Reductive Cleavage of the C–S Bond in $[Ni_2(cp)_2(\mu\text{-}SR)_2]$ (cp = η-C_5H_5) by $LiAlH_4$. Crystal Structures of $[Ni_2(cp)_2(\mu\text{-}SPh)_2]$ and $[Ni_2(cp)_2\{\mu\text{-}o\text{-}(SCH_2)_2C_6H_4\}]$†

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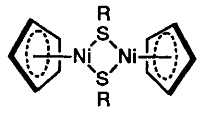
The first example of the reductive cleavage of the carbon–sulphur bond in organonickel thiolato complexes $[Ni_2(cp)_2(SR)_2]$ (cp = η-C_5H_5) by $LiAlH_4$ is reported. Preliminary mechanistic studies suggest that some kind of hydridic species may play an important role in the reduction. Electrochemical investigation of the bridged thiolatonickel complexes indicates that they undergo reversible one-electron reduction without cleavage of the C–S bond. The molecular structures of $[Ni_2(cp)_2(SPh)_2]$ (**1a**) and $[Ni_2(cp)_2\{o\text{-}(SCH_2)_2C_6H_4\}]$ (**1e**) have been determined by *X*-ray crystallography. The crystal data are: (**1a**), space group *Pbca*, a = 8.043(3), b = 12.774(3), c = 19.610(5) Å, Z = 4, R = 0.043 for 1 867 observed reflections; (**1e**), space group $P2_1/a$, a = 10.348(3), b = 10.880(3), c = 14.785(4) Å, β = 97.78(2)°, Z = 4, R = 0.046 for 1 772 observed reflections.

The reduction of carbon–sulphur bonds with organometallic reagents under homogeneous conditions is well documented.[1] Mechanistic investigations of these reactions may provide useful information on the actual mode of heterogeneous desulphurisation reactions. A free-radical mechanism,[2] an electron-transfer process,[3] as well as the involvement of metal hydridic species[4,5] have been suggested for the reductive cleavage of carbon–sulphur bonds under different conditions. It is noteworthy that complex metal hydrides in the presence of transition-metal halides are active reducing agents for the reductive cleavage of the carbon–sulphur bond.[1] We recently reported that an equimolar mixture of nickelocene and $LiAlH_4$ was an effective desulphurisation agent.[5] Preliminary examination has shown that it contains metal hydridic species. Various metallic species are highly thiophilic and a number of bridged thiolato complexes are known.[6] The ligation between the sulphur moiety and certain metals may activate the carbon–sulphur bond such that the cleavage reaction can occur thermally[7] or photolytically,[8] or upon hydrogenation.[9] To our knowledge, no report has appeared in the literature concerning the reduction with complex hydrides of the carbon–sulphur bond in complexed thiolato ligands. The reaction of $[W(cp)_2(SR)_2]$ (cp = η-C_5H_5) with 10 equivalents of $LiAlH_4$ afforded $[W(cp)_2H(SR)]$.[10] The fate of one of the SR ligands, however, was not clear.

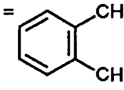
The complex $[Ni_2(cp)_2(SR)_2]$ (**1**) has been known for almost three decades,[11] but its chemistry has been studied only sporadically.[12] As mentioned above, a mixture of nickelocene and $LiAlH_4$ is an effective reducing agent for organosulphur compounds.[5] It would be intriguing to see whether (**1**) could be reduced by $LiAlH_4$. In this case, the sulphur moiety is already co-ordinated to the nickel atoms and, therefore, should be somewhat activated. In this paper, we report a detailed investigation of the reactions of complex (**1**) and crystal structures of two such molecules.[13]

Results and Discussion

Preparation and Structure of $[Ni_2(cp)_2(SR)_2]$ (**1**).—Thiolato nickel complexes (**1a**)—(**1e**) were synthesised by the reaction of mercaptans with nickelocene following the literature method.[11]



(**1a**) R = Ph
(**1b**) R = $PhCH_2$
(**1c**) R = 2–Naphthyl
(**1d**) R = n–C_8H_{17}
(**1e**) R–R =



