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# Transition metal complexes VII*. $[(\eta^5\text{-Cp})Ni(PEt_3)]_2$, a dinuclear organometallic complex with an unbridged Ni–Ni bond; structure and heteronuclear complexes thereof

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## Abstract

$[(\eta^5\text{-Cp})Ni(PEt_3)]_2$ (**1**) has been synthesized by reacting $(\eta^5\text{-Cp})Ni(PEt_3)Cl$ with activated magnesium. **1** contains an unbridged nickel–nickel bond. Reaction of **1** with elemental sulfur yields the clusters $[(\eta^5\text{-Cp})_2(PEt_3)_2(\mu_3\text{-}S)Ni_3]$ (**2**) and $[(\eta^5\text{-Cp})(PEt_3)Ni(\mu\text{-}S)Ni(\eta^5\text{-Cp})]_2$ (**3**). The homologous selenium compound $[(\eta^5\text{-Cp})(PEt_3)Ni(\mu\text{-}Se)Ni(\eta^5\text{-Cp})]_2$ (**4**) has been obtained by the reaction of **1** with elemental selenium. **1** reacts with tellurium by insertion to yield $\{[(\eta^5\text{-Cp})Ni(PEt_3)]_2Te\}$ (**5**). Tin(II) chloride can also be inserted into the nickel–nickel bond of **1** to give $\{[(\eta^5\text{-Cp})Ni(PEt_3)]_2SnCl_2\}$ (**6**). Both chlorine atoms in **6** react with alkyllithium to give compounds of the type $\{[(\eta^5\text{-Cp})Ni(PEt_3)]_2SnR_2\}$ (**7**) (**a**: R = Me, **b**: R = n-Bu). The reaction of **6** with activated magnesium yields $\{[(\eta^5\text{-Cp})Ni(PEt_3)]_3SnCl\}$ (**8**). Crystal structures of **1**, **2**, **3**, **5**, **6** and **8** have been determined.

## Introduction

The chemistry of transition metal complexes containing metal–metal bonds is one of the most interesting fields in modern coordination chemistry. This class of compounds plays an important role in catalysis [2], serves as a model for surface reactions [3] and forms a bridge between mononuclear complexes and the extended metal [4]. Nickel cluster complexes are known in great variety. In general Ni–Ni bonds are stabilized by bridging ligands. Our interest has been directed towards reactions of $\eta^3$-allylnickelhalides and nickelocene with magnesium butadiene to yield dinuclear compounds with $\eta^3,\eta^1$-bonded butadiene. The results of these investigations will be described in a separate paper. In the course of these experiments we isolated the complex $[(\eta^5\text{-Cp})Ni(PEt_3)]_2$ (**1**) containing an unbridged Ni–Ni bond. Although a great number of transition metal complexes with metal–metal interactions are known, complexes with unbridged metal–metal bonds, especially of metals of the 3d row, are still rare. In this paper we report the synthesis, the structure determination and reactions of **1** as well as a series of heteronuclear complexes obtained by insertion reactions into the Ni–Ni bond of **1**.

## Experimental

All reactions were carried out under argon atmosphere using traditional Schlenk techniques. Solvents were dried over Na/K alloy, $CaH_2$ or $NaAlEt_4$ and freshly distilled. Aluminium oxide was dried at 180 °C under high vacuum and stored under argon. Activated magnesium [5], nickelocene [6] and $(PEt_3)_2NiCl_2$ [7] were prepared by literature procedures. All other chemicals were of reagent grade quality and used without further purification.

NMR spectra were recorded on a Bruker AC 200-, Bruker AM 200- or Bruker WH 400FT spectrometer. Elemental analyses were performed by Mikroanalytisches Laboratorium Dornis & Kolbe, Mülheim an der Ruhr, Germany.

### *Bis($\eta^5$-cyclopentadienyl-triethylphosphine-nickel) (1)*

A solution of 2.6 g (13.7 mmol) nickelocene and 5.0 g (13.7 mmol) $(PEt_3)_2NiCl_2$ in 100 ml of thf was refluxed for 16 h. The red solution was cooled to 0 °C and was pipetted onto 301 mg (12.4 mmol) activated magnesium. The reaction mixture was stirred for 5 h at 0 °C, during which a slow change in colour from red to green

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†X-ray structural analyses.

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occurred. Finally the mixture was allowed to warm up to room temperature and the solvent evaporated off. The residue was extracted with pentane, and the resulting extract concentrated *in vacuo* and cooled to 0 °C. **1** was obtained in the form of large black crystals. Yield 4.8 g (80%).

$^{1}$H NMR (300 K, $C_6D_6$, 200.1 MHz): δ (ppm) = 5.32 (5H, s, C*H*–Cp), 1.62 (3H, ABX$_3$Y($J_{HHgem.} = -14.5$, $J_{HHvic.} = 7.5$, $J_{PH} = 5.1$ Hz), C*H*$_A$H$_B$–PEt$_3$), 1.29 (3H, ABX$_3$Y ($J_{HHvic.} = 7.5$, $J_{PH} = 9.1$ Hz), CH$_A$*H*$_B$–PEt$_3$), 0.90 (9H, dt ($J_{PH} = 14.5$ Hz), C*H*$_3$–PEt$_3$). $^{13}$C NMR (300 K, $C_6D_6$, 50.3 MHz): δ (ppm) = 87.0 (d, $J_{CH} = 170$ Hz, *C*H–Cp), 23.0 (ABX, $J_{CH} = 127$ Hz, *C*H$_2$–PEt$_3$), 8.8 (q, $J_{CH} = 125$ Hz, *C*H$_3$–PEt$_3$). $^{31}$P NMR (300 K, $C_6D_6$, 81.0 MHz): δ = 26.9 ppm. *Anal.* Calc. for $C_{22}H_{40}Ni_2P_2$ (483.93): C, 54.60; H, 8.33; Ni, 24.26; P, 12.80. Found: C, 54.58; H, 8.45; Ni, 24.19; P, 12.72%.

*Reaction of 1 with iodine*

To a solution of 361 mg (0.75 mmol) of **1** in ether, 189 mg (0.75 mmol) of iodine were added. Within 10 min the colour of the solution changed to red. The solvent was evaporated and the residue was extracted with a 1:1 mixture of ether and pentane. The resulting solution was concentrated *in vacuo* and cooled to 0 °C. CpNi(PEt$_3$)I was obtained in the form of red platelets. Yield 459 mg (79%).

*Reaction of 1 with sulfur*

54 mg (1.69 mmol) of elemental sulfur were added to a solution of 817 mg (1.69 mmol) of **1** in ether at −20 °C. The solution was warmed and its colour changed. At −10 °C it turned red and at room temperature orange–brown. Some aluminium oxide was added and the mixture was evaporated to dryness. The residue was placed on a column filled with aluminium oxide and chromatographed. A green brown phase was eluted with ether. The resulting solution was evaporated, the residue dissolved in pentane, filtered through celite on a glass frit to remove insoluble impurities, concentrated *in vacuo* and cooled to 0 °C. Black cube shaped crystals of **2** were obtained. Yield 114 mg (18% with respect to nickel). With thf a second brownish phase was eluted from the column. The solution was filtered through celite on a glass frit and concentrated *in vacuo*. A small amount of ether was added and the sample was cooled to 0 °C. Dark brown crystals of **3** were obtained. Yield 156 mg (23% with respect to nickel).

**2**: $^{1}$H NMR (193 K, d$^8$-toluene, 400.1 MHz): δ (ppm) = 5.32 (10H, s, C*H*–Cp), 1.45 (6H, quint. ($J_{HH} = J_{PH} = 7.4$ Hz), C*H*$_2$–PEt$_3$), 1.09 (15H, m, methyl protons of one phosphine are obscured by the methylene protons of the other phosphine), 0.73 (9H, dt ($J_{HH} = 7.4$, $J_{PH} = 14.8$ Hz), C*H*$_3$–PEt$_3$). $^{1}$H NMR (300 K, d$^8$-toluene, 400.1 MHz): δ (ppm) = 5.09 (10H, s, C*H*–Cp), 1.36 (12H, broad, C*H*$_2$–PEt$_3$), 0.93 (18H, broad, C*H*$_3$–PEt$_3$). $^{13}$C NMR (223 K, d$^8$-toluene, 100.6 MHz): δ (ppm) = 85.8 (*C*H–Cp), 20.9 ($J_{CP} = 25$ Hz, *C*H$_2$–PEt$_3$(1)), 19.3 ($J_{CP} = 22$ Hz, CH$_2$–PEt$_3$(2)), 9.4 (*C*H$_3$–PEt$_3$(1)), 8.4 (*C*H$_3$–PEt$_3$(2)). $^{13}$C NMR (300 K, $C_6D_6$, 50.3 MHz): δ (ppm) = 86.5 (*C*H–Cp), 21.3 (*C*H$_2$–PEt$_3$), 9.1 (*C*H$_3$–PEt$_3$). *Anal.* Calc. for $C_{22}H_{40}Ni_3P_2S$ (574.70): C, 45.98; H, 7.02; Ni, 30.64; P, 10.78; S, 5.58. Found: C, 45.63; H, 7.11; Ni, 30.31; P, 10.30; S, 5.61%.

**3**: $^{1}$H NMR (300 K, d$^8$-thf, 200.1 MHz): δ (ppm) = 5.48 (5H, s, C*H*–CpNiPS), 4.89 (5H, s, C*H*–CpNiSS), 1.61 (6H, quint. ($J_{HH} = J_{PH} = 7.7$ Hz), C*H*$_2$–PEt$_3$), 1.08 (9H, dt ($J_{PH} = 15.3$ Hz), C*H*$_3$–PEt$_3$). $^{13}$C NMR (300 K, d$^8$-thf, 50.3 MHz): δ (ppm) = 94.8 ($J_{CP} = 2$ Hz, *C*H–CpNiPS), 92.2 (*C*H–CpNiSS), 17.4 ($J_{CP} = 28$ Hz, *C*H$_2$–PEt$_3$), 8.1 (*C*H$_3$–PEt$_3$). $^{31}$P NMR (300 K, d$^8$-thf, 81.0 MHz): δ = 29.6 ppm. *Anal.* Calc. for $C_{32}H_{50}Ni_4P_2S_2$ (795.66): C, 48.31; H, 6.34; Ni, 29.51; P, 7.79; S, 8.06. Found: C, 47.92; H, 6.50; Ni, 28.79; P, 7.43; S, 8.26%.

