104.5(1)
C(18)-P-C(24)	107.9(1)	Cp-Ni-S	133.0
Cp-Ni-P	136.4		

^a The distance from the centroid of the C₅H₅ ring to the nickel.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$)

	x	y	z	U_{eq}^a
Ni(1)	2268(1)	2639(1)	3549(1)	35(1)
P(1)	3066(1)	1670(1)	2097(1)	30(1)
S(1)	2675(1)	4330(1)	2489(1)	51(1)
C(1)	539(5)	3212(5)	4820(4)	69(2)
C(2)	511(6)	2095(6)	4575(4)	76(2)
C(3)	1858(6)	1260(4)	4858(3)	71(2)
C(4)	2688(6)	1864(5)	5359(3)	70(2)
C(5)	1894(5)	3083(5)	5283(4)	66(2)
C(6)	4472(4)	4404(3)	2636(3)	44(1)
C(7)	5188(5)	4955(4)	1652(3)	56(1)
C(8)	6574(5)	5087(4)	1715(4)	66(2)
C(9)	7269(5)	4682(4)	2733(4)	65(2)
C(10)	6575(5)	4151(5)	3721(4)	69(2)
C(11)	5189(4)	4009(4)	3674(4)	59(2)
C(12)	3026(3)	47(3)	2416(3)	33(1)
C(13)	4239(4)	-939(3)	2531(3)	41(1)
C(14)	4092(5)	-2134(3)	2839(3)	53(1)
C(15)	2730(5)	-2359(3)	3019(3)	56(2)
C(16)	1513(4)	-1389(3)	2885(3)	51(1)
C(17)	1651(4)	-196(3)	2589(3)	44(1)
C(18)	4967(3)	1636(3)	1677(3)	33(1)
C(19)	5492(4)	1969(3)	528(3)	46(1)
C(20)	6954(4)	1923(4)	291(3)	57(2)
C(21)	7900(4)	1524(4)	1184(4)	56(1)
C(22)	7386(4)	1207(4)	2326(4)	57(1)
C(23)	5936(4)	1270(3)	2579(3)	45(1)
C(24)	2055(3)	2190(3)	759(3)	31(1)
C(25)	2436(4)	1550(3)	-197(3)	45(1)
C(26)	1658(4)	1925(4)	-1196(3)	52(1)
C(27)	464(4)	2936(3)	-1260(3)	48(1)
C(28)	58(4)	3542(3)	-310(3)	45(1)
C(29)	838(3)	3184(3)	697(3)	37(1)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

were performed on a MicroVax II computer using the SHELXTL PLUS program package [19].

A list of structure factors, a complete table of bond angles and distances, and tables of isotropic and anisotropic displacement parameters, and H-atom coordinates, are available from the author.

Acknowledgment

Financial support to J.D. by the Research and Publications Committee, University of Botswana (10.10.00.274) and the Third World Academy of Science (BC-90-075) is gratefully acknowledged. L.M.K. thanks the Northern State University for a Faculty Support Programme grant (12050). We also thank Dr. D.A. Tocher, University College London, who determined the crystal structure as a service, and Prof. F. Bottomley, University of New Brunswick, Canada for the mass spectra.

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