The *X*-ray structures of complexes (**1a**) and (**1e**) are shown in Figures 1 and 2, respectively. Molecule (**1a**) occupies a centrosymmetric site in the unit cell, and the four-membered planar Ni_2S_2 ring is nearly square with Ni–S–Ni and S–Ni–S angles of 89.9(1) and 90.1(1)° respectively. The distance between the two nickel atoms is 3.097(1) Å which greatly exceeds the shortest interatomic distance of 2.492(1) Å in metallic nickel[14] so that there is no direct metal–metal bonding. The structure of this compound is very similar to those of related phosphine complexes.[15]

The structure of (**1e**) is of interest in connection with the bridging mode of the o-$(SCH_2)_2C_6H_4$ group. As expected, the Ni_2S_2 four-membered ring is non-planar, the dihedral angle between the S(1)–Ni(1)–S(2) and S(1)–Ni(2)–S(2) fragments being 44.7°. The Ni • • • Ni distance was found to be 2.918(1) Å which is significantly shorter than that in (**1a**). However, it is unlikely to implicate metal–metal bonding.

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† Bis(μ-benzenethiolato)-bis[(η-cyclopentadienyl)nickel(II)] and μ-o-xylene-α,α'-dithiolato-κ^2S,κ^2S'-bis[(η-cyclopentadienyl)nickel(II)].
‡ To whom correspondence should be addressed concerning the *X*-ray structures.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

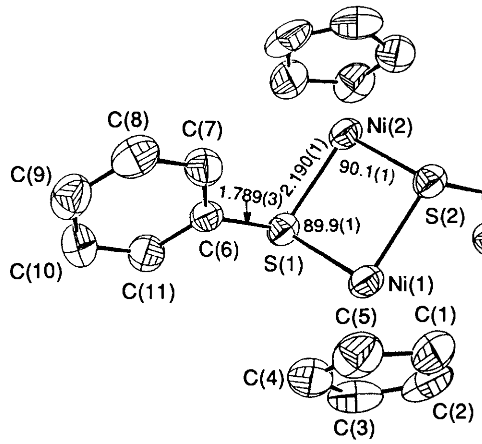

Figure 1. Perspective view of the molecular structure of complex (**1a**). Thermal ellipsoids are drawn at the 35% probability level

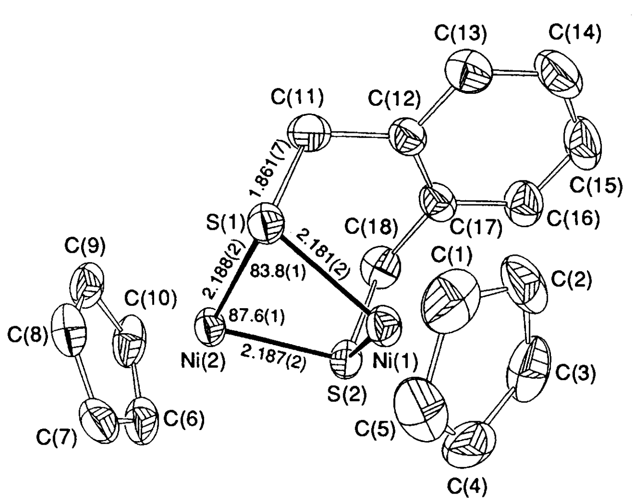

Figure 2. Perspective view of the molecular structure of complex (**1e**). Thermal ellipsoids are drawn at the 35% probability level. Other important bond distances and angles are Ni(1)–S(2) 2.191(2) and S(2)–C(18) 1.851(7) Å, Ni(1)–S(2)–Ni(2) 83.6(1) and S(1)–Ni(1)–S(2) 87.6(1)°.

Table 1. Reduction of the C–S bond in bridged thiolato complexes (**1**) and half-wave potentials for the reversible reduction of (**1**)

Complex	Product	Yield (%)	$E_{\frac{1}{2}}$ *
(**1a**)	Benzene	55	−1.43
(**1b**)	Toluene	60	−1.60
(**1c**)	Naphthalene	80	−1.41
(**1d**)	n-Decane	80	−1.66
(**1e**)	*o*-Xylene	60	−1.63

* Relative to Ag–$AgNO_3$ electrode.