*Reaction of 1 with selenium*

301 mg (3.81 mmol) of glassy selenium were added to a solution of 922 mg (1.90 mmol) of **1** in ether at −20 °C. The reaction mixture was allowed to warm up to room temperature. During warming up the selenium dissolved and the colour changed to orange–brown. The solution was evaporated to dryness and the residue was extracted exhaustively with pentane to remove Et$_3$P=Se completely. The resulting residue was dissolved in thf, filtered though celite on a glass frit, concentrated *in vacuo* and cooled to 0 °C. Black metallic glimmering crystals of **4** were obtained. The crystals contain half a molecule thf per molecule of **4**. Yield 364 mg (43%).

$^{1}$H NMR (300 K, d$^8$-thf, 200.1 MHz): δ (ppm) = 5.45 (5H, s, C*H*–CpNiPS), 4.91 (5H, s, C*H*–CpNiSS), 1.65 (6H, quint. ($J_{HH} = J_{PH} = 7.7$ Hz), C*H*$_2$–PEt$_3$), 1.08 (9H, dt ($J_{PH} = 12.5$ Hz), C*H*$_3$–PEt$_3$). $^{13}$C NMR (300 K, d$^8$-thf, 50.3 MHz): δ (ppm) = 94.9 ($J_{CP} = 2$ Hz, *C*H–CpNiPS), 90.9 (*C*H–CpNiSS), 18.4 ($J_{CP} = 28$ Hz, *C*H$_2$–PEt$_3$), 8.3 (*C*H$_3$–PEt$_3$). $^{31}$P NMR (300 K, d$^8$-thf, 81.0 MHz): δ = 30.5 ppm. *Anal.* Calc. for $C_{34}H_{54}Ni_4O_{0.5}P_2Se_2$ (925.51): C, 44.13; H, 5.88; Ni, 25.37; P, 6.69; Se, 17.06. Found: C, 44.35; H, 6.08; Ni, 25.49; P, 6.88; Se, 17.18%.

*Reaction of 1 with tellurium*

231 mg (1.81 mmol) of elemental tellurium were added to a solution of 875 mg (1.81 mmol) of **1** in thf. The reaction mixture was stirred for 3 days. During this time the tellurium completely dissolved and an orange–red solution formed. It was evaporated to dryness. The residue was extracted with pentane, the extract concentrated *in vacuo* and cooled to 0 °C. Large dark crystals of **5** were obtained. Yield 618 mg (56%).

$^1$H NMR (300 K, d$^8$-thf, 200.1 MHz): δ (ppm) = 5.32 (5H, s, C*H*–Cp), 1.66 (6H, quint. ($J_{HH}$ = $J_{PH}$ = 7.7 Hz), C*H*$_2$–PEt$_3$), 0.91 (9H, dt ($J_{PH}$ = 15.5 Hz), C*H*$_3$–PEt$_3$). $^{13}$C NMR (300 K, d$^8$-thf, 50.3 MHz): δ (ppm) = 91.3 ($J_{CTe}$ = 175 Hz, *C*H–Cp), 21.3 ($J_{CP}$ = 30 Hz, *C*H$_2$–PEt$_3$), 8.9 (*C*H$_3$–PEt$_3$). $^{31}$P NMR (300 K, d$^8$-thf, 81.0 MHZ): δ = 46.9 ppm ($J_{PTe}$ = 140 Hz). *Anal.* Calc. for $C_{22}H_{40}Ni_2P_2Te$ (611.53): C, 43.21; H, 6.59; Ni, 19.20; P, 10.13; Te, 20.87. Found: C, 43.24; H, 6.45; Ni, 19.31; P, 10.08; Te, 20.78%.

### *Reaction of 1 with tin(II) chloride*

A solution of 218 mg (1.15 mmol) of anhydrous tin(II) chloride in thf was added to a solution of 537 mg (1.11 mmol) of **1** in thf at −30 °C. The green solution turned orange within a short time. The solution was allowed to warm up to room temperature and was then evaporated to dryness. The residue was extracted exhaustively with excess ether. The extract was concentrated *in vacuo* and cooled to 0 °C. Large dark crystals of **6** were obtained. Yield 666 mg (89%).

$^1$H NMR (300 K, d$^8$-thf, 200.1 MHz): δ (ppm) = 5.18 (5H, d, ($J_{SnH}$ = 3.9 Hz), C*H*–Cp), 1.74 (6H, quint. ($J_{HH}$ = $J_{PH}$ = 7.6 Hz), C*H*$_2$–PEt$_3$), 1.08 (9H, dt ($J_{PH}$ = 16.3 Hz), C*H*$_3$–PEt$_3$). $^{13}$C NMR (300 K, d$^8$-thf, 50.3 MHz): δ (ppm) = 90.8 ($J_{CSn}$ = 10 Hz, *C*H–Cp), 18.9 ($J_{CP}$ = 29 Hz, $J_{CSn}$ = 15 Hz, *C*H$_2$–PEt$_3$), 8.3 (*C*H$_3$–PEt$_3$). $^{31}$P NMR (300 K, d$^8$-thf, 81.0 MHz): δ = 28.0 ppm ($J_{PSn}$ = 342 and 358 Hz). *Anal.* Calc. for $C_{22}H_{40}Cl_2Ni_2P_2Sn$ (673.52): C, 39.23; H, 5.99; Cl, 10.53; Ni, 17.43; P, 9.20; Sn, 17.62. Found: C, 39.18; H, 6.02; Cl, 10.62; Ni, 17.31; P, 9.16; Sn, 17.62%.

### *Reaction of 6 with alkyllithium compounds*

100 mg (0.53 mmol) anhydrous tin(II) chloride were added at −30 °C to a solution of 256 mg (0.53 mmol) of **1** in thf. The mixture was allowed to warm up to room temperature and stirred for an additional hour. The orange solution was cooled to −78 °C and 0.6 ml of a 2.0 molar methyllithium solution were added. The colour of the solution changed to green–brown. The mixture was again allowed to warm up to room temperature and aluminium oxide was added. Subsequently, the mixture was evaporated to dryness, the resulting residue was placed on a column filled with aluminium oxide and chromatographed with a mixture of pentane and ether (5:1). A green phase was eluted. The solution was evaporated to dryness, the residue dissolved in pentane, filtered through celite on a glass frit, concentrated *in vacuo* and cooled to −78 °C. Green crystals of **7a** were obtained. Yield 158 mg (47%). **7b** was synthesized by reaction of **6** with n-BuLi in the same manner. Yield 56%.

**7a**: $^1$H NMR (300 K, d$^8$-thf, 200.1 MHz): δ (ppm) = 5.05 (5H, s, C*H*–Cp), 1.56 (6H, quint. ($J_{HH}$ = $J_{PH}$ = 7.5 Hz), C*H*$_2$–PEt$_3$), 1.03 (9H, dt ($J_{PH}$ = 15.3 Hz), C*H*$_3$–PEt$_3$), 0.28 (3H, s ($J_{HSn}$ = 28.4 Hz), C*H*$_3$–SnMe). $^{13}$C NMR (300 K, d$^8$-thf, 50.3 MHz): δ (ppm) = 88.4 ($J_{CP}$ = 2, $J_{CSn}$ = 9 Hz, *C*H–Cp), 20.7 ($J_{CP}$ = 27, $J_{CSn}$ = 13 Hz, *C*H$_2$–PEt$_3$), 8.3 (*C*H$_3$–PEt$_3$), 1.7 ($J_{CSn}$ = 16 Hz, *C*H$_3$–SnMe). $^{31}$P NMR (300 K, d$^8$-thf, 81.0 MHz): δ = 29.2 ppm ($J_{PSn}$ = 315 and 323 Hz). *Anal.* Calc. for $C_{24}H_{46}Ni_2P_2Sn$ (632.69): C, 45.56; H, 7.33; Ni, 18.55; P, 9.79; Sn, 18.76. Found: C, 45.51; H, 7.30; Ni, 18.46; P, 9.94; Sn, 18.83%.

**7b**: $^1$H NMR (300 K, d$^8$-thf, 200.1 MHz): δ (ppm) = 5.05 (5H, s ($J_{HSn}$ = 9.8 Hz), C*H*–Cp), 1.61 (6H, quint. ($J_{HH}$ = $J_{PH}$ = 7.5 Hz, C*H*$_2$–PEt$_3$), 1.35 (2H, sept. ($J_{HH}$ = 7.1 Hz), CH$_2$–CH$_2$–C*H*$_2$–CH$_3$–Sn$^n$Bu), 1.03 (9H, dt ($J_{PH}$ = 15.0 Hz), C*H*$_3$–PEt$_3$), 0.93 (3H, t, CH$_2$–CH$_2$–CH$_2$–C*H*$_3$–Sn$^n$Bu), the other protons are obscured by the phosphine protons. $^{13}$C NMR (300 K, d$^8$-thf, 50.3 MHz): δ (ppm) = 88.0 ($J_{CP}$ = 2, $J_{CSn}$ = 6 Hz, C*H*–Cp), 32.6 ($J_{CSn}$ = 12 Hz, CH$_2$–CH$_2$–*C*H$_2$–CH$_3$–Sn$^n$Bu), 28.8 ($J_{CSn}$ = 44 Hz, CH$_2$–*C*H$_2$–CH$_2$–CH$_3$–Sn$^n$Bu), 21.0 ($J_{CP}$ = 24, $J_{CSn}$ = 14 Hz, CH$_2$–PEt$_3$), 18.6 ($J_{CSn}$ = 49 Hz, *C*H$_2$–CH$_2$–CH$_2$–CH$_3$–Sn$^n$Bu), 14.2 (CH$_2$–CH$_2$–CH$_2$–*C*H$_3$–Sn$^n$Bu), 8.3 (*C*H$_3$–PEt$_3$). $^{31}$P NMR (300 K, d$^8$-thf, 81.0 MHz): δ = 25.4 ppm ($J_{PSn}$ = 297 and 311 Hz). *Anal.* Calc. for $C_{30}H_{58}Ni_2P_2Sn$ (716.85): C, 50.27; H, 8.16; Ni, 16.38; P, 8.64; Sn, 16.56. Found: C, 50.25; H, 8.10; Ni, 16.32; P, 8.74; Sn, 16.64%.