Although the carbon–sulphur bonds in both complexes (Figures 1 and 2) are slightly longer than those in compounds analogous to the free sulphur ligands,† they may not reflect the reactivity of thiolato complexes toward reducing agents.

Reductive Cleavage of the Carbon–Sulphur Bond in Complex (**1**).—The complexes (**1a**)—(**1e**) were treated with 2 equivalents of $LiAlH_4$ in diethyl ether or tetrahydrofuran (thf). The corresponding hydrocarbons RH were obtained. In addition, a small amount of the disulphides RSSR (R = Ph or $PhCH_2$) were isolated from the reactions of (**1a**) and (**1b**), respectively. The results are summarized in Table 1. Aryl, benzylic, as well as simple aliphatic carbon–sulphur bonds in these substrates were reduced readily under the reaction conditions. There was no apparent difference in reactivity among these substrates. When $LiAlD_4$ was used in the reduction of (**1b**), $C_6H_5CH_2D$ was isolated in 60% yield with more than 90% of deuterium incorporated. Low-valent organonickel reagents can reduce mercaptans to the corresponding hydrocarbons.[3–5] It is highly desirable to investigate whether the organosulphur moiety remains ligated to nickel at (**1a**)—(**1e**) during the course of reduction. Accordingly, an equimolar mixture of 2-naphthylmethanethiol and (**1b**) was allowed to react with $LiAlH_4$ as usual; after work-up, the thiol was recovered in essentially quantitative yield and the yield of toluene was 60%. This result demonstrates that only the C–S bond of the complexed thiolato ligand was reduced and no exchange between organosulphur ligands occurred under these conditions. It can also rule out the possibility that the bridged thiolato ligand in (**1b**) is first liberated and then reduced *in situ*. It is also worth mentioning that complexes (**1**) are stable toward $NaBH_4$, catalytic hydrogenation, and photolysis, the starting materials being recovered in *ca.* 95% yield.

The reaction of complex (**1b**) was followed by ^1H n.m.r. spectroscopy. At −10 °C $LiAlH_4$ was instantaneously consumed upon treatment with 0.5 equivalent of (**1b**) in $[^2H_8]$-tetrahydrofuran; a new broad singlet at *ca.* δ −7.0 was observed at the beginning of the reaction {the ^1H n.m.r. absorption for $LiAlH_4$ in $[^2H_8]$tetrahydrofuran appeared at δ 1.83 as a broad sextet [J(Al–H) = 167 Hz]} which was absent when $LiAlD_4$ was employed. This absorption was assigned to be some kind of metal hydridic species.[16] It disappeared very rapidly as the reaction proceeded. The absorption of the cyclopentadienyl ligand changed gradually from δ 4.50 to 5.80. Complete transformation was achieved after 20 h. No organic product other than toluene and a η^5-cyclopentadienyl compound was detected. In other words, the formation of these products was essentially quantitative. The n.m.r. results indicates that the cyclopentadienyl moiety is still co-ordinated symmetrically to the metal in the product. By consideration of the stoicheiometry of the reaction, the structure $Li_2[(cp)Ni(\mu\text{-}S)_2Ni(cp)]$ is proposed. Attempts to isolate the product were unsuccessful. After removal of the solvent and other volatile materials (*e.g.* product of the reaction), the residue decomposed rapidly and could not be redissolved in any organic solvent.

Triphenylphosphine reacted smoothly with nickel sulphide at room temperature to form triphenylphosphine sulphide in 73% yield. In a similar experiment, a mixture of complex (**1b**) and $LiAlH_4$ was allowed to react first as usual followed by treatment of the reaction mixture with triphenylphosphine. After work-up, PPh_3S was isolated in 12% yield. It is noteworthy that triphenylphosphine did not react with (**1b**) in the absence of $LiAlH_4$.

Although the actual mode of reduction of complexes (**1a**)—(**1e**) is not well understood at this stage, the nature of the reaction is intriguing. Our results suggested that metal hydride may be formed and would be responsible for the reduction of the carbon–sulphur bond. Recently, Yamamoto and his co-workers[17] reported that C–S bond reduction may occur upon thermolysis of hydridothiolatonickel phosphine complexes. Phosphine sulphide was also obtained from these reactions. Our results are compatible with their observations.

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† The carbon–sulphur distances for di(4-tolyl) sulphide and dibenzyl disulphide are 1.75(3) and 1.844(12) Å, respectively (W. R. Blackmore and S. C. Abrahams, *Acta Crystallogr.*, 1955, **8**, 329; B. V. Dijk and G. J. Visser, *Acta Crystallogr., Sect. B*, 1971, **27**, 846).

Electrochemical Study.—The nickel-mediated hydrodesulphurisation of dibenzothiophene and related compounds has been suggested to proceed *via* an electron-transfer mechanism.[3] It is of interest to investigate whether such a process may also occur in the reduction of (**1**). Electrochemical oxidation of certain nickel thiolato complexes such as (**1a**) and (**1b**) has been reported.[12] The reduction process has been only briefly investigated. When a reduction potential was applied to the nickel substrates (**1a**)—(**1e**) in CH_3CN a reversible couple was found at *ca.* −1.6 V (against Ag–$AgNO_3$). Individual runs showed that all the electron-transfer processes were indeed reversible and each involved one electron with the peak-to-peak separation current approaching the theoretical limit of 60 mV.[18] Furthermore, rotating-disc electrolysis at −2.0 V confirmed that this couple is a one-electron redox process. The complex may accept one electron to yield a radical anion $[(cp)Ni(\mu\text{-}SR)_2Ni(cp)]^{\cdot -}$. The half-wave potentials for the reduction of (**1a**)—(**1e**) are also outlined in Table 1. The ease of reduction follows the order: 2-naphthyl > phenyl > benzyl > n-decyl > o-$(CH_2)_2C_6H_4$. The fact that the reduction of the o-$(CH_2)_2C_6H_4$ species is harder than that of the benzyl-substituted species may arise from the puckered structure of the former complex. The reversibility suggested that a simple one-electron-transfer process would not lead to reductive cleavage of the carbon–sulphur bond of these nickel thiolato complexes.

Conclusion

We have reported the first example of the reduction of thiolato ligands in organonickel complexes by $LiAlH_4$. The model suggests that the carbon–sulphur bond is indeed activated by complexation with nickel and subsequent hydride transfer affords the corresponding reduced hydrocarbon. The hydridic species may play an important role in the reduction. A simple one-electron transfer process as described in the electrochemical study will not lead to reductive cleavage of the carbon–sulphur bond of nickel thiolato complexes.

Experimental

All n.m.r. spectra were recorded on JEOL PMX-60 and Bruker WM-250 spectrometers using tetramethylsilane as the internal standard. Chemical shifts are reported on the δ scale. Infrared spectra were measured on a Perkin-Elmer 283 spectrophotometer, mass spectra on a VG 7070G mass spectrometer, and gas chromatography on a Hitachi G-3000 gas chromatograph. Melting points were uncorrected. Tetrahydrofuran was distilled from sodium diphenylketyl. Other solvents were purified according to the literature procedure.[19] All reactions were carried out by using a standard inert-gas atmosphere technique.[20] The electrochemical measurements were performed with a Princeton Applied Research (PARC) model 173 potentiostat, a model 175 universal programmer, and a model 179 digital coulombmeter. Mercaptans were prepared according to the literature method.[21]

General Procedure for the Synthesis of Complexes (**1**).—According to the literature procedure,[11] thiol in benzene was added dropwise to a solution of 1 equivalent of nickelocene and the mixture was stirred at room temperature for 16 h. Solvent was removed *in vacuo* and the residue was recrystallised from diethyl ether to afford a black crystalline solid: (**1a**) yield 78%, m.p. 126—128 °C (lit.,[11] 125 °C), ^1H n.m.r. δ 4.50 (10 H, br s) and 7.09 (10 H, br s), *m/z* 466; (**1b**), 85%, 155—157 °C, δ 3.3 (4 H, br s), 4.50 (10 H, br s), and 7.20 (10 H, br s), *m/z* 494; (**1c**), 72%, 180—182 °C, δ 4.54 (10 H, br s) and 7.2—8.5 (14 H, br m), *m/z* 566; (**1d**) 50%, 50—51 °C, δ 4.0 (10 H, br s), 2.8 (4 H, br s), 1.14 (32 H, br s), and 0.84 (6 H, br s), *m/z* 594; (**1e**), 35%, 173—174 °C, δ 7.10 (4 H, br s) and 4.10 (14 H, br s), *m/z* 416.