### *Reaction of 6 with activated magnesium*

A solution of **6** in thf was prepared from 550 mg (1.14 mmol) of **1** and 215 mg (1.14 mmol) of anhydrous tin(II) chloride, as described above. This solution was added to 32 mg (1.30 mmol) of activated magnesium at room temperature. The colour changed to red–brown within 4 h. The mixture was evaporated to dryness and the residue was extracted with pentane. The extract was concentrated *in vacuo* and cooled to 0 °C. **8** was obtained as black crystals. Yield 230 mg (38% with respect to **1**).

$^1$H NMR (300 K, d$^8$-thf, 200.1 MHz): δ (ppm) = 5.25 (5H, s ($J_{HSn}$ = 5.4 Hz), C*H*–Cp), 1.80 (6H, broad, C*H*$_2$–PEt$_3$), 1.07 (9H, dt ($J_{HH}$ = 7.1 Hz, $J_{PH}$ = 15.1 Hz), C*H*$_3$–PEt$_3$). $^{13}$C NMR (300 K, d$^8$-thf, 50.3 MHz): δ (ppm) = 90.5 (*C*H–Cp), 19.1 ($J_{CP}$ = 27 Hz, *C*H$_2$–PEt$_3$), 8.4 (*C*H$_3$–PEt$_3$). $^{31}$P NMR (300 K, d$^8$-thf, 81.0 MHz): δ = 20.3 ppm ($J_{PSn}$ = 180 and 181 Hz). *Anal.* Calc. for $C_{33}H_{60}ClNi_3P_3Sn$ (880.04): C, 45.04; H, 6.87; Cl, 4.03; Ni, 20.01; P, 10.56; Sn, 13.49. Found: C, 44.62; H, 7.02; Cl, 3.67; Ni, 20.82; P, 9.84; Sn, 13.72%.

### *X-ray structural determinations*

Suitable crystals of the compounds **1**, **2**, **3**, **5**, **6** and **8** were sealed in glass capillaries under argon and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from 75 reflec-

TABLE 1. Crystallographic and data collection parameters for compounds **1–3**, **5**, **6** and **8**

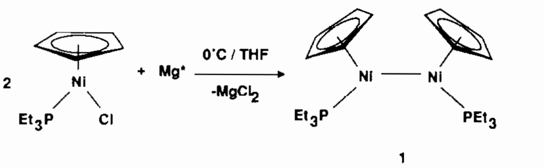
| | **1**[b] | **2**[a] | **3**[a] | **5**[a] | **6**[a] | **8**[a] |
|---|---|---|---|---|---|---|
| Formula | $C_{22}H_{40}Ni_2P_2$ | $C_{22}H_{40}Ni_3P_2S$ | $C_{32}H_{50}Ni_4P_2S_2$ | $C_{22}H_{40}Ni_2P_2Te$ | $C_{22}H_{40}Cl_2Ni_2P_2Sn$ | $C_{33}H_{60}ClNi_3P_3Sn$ |
| Formula weight (g mol$^{-1}$) | 483.9 | 574.7 | 795.7 | 611.5 | 673.5 | 880.0 |
| Crystal size (mm) | 0.32 × 0.21 × 0.25 | 0.32 × 0.53 × 0.32 | 0.25 × 0.49 × 0.39 | 0.39 × 0.42 × 0.39 | 0.39 × 0.25 × 0.32 | 0.28 × 0.53 × 0.53 |
| Crystal system | orthorhombic | monoclinic | monoclinic | tetragonal | orthorhombic | orthorhombic |
| Space group (No.) | $P2_12_12$ (18) | $P2_1/a$ (14) | $P2_1/n$ (14) | $P4_32_12_1$ (96) | $Pbca$ (61) | $P2_12_12_1$ (19) |
| $a$ (Å) | 10.525(1) | 9.822(1) | 8.625(1) | 11.324(1) | 14.335(4) | 11.446(1) |
| $b$ (Å) | 13.349(1) | 30.093(1) | 10.796(1) | 11.324(1) | 18.027(5) | 16.321(1) |
| $c$ (Å) | 8.656(1) | 10.098(1) | 18.911(1) | 20.935(1) | 21.731(8) | 21.294(1) |
| $\alpha$ (°) | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 |
| $\beta$ (°) | 90.0 | 116.47(1) | 101.07(1) | 90.0 | 90.0 | 90.0 |
| $\gamma$ (°) | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 |
| $V$ (Å$^3$) | 1216.2 | 2672.0 | 1728.1 | 2684.6 | 5615.9 | 3978.0 |
| $Z$ | 2 | 4 | 2 | 4 | 8 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.32 | 1.43 | 1.53 | 1.51 | 1.59 | 1.47 |
| $\mu$ (cm$^{-1}$) | 31.81 (Cu K$\alpha$) | 43.46 (Cu K$\alpha$) | 23.87 (Mo K$\alpha$) | 26.02 (Mo K$\alpha$) | 25.35 (Mo K$\alpha$) | 22.37 (Mo K$\alpha$) |
| $F(000)$ (e) | 516 | 1208 | 832 | 1240 | 2736 | 1816 |
| $T$ (K) | 293 | 293 | 293 | 293 | 293 | 293 |
| $[\sin \Theta/\lambda]_{max}$ | 0.63 | 0.63 | 0.65 | 0.65 | 0.65 | 0.65 |
| Absorption correction | spherical | empirical | spherical | spherical | spherical | analytical |
| (min.–max.) | 0.307–0.378 | 0.953–0.999 | 0.519–0.526 | 0.468–0.477 | 0.551–0.557 | 0.786–1.000 |
| No. measured reflections | 7815 ($\pm h \pm k \pm l$) | 7883 ($\pm h \pm k + l$) | 4271 ($\pm h + k + l$) | 12855 ($\pm h \pm k + l$) | 6200 ($\pm h + k + l$) | 10137 ($\pm h + k + l$) |
| No. of independent reflections | 2496 | 5498 | 3938 | 3084 | 3886 | 9081 |
| No. of observed reflections ($I > 2\sigma(I)$) | 2397 | 5072 | 3220 | 2797 | 2626 | 8120 |
| No. refined parameters | 198 | 253 | 181 | 123 | 262 | 218 |
| $R$, $R_w$ ($w = 1/\sigma^2(F_o)$) | 0.028, 0.030 | 0.051, 0.057 | 0.033, 0.040 | 0.046, 0.054 | 0.035, 0.038 | 0.054, 0.052 |
| Residual electron density (e Å$^{-3}$) | 0.25 | 0.33 | 0.63 | 1.57 | 0.31 | 1.40 |

[a] H atom positions were calculated and kept fixed in the final refinement stages. [b] H atom positions were refined in the final refinement stages.

tions ($6 < \Theta < 28°$) and refined by least-squares. Intensities were collected with graphite monochromated Cu K$\alpha$ radiation ($\lambda = 1.54178$ Å) for **1** and **2** and Mo K$\alpha$ radiation ($\lambda = 0.71069$ Å) for **3**, **5**, **6** and **8** by using the $\omega$–$2\Theta$ scan mode. Three standard reflections were monitored every 60 min. Corrections for decay, Lorentz and polarization and absorption effects were applied. The structures were solved by Patterson and direct methods [8] and refined by full-matrix least-squares [9]. The positions of the H atoms were calculated for all structures [10] and refined isotropically for **1**. The non-hydrogen atoms in **1**, **2**, **3**, **5** and **6** were refined anisotropically; in **8** all carbon atoms were refined isotropically and two ethyl groups were disordered (C28–C31). Crystal parameters, data collection and results of the refinements are summarized in Table 1. Final atomic coordinates are listed in Tables 2–7 for compounds **1**, **2**, **3**, **5**, **6** and **8**, respectively.

## Results and discussion

The reaction of ($\eta^5$-Cp)Ni(PEt$_3$)Cl with activated magnesium [5] yields the diamagnetic complex [($\eta^5$-Cp)Ni(PEt$_3$)]$_2$ (**1**) (eqn. (1)) in the form of large black crystals in 80% yield. The molecular composition was evident from elemental analysis, and first indications of its molecular structure were deduced from its NMR spectrum. The X-ray crystal structure determination (Fig. 1, experimental details are given in Table 1)



(1)

TABLE 2. Atomic coordinates and isotropic thermal parameters (Å$^2$) for **1**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$$^a$ |
|---|---|---|---|---|
| Ni | 0.0198(1) | 0.0888(1) | 0.7916(1) | 0.047(1) |
| P | 0.1744(1) | 0.0755(1) | 0.6356(1) | 0.048(1) |
| C(1) | 0.1746(2) | −0.0113(2) | 0.4693(2) | 0.059(1) |
| C(2) | 0.2862(3) | −0.0092(3) | 0.3600(3) | 0.080(1) |
| C(3) | 0.3296(2) | 0.0465(2) | 0.7209(3) | 0.066(1) |
| C(4) | 0.3633(3) | 0.1061(3) | 0.8633(5) | 0.094(2) |
| C(5) | 0.2066(2) | 0.1974(2) | 0.5415(3) | 0.066(1) |
| C(6) | 0.0978(3) | 0.2333(2) | 0.4406(4) | 0.079(1) |
| C(7) | −0.1212(3) | 0.1175(2) | 0.9581(3) | 0.086(2) |
| C(8) | −0.0026(5) | 0.1358(3) | 1.0282(3) | 0.105(2) |
| C(9) | 0.0539(3) | 0.2127(3) | 0.9477(5) | 0.095(2) |
| C(10) | −0.0301(3) | 0.2436(2) | 0.8303(3) | 0.081(1) |
| C(11) | −0.1367(3) | 0.1874(2) | 0.8407(3) | 0.075(1) |

$^a U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \bar{a}_i \cdot \bar{a}_j$.