General Procedure for Desulphurization of Complexes (**1**) *with* $LiAlH_4$.—In a Schlenk tube (100 cm^3) an equimolar mixture of complex (**1**) and $LiAlH_4$ in ether or thf was stirred at room temperature for 16 h and then quenched with water. After filtration, the solution was extracted with ether and the solution dried over anhydrous magnesium sulphate, filtered, and the filtrate evaporated at atmospheric pressure. The residue was subjected to analysis. The volatile desulphurisation product was analyzed by gas chromatography using OV-17 as the stationary phase.

A mixture of complex (**1a**) (200 mg, 0.43 mmol) and $LiAlH_4$ (33 mg, 0.86 mmol) in ether (20 cm^3) was converted into benzene in 55% yield. In another run under identical reaction conditions, diphenyl disulphide (5 mg, 5%), m.p. 56—58 °C (lit.,[22] 58—60 °C), was isolated from the residue by preparative t.l.c. using hexane as eluant.

A mixture of complex (**1b**) (220 mg, 0.44 mmol) and $LiAlH_4$ (34 mg, 0.9 mmol) in ether (15 cm^3) was transformed into toluene (60% yield). In addition, $PhCH_2S_2CH_2Ph$ (5 mg, 5%), m.p. 68—70 °C (lit.,[23] 71—72 °C), was isolated from another identical run.

Complex (**1c**) (200 mg, 0.35 mmol) was allowed to react with $LiAlH_4$ (27 mg, 0.7 mmol) to give naphthalene (179 mg, 80%) which showed identical physical properties to those of an authentic sample.

A tetrahydrofuran solution (20 cm^3) of complex (**1d**) (250 mg, 0.42 mmol) and $LiAlH_4$ (32 mg, 0.84 mmol) was converted into n-decane (80% yield).

Complex (**1e**) (200 mg, 0.51 mmol) was treated with $LiAlH_4$ (39 mg, 1.02 mmol) in thf (25 cm^3) to give *o*-xylene (60% yield).

Reaction of complex (**1b**) *in the presence of* 2-*naphthalenemethanethiol.* A mixture of complex (**1b**) (220 mg, 0.44 mmol) and the thiol (76 mg, 0.44 mmol) was treated with $LiAlH_4$ (35 mg, 0.9 mmol) in ether (15 cm^3) for 2 h. The mixture was quenched with dilute HCl. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulphate. After filtration, the filtrate was subjected to g.c. analysis. The yield of toluene was 60%. In a separate run, the filtrate thus obtained was evaporated *in vacuo* and the residue (70 mg, 92%) identified as unreacted thiol.

Proton n.m.r. study of the reaction of complex (**1b**) *in* $[^2H_8]$*tetrahydrofuran.* Compound (**1b**) (30 mg, 0.06 mmol) and $LiAlH_4$ (5 mg, 0.13 mmol) were mixed in an n.m.r. tube to which $[^2H_8]$tetrahydrofuran (*ca.* 0.5 cm^3) was added. The tube was immersed in a liquid-nitrogen Dewar, evacuated, and sealed under a nitrogen atmosphere. The sample was warmed to −10 °C and immediately subjected to n.m.r. analysis.

Reactions of Complex (**1b**).—(*a*) *With* $LiAlD_4$. A mixture of complex (**1b**) (150 mg, 0.3 mmol) and $LiAlD_4$ (23 mg, 0.6 mmol) in thf (20 cm^3) was stirred at room temperature for 16 h and the reaction mixture was worked up according to the general procedure to give $C_6H_5CH_2D$ (34 mg, 60%), *m/z* 93.