TABLE 3. Atomic coordinates and isotropic thermal parameters (Å$^2$) for **2**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$$^a$ |
|---|---|---|---|---|
| Ni(1) | 0.2073(1) | 0.6284(1) | 0.1540(1) | 0.041(1) |
| Ni(2) | 0.1977(1) | 0.5899(1) | 0.3770(1) | 0.044(1) |
| Ni(3) | 0.2795(1) | 0.6669(1) | 0.4074(1) | 0.047(1) |
| S | 0.0649(1) | 0.6439(1) | 0.2545(1) | 0.046(1) |
| P(1) | 0.0512(1) | 0.6514(1) | −0.0667(1) | 0.045(1) |
| P(2) | 0.4095(1) | 0.6029(1) | 0.1406(1) | 0.054(1) |
| C(1) | 0.2651(8) | 0.5223(2) | 0.3943(7) | 0.077(6) |
| C(2) | 0.3626(6) | 0.5444(2) | 0.5194(7) | 0.072(5) |
| C(3) | 0.2823(7) | 0.5603(2) | 0.5906(6) | 0.076(5) |
| C(4) | 0.1329(7) | 0.5487(2) | 0.5127(7) | 0.073(5) |
| C(5) | 0.1174(7) | 0.5252(2) | 0.3884(7) | 0.083(5) |
| C(6) | 0.453(1) | 0.6764(3) | 0.6214(8) | 0.115(7) |
| C(7) | 0.5058(6) | 0.6894(2) | 0.5225(8) | 0.082(5) |
| C(8) | 0.4180(8) | 0.7239(2) | 0.4434(7) | 0.085(6) |
| C(9) | 0.3130(8) | 0.7315(2) | 0.495(1) | 0.119(9) |
| C(10) | 0.335(1) | 0.7030(4) | 0.603(1) | 0.14(1) |
| C(11) | 0.0382(6) | 0.7126(2) | −0.0763(5) | 0.063(4) |
| C(12) | 0.1811(8) | 0.7351(2) | −0.0583(8) | 0.094(7) |
| C(13) | −0.1474(6) | 0.6370(2) | −0.1208(6) | 0.073(4) |
| C(14) | −0.1790(8) | 0.5887(3) | −0.1282(9) | 0.121(7) |
| C(15) | 0.0774(6) | 0.6363(2) | −0.2301(5) | 0.060(4) |
| C(16) | −0.0337(7) | 0.6550(2) | −0.3794(5) | 0.085(5) |
| C(17) | 0.5128(7) | 0.6411(3) | 0.0742(7) | 0.093(6) |
| C(18) | 0.5932(9) | 0.6773(3) | 0.176(1) | 0.14(1) |
| C(19) | 0.3703(8) | 0.5574(3) | 0.0077(6) | 0.105(6) |
| C(20) | 0.284(1) | 0.5205(2) | 0.022(1) | 0.14(1) |
| C(21) | 0.5633(5) | 0.5823(2) | 0.3111(5) | 0.066(4) |
| C(22) | 0.7063(6) | 0.5647(2) | 0.3080(7) | 0.085(5) |

$^a U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \bar{a}_i \cdot \bar{a}_j$.

TABLE 4. Atomic coordinates and isotropic thermal parameters (Å$^2$) for **3**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$$^a$ |
|---|---|---|---|---|
| Ni(1) | 0.1422(1) | 0.2850(1) | 0.9180(1) | 0.036(1) |
| Ni(2) | 0.0656(1) | 0.6027(1) | 0.9517(1) | 0.041(1) |
| S | −0.0369(1) | 0.4188(1) | 0.9373(1) | 0.038(1) |
| P | −0.0150(1) | 0.2206(1) | 0.8232(1) | 0.038(1) |
| C(1) | 0.3128(4) | 0.1418(3) | 0.9524(3) | 0.079(3) |
| C(2) | 0.2937(4) | 0.2090(5) | 1.0116(2) | 0.079(3) |
| C(3) | 0.3330(4) | 0.3324(4) | 0.9986(2) | 0.074(2) |
| C(4) | 0.3877(3) | 0.3366(4) | 0.9346(2) | 0.064(2) |
| C(5) | 0.3691(4) | 0.2211(4) | 0.9053(2) | 0.073(3) |
| C(6) | 0.2533(5) | 0.6584(4) | 0.8967(2) | 0.078(3) |
| C(7) | 0.2378(4) | 0.7469(3) | 0.9463(2) | 0.060(2) |
| C(8) | 0.0851(4) | 0.7972(3) | 0.9288(2) | 0.052(2) |
| C(9) | 0.0049(4) | 0.7417(3) | 0.8663(2) | 0.063(2) |
| C(10) | 0.1059(6) | 0.6501(4) | 0.8483(2) | 0.085(3) |
| C(11) | −0.0475(3) | 0.3341(3) | 0.7508(2) | 0.053(2) |
| C(12) | 0.1012(4) | 0.3742(3) | 0.7255(2) | 0.068(2) |
| C(13) | 0.0503(4) | 0.0811(3) | 0.7824(2) | 0.057(2) |
| C(14) | −0.0586(5) | 0.0305(4) | 0.7165(2) | 0.084(3) |
| C(15) | −0.2164(3) | 0.1836(3) | 0.8336(2) | 0.049(2) |
| C(16) | −0.2257(4) | 0.0734(3) | 0.8815(2) | 0.059(2) |

$^a U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \bar{a}_i \cdot \bar{a}_j$.

TABLE 5. Atomic coordinates and isotropic thermal parameters (Å$^2$) for **5**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Te | 0.0586(1) | 0.0586(1) | 0.0000 | 0.060 |
| Ni | 0.0863(1) | −0.1528(1) | 0.0288(1) | 0.060 |
| P | 0.2357(1) | −0.1668(2) | −0.0314(1) | 0.067 |
| C(1) | −0.0716(7) | −0.1889(9) | 0.0752(4) | 0.098 |
| C(2) | 0.011(1) | −0.160(1) | 0.1202(4) | 0.107 |
| C(3) | 0.099(1) | −0.246(2) | 0.1166(7) | 0.163 |
| C(4) | 0.065(1) | −0.3225(9) | 0.0672(8) | 0.151 |
| C(5) | −0.042(1) | −0.2900(8) | 0.0443(5) | 0.105 |
| C(6) | 0.3142(8) | −0.3088(8) | −0.0166(4) | 0.109 |
| C(7) | 0.424(1) | −0.332(1) | −0.0482(6) | 0.154 |
| C(8) | 0.3513(5) | −0.0558(8) | −0.0212(4) | 0.080 |
| C(9) | 0.3923(7) | −0.0406(8) | 0.0448(4) | 0.095 |
| C(10) | 0.2108(8) | −0.1637(9) | −0.1159(4) | 0.104 |
| C(11) | 0.120(1) | −0.243(1) | −0.1422(6) | 0.162 |

[a] $U_{eq}=\frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \bar{\mathbf{a}}_i \cdot \bar{\mathbf{a}}_j$.

TABLE 6. Atomic coordinates and isotropic thermal parameters (Å$^2$) for **6**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Sn | 0.7604(1) | 0.1492(1) | 0.6246(1) | 0.039(1) |
| Ni(1) | 0.6970(1) | 0.1774(1) | 0.5217(1) | 0.043(1) |
| Ni(2) | 0.6899(1) | 0.1337(1) | 0.7272(1) | 0.048(1) |
| Cl(1) | 0.8616(1) | 0.0402(1) | 0.6130(1) | 0.063(1) |
| Cl(2) | 0.8962(1) | 0.2310(1) | 0.6389(1) | 0.073(1) |
| P(1) | 0.6628(1) | 0.2906(1) | 0.5396(1) | 0.040(1) |
| P(2) | 0.6340(1) | 0.0251(1) | 0.7134(1) | 0.052(1) |
| C(1) | 0.6204(6) | 0.0945(5) | 0.4741(4) | 0.080(7) |
| C(2) | 0.7074(6) | 0.0699(4) | 0.4907(4) | 0.069(6) |
| C(3) | 0.7747(5) | 0.1124(4) | 0.4599(4) | 0.073(7) |
| C(4) | 0.7259(8) | 0.1648(4) | 0.4265(4) | 0.088(9) |
| C(5) | 0.6309(8) | 0.1544(5) | 0.4360(5) | 0.086(8) |
| C(6) | 0.6328(7) | 0.2295(5) | 0.7712(5) | 0.086(8) |
| C(7) | 0.7262(8) | 0.2392(4) | 0.7544(4) | 0.089(7) |
| C(8) | 0.7808(6) | 0.1888(6) | 0.7877(5) | 0.094(8) |
| C(9) | 0.7193(8) | 0.1455(5) | 0.8226(4) | 0.087(9) |
| C(10) | 0.6289(6) | 0.1720(6) | 0.8102(4) | 0.084(8) |
| C(11) | 0.5965(5) | 0.3308(3) | 0.4767(3) | 0.058(5) |
| C(12) | 0.5753(5) | 0.4131(4) | 0.4797(4) | 0.088(7) |
| C(13) | 0.7600(4) | 0.3542(3) | 0.5494(4) | 0.052(5) |
| C(14) | 0.8312(5) | 0.3514(4) | 0.5010(4) | 0.086(7) |
| C(15) | 0.5913(5) | 0.3118(3) | 0.6065(3) | 0.058(5) |
| C(16) | 0.5004(5) | 0.2721(4) | 0.6069(4) | 0.102(7) |
| C(17) | 0.5424(5) | 0.0028(5) | 0.7676(4) | 0.087(6) |
| C(18) | 0.5047(7) | −0.0754(6) | 0.7664(5) | 0.15(1) |
| C(19) | 0.7150(5) | −0.0517(4) | 0.7224(4) | 0.080(7) |
| C(20) | 0.7612(7) | −0.0543(5) | 0.7843(5) | 0.13(1) |
| C(21) | 0.5805(5) | 0.0024(4) | 0.6397(3) | 0.072(6) |
| C(22) | 0.4967(7) | 0.0490(5) | 0.6264(4) | 0.109(8) |

[a] $U_{eq}=\frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \bar{\mathbf{a}}_i \cdot \bar{\mathbf{a}}_j$.

TABLE 7. Atomic coordinates and isotropic thermal parameters (Å$^2$) for **8**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Sn | 0.9568(1) | 0.9812(1) | 0.9387(1) | 0.044(1) |
| Ni(1) | 0.8396(1) | 1.1103(1) | 0.9574(1) | 0.054(1) |
| Ni(2) | 1.0164(1) | 0.9618(1) | 0.8258(1) | 0.068(1) |
| Ni(3) | 1.1230(1) | 0.9583(1) | 1.0147(1) | 0.059(1) |
| Cl | 0.8186(2) | 0.8638(1) | 0.9600(1) | 0.064(1) |
| P(1) | 0.6717(2) | 1.0638(1) | 0.9307(1) | 0.054(1) |
| P(2) | 1.0190(3) | 0.8309(1) | 0.8250(1) | 0.078(2) |
| P(3) | 1.0256(3) | 0.9165(2) | 1.0937(1) | 0.086(2) |
| C(1) | 0.980(1) | 1.1909(6) | 0.9569(6) | 0.097(4) |
| C(2) | 0.956(1) | 1.1641(6) | 1.0180(5) | 0.093(3) |
| C(3) | 0.854(1) | 1.1909(7) | 1.0374(6) | 0.097(4) |
| C(4) | 0.809(1) | 1.2330(7) | 0.9866(6) | 0.096(4) |
| C(5) | 0.882(1) | 1.2358(7) | 0.9317(6) | 0.102(4) |
| C(6) | 0.959(1) | 1.0767(7) | 0.7956(6) | 0.108(4) |
| C(7) | 0.954(1) | 1.0254(9) | 0.7431(6) | 0.134(5) |
| C(8) | 1.070(1) | 0.9976(7) | 0.7339(5) | 0.100(4) |
| C(9) | 1.146(1) | 1.0360(7) | 0.7747(6) | 0.107(4) |
| C(10) | 1.074(1) | 1.0842(7) | 0.8140(6) | 0.104(4) |
| C(11) | 1.2459(9) | 1.0313(6) | 0.9674(5) | 0.087(3) |
| C(12) | 1.274(1) | 1.0294(7) | 1.0295(6) | 0.103(4) |
| C(13) | 1.295(1) | 0.9476(7) | 1.0487(6) | 0.096(4) |
| C(14) | 1.2908(8) | 0.9020(6) | 0.9956(5) | 0.075(3) |
| C(15) | 1.2515(9) | 0.9503(6) | 0.9460(6) | 0.093(3) |
| C(16) | 0.6586(7) | 0.9974(5) | 0.8622(4) | 0.064(2) |
| C(17) | 0.540(1) | 0.9687(7) | 0.8462(5) | 0.102(4) |
| C(18) | 0.5939(7) | 1.0080(5) | 0.9919(4) | 0.063(2) |
| C(19) | 0.5895(8) | 1.0535(6) | 1.0551(5) | 0.082(3) |
| C(20) | 0.5691(9) | 1.1448(6) | 0.9135(5) | 0.086(3) |
| C(21) | 0.601(1) | 1.1949(7) | 0.8586(6) | 0.112(4) |
| C(22) | 1.0712(9) | 0.7731(6) | 0.8944(5) | 0.080(3) |
| C(23) | 1.071(1) | 0.6843(8) | 0.8905(6) | 0.115(4) |
| C(24) | 0.884(1) | 0.7809(7) | 0.8062(6) | 0.108(4) |
| C(25) | 0.831(2) | 0.815(1) | 0.7490(8) | 0.173(7) |
| C(26) | 1.118(1) | 0.7920(7) | 0.7629(6) | 0.108(4) |
| C(27) | 1.242(2) | 0.806(1) | 0.7805(8) | 0.187(7) |
| C(28) | 0.879(1) | 0.9542(7) | 1.1075(6) | 0.100(4) |
| C(29a) | 0.827(2) | 0.941(1) | 1.1695(9) | 0.119(7) |
| C(29b) | 0.885(3) | 1.025(3) | 1.147(2) | 0.11(1) |
| C(30a) | 1.099(2) | 0.958(1) | 1.168(1) | 0.133(7) |
| C(30b) | 1.114(4) | 0.868(3) | 1.157(2) | 0.11(1) |
| C(31a) | 1.100(1) | 1.054(1) | 1.1715(8) | 0.100(5) |
| C(31b) | 1.066(4) | 0.850(3) | 1.208(2) | 0.13(2) |

[a] $U_{eq}=\frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \bar{\mathbf{a}}_i \cdot \bar{\mathbf{a}}_j$.

reveals an unbridged Ni–Ni bonded system. As far as we are aware **1** is the first example of a structurally characterized dinuclear nickel complex containing an unbridged metal–metal bond. There is a report in the literature of deep purple crystals of $[Ni_2(CNMe)_8][PF_6]_2$ and a symmetrical structure containing an unbridged Ni–Ni bond with equivalent MeNC ligands has been proposed for the dication on the basis of $^1$H NMR data but no crystal structure has yet been reported [11].

The Ni–Ni bond length in **1** of 2.407(1) Å (Table 8) is normal for a Ni–Ni single bond [12]. The molecule crystallizes about a crystallographic twofold axis of symmetry which passes through the midpoint of the Ni–Ni bond. Each Ni atom, its neighbour, the midpoint of the attached cyclopentadienyl ring and the phosphor atom are coplanar (maximum deviation from the mean plane 0.1 Å [Ni]) and the two coordination planes

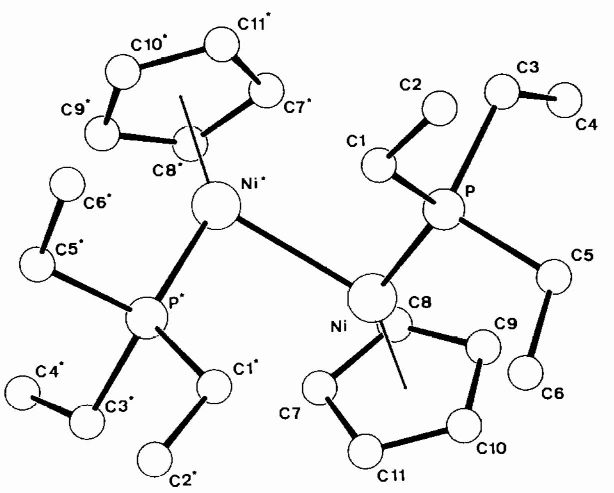


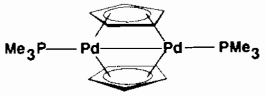
Fig. 1. Molecular structure of **1**.

TABLE 8. Selected distances (Å) and angles (°) for **1**

| | | | |
|---|---|---|---|
| Ni–P | 2.122(1) | Ni–C(7) | 2.105(3) |
| Ni–C(8) | 2.156(2) | Ni–C(9) | 2.166(4) |
| Ni–C(10) | 2.160(2) | Ni–C(11) | 2.152(3) |
| Ni–Ni* | 2.407(1) | P–C(1) | 1.849(2) |
| P–C(3) | 1.835(2) | P–C(5) | 1.851(2) |
| C(1)–C(2) | 1.510(4) | C(3)–C(4) | 1.511(5) |
| C(5)–C(6) | 1.518(4) | C(7)–C(8) | 1.409(5) |
| C(7)–C(11) | 1.390(4) | C(8)–C(9) | 1.376(5) |
| C(9)–C(10) | 1.410(5) | C(10)–C(11) | 1.354(4) |
| Ni*–Ni–C(11) | 118.0(1) | Ni*–Ni–C(10) | 154.2(1) |
| Ni*–Ni–C(9) | 141.3(1) | Ni*–Ni–C(8) | 105.5(1) |
| Ni*–Ni–C(7) | 93.3(1) | Ni*–Ni–P | 92.9(1) |
| C(11)–Ni–C(10) | 36.6(1) | C(11)–Ni–C(9) | 62.4(1) |
| C(11)–Ni–C(8) | 63.2(1) | C(11)–Ni–C(7) | 38.1(1) |
| C(11)–Ni–P | 139.8(1) | C(10)–Ni–C(9) | 38.0(1) |
| C(10)–Ni–C(8) | 63.1(1) | C(10)–Ni–C(7) | 63.1(1) |
| C(10)–Ni–P | 111.4(1) | C(9)–Ni–C(8) | 37.1(1) |
| C(9)–Ni–C(7) | 63.3(1) | C(9)–Ni–P | 109.5(1) |
| C(8)–Ni–C(7) | 38.6(2) | C(8)–Ni–P | 135.5(1) |
| C(7)–Ni–P | 172.7(1) | C(5)–P–C(3) | 101.5(1) |
| C(5)–P–C(1) | 102.1(1) | C(5)–P–Ni | 110.3(1) |
| C(3)–P–C(1) | 100.3(1) | C(3)–P–Ni | 116.4(1) |
| C(1)–P–Ni | 123.3(1) | C(2)–C(1)–P | 118.5(2) |
| C(4)–C(3)–P | 115.2(2) | C(6)–C(5)–P | 113.1(2) |
| C(11)–C(7)–C(8) | 107.6(3) | C(11)–C(7)–Ni | 72.8(2) |
| C(8)–C(7)–Ni | 72.6(2) | C(9)–C(8)–C(7) | 107.1(3) |
| C(9)–C(8)–Ni | 71.9(2) | C(7)–C(8)–Ni | 68.8(2) |
| C(10)–C(9)–C(8) | 108.2(3) | C(10)–C(9)–Ni | 70.7(2) |
| C(8)–C(9)–Ni | 71.0(2) | C(11)–C(10)–C(9) | 108.0(2) |
| C(11)–C(10)–Ni | 71.4(1) | C(9)–C(10)–Ni | 71.2(2) |
| C(10)–C(11)–C(7) | 108.9(3) | C(10)–C(11)–Ni | 72.0(2) |
| C(7)–C(11)–Ni | 69.1(2) | | |