(*b*) *With* $NaBH_4$. A mixture of complex (**1b**) (150 mg, 0.3 mmol) and $NaBH_4$ (23 mg, 0.6 mmol) in ether (15 cm^3) was allowed to react according to the general procedure. After work-up, the starting material (**1b**) (142 mg, 95%) was recovered in addition to $PhCH_2S_2CH_2Ph$ (3 mg, 3%).

(*c*) *Irradiation.* An ether solution of complex (**1b**) (250 mg, 0.51 mmol) was irradiated by a broad-band u.v. lamp (Hanovia 150 W) for 16 h. After usual work up, (**1b**) (238 mg, 95%) was recovered.

(*d*) *Attempted hydrogenation.* Compound (**1b**) (250 mg, 0.51 mmol) was dissolved in thf (100 cm^3) in a Teflon container

Table 2. Data collection and processing parameters *

Compound	**(1a)**	**(1e)**
a/Å	8.043(3)	10.348(3)
b/Å	12.774(3)	10.880(3)
c/Å	19.610(5)	14.785(4)
β/°		97.78(2)
U/Å^3	2 014.8(9)	1 649.2(8)
Z	4	4
F(000)	960	856
D_m/g cm^{-3}	1.539 (KI–water)	1.673 (CCl_4–$BrCH_2CH_2Br$)
D_c/g cm^{-3}	1.536	1.675
Space group	*Pbca*	$P2_1/a$
μ/cm^{-1}	20.81	25.31
Crystal size (mm)	0.30 × 0.26 × 0.10	0.32 × 0.30 × 0.06
Mean μr	0.12	0.16
Transmission factors	0.685—0.757	0.512—0.824
Collection range	$h, k, l; 2\theta_{max.} = 60°$	$h, k, \pm l; 2\theta_{max.} = 45°$
Unique data measured	2 410	2 043
Observed data with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$, n	1 867	1 772
Number of variables, p	118	199
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.043	0.046
g in weighting scheme $w = [\sigma^2(\lvert F_o\rvert) + g\lvert F_o\rvert^2]^{-1}$	0.0005	0.0010
$R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.047	0.055
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - p)]^{\frac{1}{2}}$	1.300	1.310
Residual extrema in final difference map (e Å^{-3})	+0.46 to −0.34	+0.50 to −0.79

* Details in common: black plates; intensity variation, ±0.5%; scan type, ω—2θ; scan speed, 2.02—8.37° min^{-1}; scan range, 1° below K_{α_1} to 1° above K_{α_2}; background counting, stationary counts for one half of scan time at each end of scan range.

Table 3. Atomic co-ordinates (× 10^5 for Ni and S, × 10^4 for others) for compound (**1a**)

Atom	x	y	z
Ni(1)	9 571(5)	7 580(3)	4 741(2)
S(1)	−16 277(11)	2 328(6)	3 955(4)
C(1)	3 263(6)	1 335(4)	760(2)
C(2)	2 292(7)	2 222(3)	558(2)
C(3)	948(7)	2 242(3)	982(2)
C(4)	1 074(5)	1 391(4)	1 455(2)
C(5)	2 559(6)	877(4)	1 336(2)
C(6)	−2 001(4)	−583(2)	1 122(2)
C(7)	−1 198(4)	−1 536(2)	1 220(2)
C(8)	−1 548(5)	−2 126(3)	1 793(2)
C(9)	−2 696(5)	−1 796(3)	2 266(2)
C(10)	−3 481(5)	−857(3)	2 170(2)
C(11)	−3 139(4)	−252(3)	1 597(2)

Table 4. Atomic co-ordinates (× 10^5 for Ni, × 10^4 for others) for compound (**1e**)