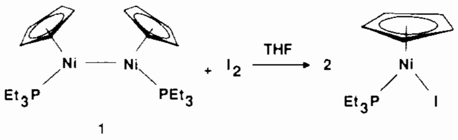
An asterisk indicates a symmetry related atom.

make an angle of 93(2)° to one another. Inspection of the $^1H$ NMR spectrum reveals that free rotation about the Ni–Ni axis is hindered in solution since the $CH_2$ protons of the ethyl groups of the phosphine ligand are diastereotopic [13]. This can be attributed to steric hindrance of the ligands about the Ni atoms. The P–Ni–Ni angle is 92.9(1)° and is only slightly smaller than the P–Ni–C angle of 93.4(2)° in $[(\eta^5\text{-Cp})Ni(Ph_3P)Ph]$ [14] and thus appears to be within the expected range. The fact that we were unable to synthesize analogous compounds with $PPh_3$ or $CpMe_5$ suggests that the molecule is stabilized by steric effects alone. This is supported by molecular modelling studies and an inspection of space filling models. Interestingly the homologous Pd compound $[PMe_3Pd_2(Cp)_2PMe_3]$ with trimethylphosphine as ligand has *bridging* Cp ligands across the metal–metal bond [15] (eqn. (2)).

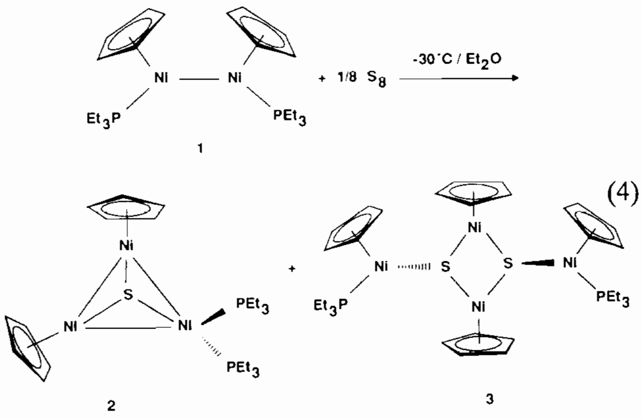


(2)

Subsequent investigations were concerned with a detailed investigation of the reactivity of the unbridged Ni–Ni entity. Whereas treatment with olefins was unsuccessful in all cases, alkynes react under vigorous conditions by displacement of the phosphine ligands to give the alkyne bridged species. Thus diphenylethyne affords $(\eta^5\text{-CpNi})_2(\mu\text{-}C_2Ph_2)$ in good yield. The Ni–Ni bond in **1** can be easily cleaved by iodine to yield the mononuclear $(\eta^5\text{-Cp})Ni(PEt_3)I$ (eqn. (3)). The reaction of **1** with elemental sulfur is more complicated (eqn. (4)). Two compounds were isolated and subsequently characterized by X-ray crystallography. One is the trinuclear cluster **2** and the other the tetranuclear cluster **3**. The results of both crystal structure analyses are depicted in Figs. 2 and 3, respectively.



(3)



(4)

In **2** one sulfur atom is located on a triangle of Ni atoms. The triangle is not regular and the Ni2–Ni3 distance is shortened as compared to the other two Ni–Ni distances (Table 9). The two phosphine ligands are attached to Ni1 and lie above and below the metal

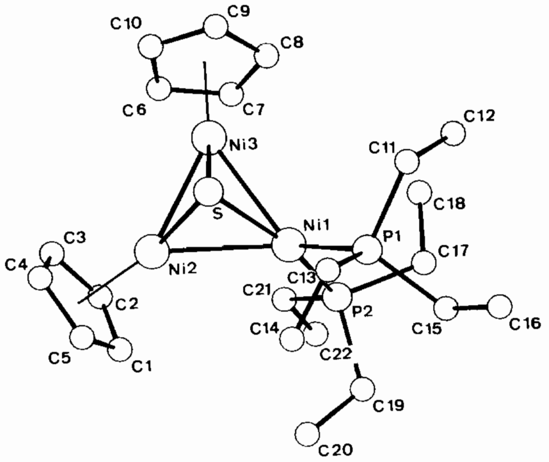
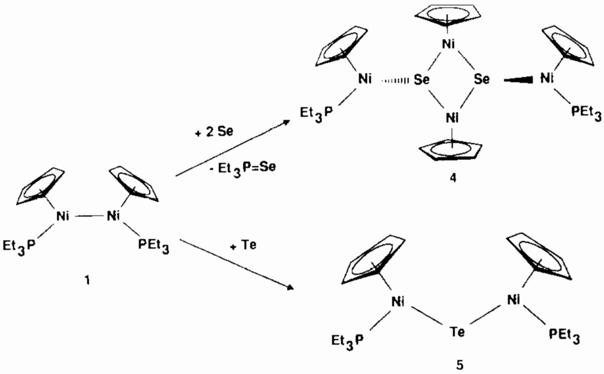


Fig. 2. Molecular structure of **2**.

triangle. The P–Ni–P angle is 107.0(1)°. The compound is diamagnetic and the $^1H$ and $^{13}C$ NMR spectra of **2** show sharp signals for the cyclopentadienyl ligands over a broad range of temperatures, but broad signals at room temperature for the phosphine ligands. At $-80$ °C the $^1H$ NMR for the phosphine protons show three signals in the ratio of 2:5:3 and at $+80$ °C two signals in the ratio 2:3. The results of the $^{31}P$ NMR measurements are given in Table 10. No $^{31}P$–$^{31}P$ coupling was detected. These observations are consistent with the assumption of a dissociation equilibrium of the phosphine ligands. The shift of $\delta_{P2}$ at $+80$ °C corresponds to the shift $\delta_{PEt_3}$ of the uncoordinated phosphine [16] supporting a dissociative mechanism [17].

The results of the crystal structure analysis of **3** are summarized in Fig. 3 which shows the molecule to be made up of a central Ni–S–Ni–S unit substituted at the sulfur atoms by ($\eta^5$-Cp)Ni(PEt$_3$) fragments. The molecule crystallizes about a centre of symmetry; as a result the central four-membered ring is of necessity planar. Ni–S distances are similar within the ring (Table 11) and angles are 84.5(1)° at Ni and 95.5(1)° at S. These angles result in a relatively short S···S distance (2.919(1) Å) across the ring which is appreciably shorter than the sum of the van der Waals radii of two sulfur atoms (3.64 Å) [18].

**1** also readily reacts with elemental selenium. The only nickel containing complex that could be identified on the basis of spectroscopic data was the selenium analog to **3** $\{[(\eta^5\text{-Cp})Ni(PEt_3)](\mu\text{-Se})Ni(\eta^5\text{-Cp})\}_2$ (**4**) (eqn. (5)). The crystal structure of the triphenylphosphine analog $\{[(\eta^5\text{-Cp})Ni(PPh_3)](\mu\text{-Se})Ni(\eta^5\text{-Cp})\}_2$ is already known [19]. Tellurium also reacts with **1** with insertion into the Ni–Ni bond yielding $\{[(\eta^5\text{-Cp})Ni(PEt_3)]_2Te\}$ (**5**) (eqn. (5)). In contrast to the reactions with sulfur and selenium no subsequent loss of phosphine is observed. A possible explanation may be that tellurium is a weak donor by virtue of its highly diffused orbitals and is thus not able to displace a phosphine ligand. The molecular structure of **5** is shown in Fig. 4. The tellurium atom is located on a crystallographic twofold axis of symmetry which also passes through the mid-point between the two Ni atoms. The Ni–Te–Ni angle at 107.5(1)° is close to tetrahedral (Table 12). Figure 5 gives a Newman projection along the Ni···Ni vector.



(5)

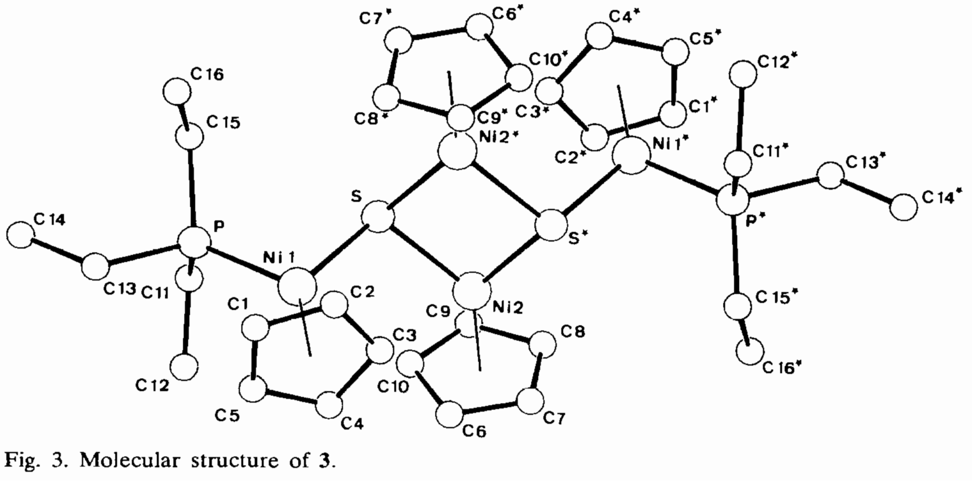


Fig. 3. Molecular structure of **3**.

TABLE 9. Selected distances (Å) and angles (°) for **2**

| | | | |
|---|---|---|---|
| Ni(1)–Ni(2) | 2.571(1) | Ni(1)–Ni(3) | 2.604(1) |
| Ni(1)–S | 2.114(1) | Ni(1)–P(1) | 2.180(1) |
| Ni(1)–P(2) | 2.189(1) | Ni(2)–Ni(3) | 2.426(1) |
| Ni(2)–S | 2.104(1) | Ni(2)–C(1) | 2.124(5) |
| Ni(2)–C(2) | 2.121(6) | Ni(2)–C(3) | 2.131(5) |
| Ni(2)–C(4) | 2.146(6) | Ni(2)–C(5) | 2.125(6) |
| Ni(3)–S | 2.099(1) | Ni(3)–C(6) | 2.090(8) |
| Ni(3)–C(7) | 2.109(7) | Ni(3)–C(8) | 2.119(7) |
| Ni(3)–C(9) | 2.102(8) | Ni(3)–C(10) | 2.10(1) |
| P(1)–C(11) | 1.845(5) | P(1)–C(13) | 1.828(6) |
| P(1)–C(15) | 1.837(5) | P(2)–C(17) | 1.847(7) |
| P(2)–C(19) | 1.834(7) | P(2)–C(21) | 1.820(6) |
| P(2)–Ni(1)–P(1) | 107.0(1) | P(2)–Ni(1)–S | 156.9(1) |
| P(2)–Ni(1)–Ni(3) | 111.1(1) | P(2)–Ni(1)–Ni(2) | 106.6(1) |
| P(1)–Ni(1)–S | 96.1(1) | P(1)–Ni(1)–Ni(3) | 128.5(1) |
| P(1)–Ni(1)–Ni(2) | 139.0(1) | S–Ni(1)–Ni(3) | 51.6(1) |
| S–Ni(1)–Ni(2) | 52.3(1) | Ni(3)–Ni(1)–Ni(2) | 55.9(1) |
| S–Ni(2)–Ni(3) | 54.6(1) | S–Ni(2)–Ni(1) | 52.6(1) |
| Ni(3)–Ni(2)–Ni(1) | 62.7(1) | S–Ni(3)–Ni(2) | 54.9(1) |
| S–Ni(3)–Ni(1) | 52.1(1) | Ni(2)–Ni(3)–Ni(1) | 61.4(1) |
| Ni(3)–S–Ni(2) | 70.5(1) | Ni(3)–S–Ni(1) | 76.4(1) |
| Ni(2)–S–Ni(1) | 75.1(1) | | |

TABLE 10. $^{31}P$ NMR data of **2** in $d^8$-toluene at different temperatures in a 162.0 MHz experiment

| $T$(K) | $\delta_{P1}$ (ppm) | $\delta_{P2}$ (ppm) |
|---|---|---|
| 353[a] | ~10 | ~ −22 |
| 300 | 18.7 | −15.2 |
| 243 | 19.8 | −9.5 |
| 223 | 19.9 | −8.6 |
| 193 | 20.1 | −7.5 |

[a]Halfwidth *c.* 3900 Hz.

TABLE 11. Selected distances (Å) and angles (°) for **3**

| | | | |
|---|---|---|---|
| Ni(1)–S | 2.197(1) | Ni(1)–P | 2.146(1) |
| Ni(1)–C(1) | 2.147(4) | Ni(1)–C(2) | 2.151(4) |
| Ni(1)–C(3) | 2.082(4) | Ni(1)–C(4) | 2.154(3) |
| Ni(1)–C(5) | 2.132(3) | Ni(2)–S | 2.169(1) |
| Ni(2)–C(6) | 2.171(4) | Ni(2)–C(7) | 2.168(3) |
| Ni(2)–C(8) | 2.158(3) | Ni(2)–C(9) | 2.194(3) |
| Ni(2)–C(10) | 2.114(4) | Ni(2)–S* | 2.173(1) |
| P–Ni(1)–S | 90.0(1) | Ni(2)*–S–Ni(1) | 107.8(1) |
| Ni(2)*–S–Ni(2) | 95.5(1) | S*–Ni(2)–S | 84.5(1) |
| Ni(2)–S–Ni(1) | 109.9(1) | | |

An asterisk indicates a symmetry related atom.

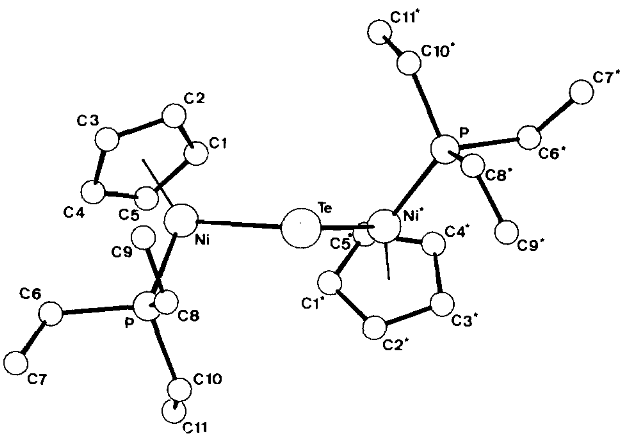


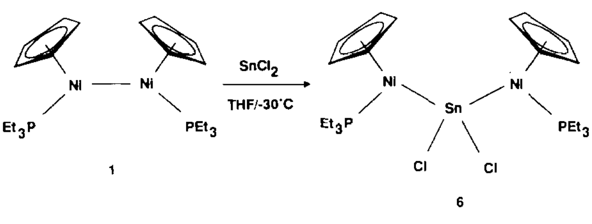
Fig. 4. Molecular structure of **5**.

TABLE 12. Selected distances (Å) and angles (°) for **5**

| | | | |
|---|---|---|---|
| Te–Ni | 2.489(1) | Ni–P | 2.117(2) |
| Ni–C(1) | 2.076(8) | Ni–C(2) | 2.097(8) |
| Ni–C(3) | 2.13(1) | Ni–C(4) | 2.10(1) |
| Ni–C(5) | 2.15(1) | P–C(6) | 1.86(1) |
| P–C(8) | 1.828(7) | P–C(10) | 1.792(9) |
| C(1)–C(2) | 1.37(1) | C(1)–C(5) | 1.36(1) |
| C(2)–C(3) | 1.40(2) | C(3)–C(4) | 1.40(2) |
| C(4)–C(5) | 1.35(2) | C(6)–C(7) | 1.43(2) |
| C(8)–C(9) | 1.47(1) | C(10)–C(11) | 1.47(2) |
| Ni*–Te–Ni | 107.5(1) | C(5)–Ni–C(4) | 37.1(5) |
| C(5)–Ni–C(3) | 63.6(5) | C(5)–Ni–C(2) | 64.0(4) |
| C(5)–Ni–C(1) | 37.5(4) | C(5)–Ni–P | 125.0(3) |
| C(5)–Ni–Te | 130.4(3) | C(4)–Ni–C(3) | 38.7(6) |
| C(4)–Ni–C(2) | 64.5(5) | C(4)–Ni–C(1) | 62.8(5) |
| C(4)–Ni–P | 104.5(4) | C(4)–Ni–Te | 163.8(4) |
| C(3)–Ni–C(2) | 38.7(5) | C(3)–Ni–C(1) | 63.6(4) |
| C(3)–Ni–P | 115.1(3) | C(3)–Ni–Te | 134.2(5) |
| C(2)–Ni–C(1) | 38.3(4) | C(2)–Ni–P | 150.0(3) |
| C(2)–Ni–Te | 101.9(3) | C(1)–Ni–P | 162.3(3) |
| C(1)–Ni–Te | 101.2(3) | P–Ni–Te | 91.6(1) |
| C(10)–P–C(8) | 102.4(4) | C(10)–P–C(6) | 104.9(4) |
| C(10)–P–Ni | 117.5(3) | C(8)–P–C(6) | 103.4(4) |
| C(8)–P–Ni | 116.8(2) | C(6)–P–Ni | 110.3(3) |
| C(5)–C(1)–C(2) | 111.1(9) | C(5)–C(1)–Ni | 74.2(6) |
| C(2)–C(1)–Ni | 71.7(5) | C(3)–C(2)–C(1) | 106.3(9) |
| C(3)–C(2)–Ni | 71.8(7) | C(1)–C(2)–Ni | 70.0(5) |
| C(4)–C(3)–C(2) | 106(1) | C(4)–C(3)–Ni | 69.5(8) |
| C(2)–C(3)–Ni | 69.5(7) | C(5)–C(4)–C(3) | 110(1) |
| C(5)–C(4)–Ni | 73.5(6) | C(3)–C(4)–Ni | 71.7(8) |
| C(4)–C(5)–C(1) | 106.6(9) | C(4)–C(5)–Ni | 69.4(6) |
| C(1)–C(5)–Ni | 68.3(5) | C(7)–C(6)–P | 119.5(8) |
| C(9)–C(8)–P | 114.7(6) | C(11)–C(10)–P | 117.9(8) |

An asterisk indicates a symmetry related atom.

All attempts to add carbenes across the Ni–Ni bond in **1** have so far been unsuccessful. **1** does not react with 2-diazopropane at low temperatures. It does, however, react with tin(II) chloride, which may be regarded as an inorganic carbene and which is known to undergo insertion reactions into metal–metal bonds [20], to give the insertion product **6** (eqn. (6)).



(6)

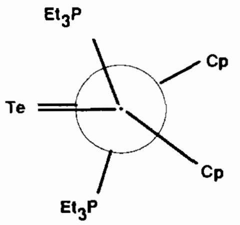


Fig. 5. Newman-projection of **5** along the nickel–nickel vector.