Atom	x	y	z
Ni(1)	10 178(7)	−2 090(7)	25 615(5)
Ni(2)	22 850(7)	6 412(7)	43 342(5)
S(1)	2 971(1)	−515(1)	3 286(1)
S(2)	1 049(1)	1 588(1)	3 233(1)
C(1)	713(7)	−1 791(7)	1 782(5)
C(2)	575(7)	−803(7)	1 163(4)
C(3)	−393(7)	−71(7)	1 401(5)
C(4)	−951(6)	−640(8)	2 121(5)
C(5)	−301(7)	−1 706(7)	2 339(5)
C(6)	1 634(7)	1 359(7)	5 506(4)
C(7)	1 730(7)	55(7)	5 602(4)
C(8)	3 035(7)	−236(6)	5 546(4)
C(9)	3 765(6)	875(6)	5 509(4)
C(10)	2 913(7)	1 847(6)	5 486(4)
C(11)	4 083(6)	483(6)	2 722(4)
C(12)	3 481(5)	1 020(6)	1 829(4)
C(13)	3 780(7)	555(7)	1 019(5)
C(14)	3 242(7)	1 021(7)	189(5)
C(15)	2 344(7)	1 961(7)	157(5)
C(16)	2 023(7)	2 431(6)	958(4)
C(17)	2 588(6)	1 995(6)	1 803(4)
C(18)	2 190(6)	2 528(5)	2 661(4)

placed in an autoclave. Hydrogen (35 atm, *ca.* 3.55 × 10^6 Pa) was charged and the mixture was stirred at room temperature for 4 h. The hydrogen gas was released and the starting material (**1b**) (250 mg, 95%) was recovered after work-up.

Reactions of PPh_3.—(*a*) *With* NiS. A slurry of PPh_3 (100 mg, 0.38 mmol) and NiS (33 mg, 0.36 mmol) in thf (25 cm^3) was stirred at room temperature for 16 h. Solvent was then removed *in vacuo* and the residue was chromatographed on a silica gel column using hexane–ethyl acetate (10:1) as eluant to give PPh_3S (82 mg, 73%), m.p. 161—162 °C, which exhibited identical physical properties to those of an authentic sample.

(*b*) *With complex* (**1b**) *and* $LiAlH_4$. A mixture of complex (**1b**) (1.0 g, 2.03 mmol) and $LiAlH_4$ (0.155 g, 4.06 mmol) in thf (50 cm) was allowed to react according to the general procedure for 3 h. To this mixture PPh_3 (1.1 g, 4.06 mmol) was added and the solution was stirred for 16 h. Solvent was removed *in vacuo* and the residue was chromatographed on a silica gel column using hexane–ethyl acetate (10:1) as eluant to afford PPh_3S (0.14 g, 12%) and $PhCH_2S_2CH_2Ph$ (25 mg, 5%).

General Procedure for Cyclic Voltammetry Experiments.—A three-electrode configuration was used in a divided electrochemical cell of capacity *ca.* 10 cm^3. A glassy carbon electrode (area *ca.* 0.04 cm^2) and platinum foil (area *ca.* 0.03 cm^2) were used as working and counter electrodes, respectively. The counter electrode was separated from the working electrode compartment by a sintered glass frit. An Ag–$AgNO_3$ (0.1 mol

dm^{-3} $AgNO_3$ in CH_3CN) electrode was used as the reference electrode. Ferrocene was used as internal standard and 0.1 mol dm^{-3} tetra-n-butylammonium perchlorate as the supporting electrolyte, and the cell was deaerated using purified nitrogen.

The complex was dissolved in CH_3CN containing 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ in a volumetric flask (10 cm^3) to form a 5×10^{-4} mol dm^{-3} solution. The solution was placed in an electrochemical cell and deaerated with nitrogen for 5 min. A potential was applied to the solution and the cyclo voltammogram recorded. Ferrocene was then added to the solution as an internal standard to calibrate the potential at the end of each experiment.

X-Ray Crystallography.—*X*-Ray measurements were performed at 18 °C on a Nicolet R3m/V diffractometer using monochromatic Mo-K_α radiation (λ = 0.710 73 Å). The raw data were corrected for absorption effects using ψ-scan data,[24] and the structures were solved by direct methods. The hydrogen atoms of the benzene rings were introduced in computed positions, while those of the cyclopentadienyl groups were allowed to vary. All non-hydrogen atoms were refined anisotropically, and isotropic thermal parameters were assigned to the hydrogen atoms. Computations were carried out using the SHELXTL-PLUS program package,[25] and neutral atomic scattering factors incorporating anomalous dispersion terms were employed. Crystal data collection and processing parameters are given in Table 2, fixed atomic co-ordinates in Tables 3 and 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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