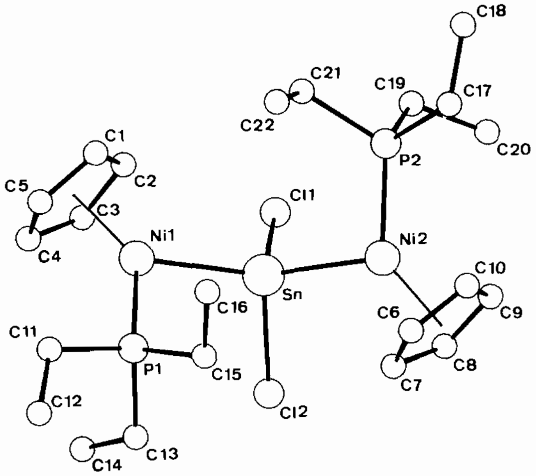


Fig. 6. Molecular structure of **6**.

TABLE 13. Selected distances (Å) and angles (°) for **6**

| | | | |
|---|---|---|---|
| Sn–Ni(1) | 2.468(1) | Sn–Ni(2) | 2.465(1) |
| Sn–Cl(1) | 2.455(2) | Sn–Cl(2) | 2.462(2) |
| Ni(1)–P(1) | 2.135(2) | Ni(1)–C(1) | 2.123(9) |
| Ni(1)–C(2) | 2.057(7) | Ni(1)–C(3) | 2.102(8) |
| Ni(1)–C(4) | 2.123(9) | Ni(1)–C(5) | 2.13(1) |
| Ni(2)–P(2) | 2.139(2) | Ni(2)–C(6) | 2.136(9) |
| Ni(2)–C(7) | 2.058(8) | Ni(2)–C(8) | 2.10(1) |
| Ni(2)–C(9) | 2.13(1) | Ni(2)–C(10) | 2.119(9) |
| Cl(2)–Sn–Cl(1) | 91.4(1) | Cl(2)–Sn–Ni(2) | 106.2(1) |
| Cl(2)–Sn–Ni(1) | 106.4(1) | Cl(1)–Sn–Ni(2) | 104.2(1) |
| Cl(1)–Sn–Ni(1) | 106.8(1) | Ni(2)–Sn–Ni(1) | 133.8(1) |

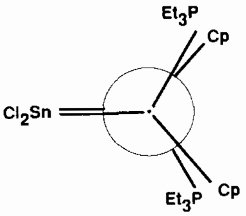
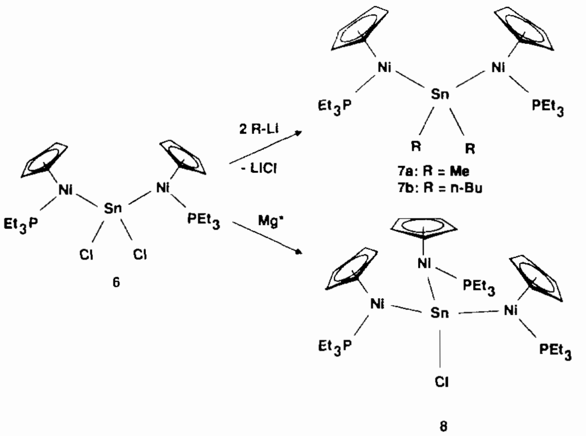


Fig. 7. Newman-projection of **6** along the nickel–nickel vector.

**6** is insoluble in apolar solvents, sparingly soluble in ether and highly soluble in thf. Its solubility appears to be related to the $\sigma$-donor ability of the solvent. The crystal structure of **6** (Fig. 6) shows that a tin dichloride unit has inserted between the two nickel atoms. The coordination around the tin atom is distorted tetrahedral: the Ni–Sn–Ni angle is 133.8(1)° whereas the Cl–Sn–Cl angle is 91.4(1)° (Table 13). A similar Newman projection of **6** along the Ni···Ni vector to that shown for **5** in Fig. 5 is given in Fig. 7 and clearly shows a different arrangement of the ligands around the Ni atoms.

Reaction of **6** with two equivalents of alkyllithium (n-BuLi and MeLi) results in a clean substitution of both chlorine atoms by the respective alkyl groups (eqn. (7)). Complexes of the type **7a** and **7b** contain Sn attached to Ni atoms and butyl ligands and as such are similar to the proposed structures for the nickel tin clusters used for the selective hydrogenation of cinnamic aldehyde to cinnamic alcohol [21]. However, compound **7b** shows no such catalytic activity and cinnamic aldehyde is not hydrogenated in the presence of **7b**.



(7)

Attempts to couple two molecules of **6** by reductive coupling with activated magnesium led to the replacement of one Cl atom in **6** by an $(\eta^5\text{-}C_5H_5)Ni(Et_3P)$ unit and formation of red **8** in which three such units are bonded to SnCl (Fig. 8). Chlorotris(metallato)tin(IV) complexes are known for metal carbonyls and the crystal structure of $[Cp(CO)_2Fe][Cp(CO)Ni][(CO)_4Co]SnCl$ has been reported [22]. The geometry around the Sn atom in **8** is similar to that of the mixed metal complex [22] with the Cl–Sn–M angles at 104.7(9)° (av.) somewhat smaller than the M–Sn–M angles (114(1)°, av.). In **8** each $(\eta^5\text{-}C_5H_5)Ni(Et_3P)$ group is twisted in the same direction relative to the Sn–Cl bond (torsion angles: Cl–Sn–Ni1–P1 + 30.6°; Cl–Sn–Ni2–P2 + 36.3°; Cl–Sn–Ni3–P3 + 38.4°) so that although the three groups are the same, the molecule as a whole is chiral. A comparison of the Ni–Sn and Cl–Sn distances in **8** (Table 14) with those in **6** (Table 13) shows that substitution of one Cl atom in **6** by an $(\eta^5\text{-}C_5H_5)Ni(Et_3P)$ unit results in a significant increase in bond length. In spite of using excess activated magnesium it was not

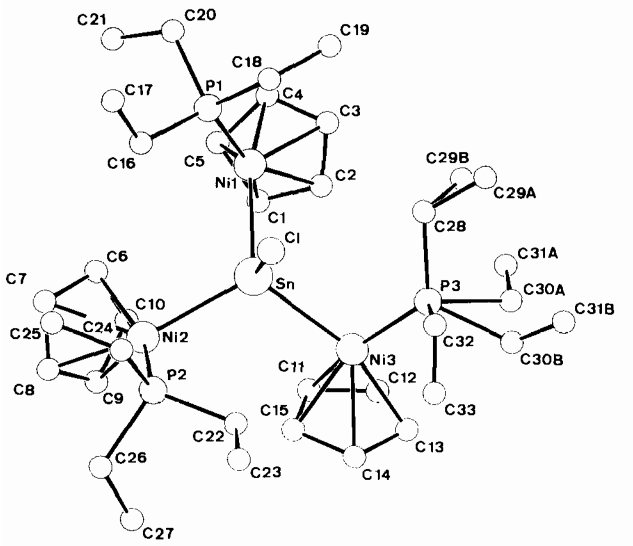


Fig. 8. Molecular structure of **8**.

TABLE 14. Selected distances (Å) and angles (°) for **8**

| | | | |
|---|---|---|---|
| Sn–Ni(1) | 2.531(1) | Sn–Ni(2) | 2.519(1) |
| Sn–Ni(3) | 2.526(1) | Sn–Cl | 2.527(2) |
| Ni(1)–P(1) | 2.144(2) | Ni(1)–C(1) | 2.09(1) |
| Ni(1)–C(2) | 2.05(1) | Ni(1)–C(3) | 2.15(1) |
| Ni(1)–C(4) | 2.13(1) | Ni(1)–C(5) | 2.17(1) |
| Ni(2)–P(2) | 2.136(3) | Ni(2)–C(6) | 2.09(1) |
| Ni(2)–C(7) | 2.15(1) | Ni(2)–C(8) | 2.14(1) |
| Ni(2)–C(9) | 2.21(1) | Ni(2)–C(10) | 2.11(1) |
| Ni(3)–P(3) | 2.128(3) | Ni(3)–C(11) | 2.11(1) |
| Ni(3)–C(12) | 2.12(1) | Ni(3)–C(13) | 2.12(1) |
| Ni(3)–C(14) | 2.17(1) | Ni(3)–C(15) | 2.09(1) |
| Cl–Sn–Ni(3) | 104.1(1) | Cl–Sn–Ni(2) | 104.3(1) |
| Cl–Sn–Ni(1) | 105.7(1) | Ni(3)–Sn–Ni(2) | 112.8(1) |
| Ni(3)–Sn–Ni(1) | 114.9(1) | Ni(2)–Sn–Ni(1) | 113.5(1) |
| P(1)–Ni(1)–Sn | 98.0(1) | P(2)–Ni(2)–Sn | 97.9(1) |
| P(3)–Ni(3)–Sn | 99.3(1) | | |

possible to replace the Cl atom in **8** by a further Ni fragment so it would appear that although the Sn–Cl bond length increases in going from **6** to **8** the Cl atom is less easily abstracted.

## Conclusions

The reaction of ($\eta^5$-Cp)Ni(PEt$_3$)Cl with activated magnesium yields [($\eta^5$-Cp)Ni(PEt$_3$)]$_2$ containing an unbridged Ni–Ni bond. The unexpected stability of the Ni–Ni bond can be attributed to steric shielding by the ligands. [($\eta^5$-Cp)Ni(PEt$_3$)]$_2$ reacts with oxidizing agents such as elemental iodine, sulfur, selenium and tellurium with opening of the Ni–Ni bond. Sulfur, selenium and tellurium insert into the Ni–Ni bond to give Ni–X–Ni complexes characterized by NMR and X-ray analyses. SnCl$_2$ also inserts into the Ni–Ni bond to give a Ni–Sn(Cl$_2$)–Ni unit which can be alkylated with alkyllithium. Treatment of, ($\eta^5$-Cp)Ni(Et$_3$P)Sn(Cl)$_2$($\eta^5$-Cp)Ni(Et$_3$P) with activated magnesium results in substitution of only one Cl atom by a ($\eta^5$-C$_5$H$_5$)Ni(Et$_3$P) unit in spite of using excess magnesium.

## Supplementary material

Further details of the crystal structure investigations (listings of structure factors, hydrogen atom positional parameters, anisotropic thermal parameters, distances and angles) may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-57127, the names of the authors and the journal citation.

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