

Synthesis of phosphido-bridged dinuclear complexes through sodium reduction of *cis*-[M{P(C₆H₁₁)₂H}₂Cl₂] (M = Ni or Pd)

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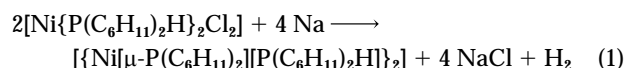
Reduction of *cis*-[Ni{P(C₆H₁₁)₂H}₂Cl₂] with sodium afforded the dinuclear nickel complex [{Ni[μ-P(C₆H₁₁)₂]-P(C₆H₁₁)₂H}]₂ which, in turn, reacted with CO producing [{Ni[μ-P(C₆H₁₁)₂](CO)₂}]₂. The reduction of *cis*-[Pd{P(C₆H₁₁)₂H}₂Cl₂] occurred in two steps giving first [Pd₂{μ-P(C₆H₁₁)₂Cl}{P(C₆H₁₁)₂H}]₂, then [Pd[μ-P(C₆H₁₁)₂][P(C₆H₁₁)₂H]]₂. The structure of the chloride complex was determined.

Low-valent transition-metal complexes are the foundations for activating small molecules and for achieving organic syntheses through metal-catalysed reactions. In the framework of our studies on sodium-promoted reduction of metal complexes,¹ we decided to address the divalent metal dicyclohexylphosphino complexes of general formula *cis*-[M{P(C₆H₁₁)₂H}₂Cl₂] (M = Ni or Pd).

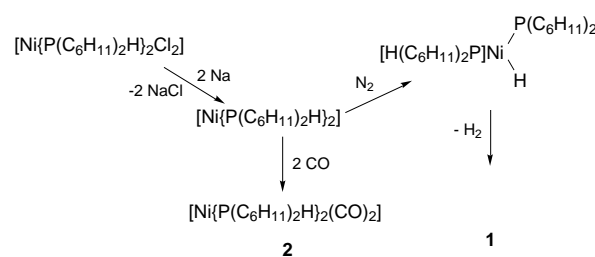
Results and Discussion

The sodium-promoted reduction of [Ni{P(C₆H₁₁)₂H}₂Cl₂] in toluene proceeded with evolution of dihydrogen (revealed by GC analyses) and resulted in the synthesis of a brown-red compound the elemental analysis and spectroscopic features of which indicate the formula [{Ni[μ-P(C₆H₁₁)₂][P(C₆H₁₁)₂H}]₂ **1**. This compound shows an UV/VIS spectrum under argon (or under nitrogen) consisting of three peaks located at 332 (19 500), 370 (14 700) and 510 nm (ε 2800 dm³ mol⁻¹ cm⁻¹) which is very similar to that of [{Ni[μ-P(C₆H₁₁)₂][P(C₆H₁₁)₂Ph}]₂]² (λ_{max} = 340, 380 and 526 nm). Its IR spectrum shows a sharp strong band at 2236 cm⁻¹ ascribable to the P–H stretching of the co-ordinated dicyclohexylphosphine. The ³¹P NMR spectrum consists of two triplets centred at δ 16 and 118 with a P–P coupling constant of 31.0 Hz. The first is attributable to the co-ordinated dicyclohexylphosphine whereas the second is ascribed to a bridging phosphide. The resonance of the latter at lower fields with respect to the corresponding trisubstituted phosphine is also a clue to the presence of a three-membered Ni₂P ring,³ thus substantiating the presence of a Ni–Ni bond in the molecule. This is further confirmed by the fact that **1** was found to be diamagnetic. The structure proposed resembles therefore those found for [{Ni[μ-P(C₆H₁₁)₂][P(C₆H₁₁)₂Ph}]₂]², [{Ni[μ-P(SiMe₃)₂](PR₃)₂}]₂ (R = Me, Et or Buⁿ),⁴ [{Ni(μ-PBu₂^t)(PR₃)₂}]₂ (R = Me, Et or OMe)^{5,6} or [{Ni(μ-PBu^tH)(PMe₃)₂}]₂.⁷

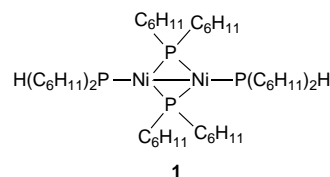
The stoichiometry of the reduction reaction can be written as in equation (1). A mechanism similar to that proposed for the



formation of the dimeric palladium(II) complex [Pd(μ-PBu^t)-(PBu^tH)]₂⁸ can be invoked. In this case the sodium can cleave the two chlorine atoms leading to Ni[P(C₆H₁₁)₂H]₂ which evolves *via* intramolecular oxidative addition to [NiH{P(C₆H₁₁)₂}-P(C₆H₁₁)₂H]. This latter can easily couple giving rise to H₂ and **1**. When the reduction of [Ni{P(C₆H₁₁)₂H}₂Cl₂] was carried out under atmospheric pressure of carbon monoxide the expected



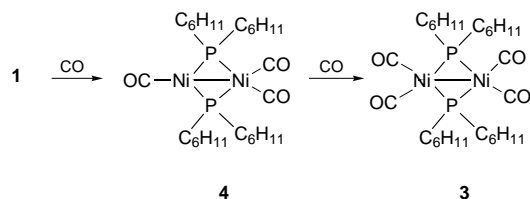
Scheme 1 Proposed mechanism of formation of complex **1**



[Ni{P(C₆H₁₁)₂H}₂(CO)₂] **2** formed according to Scheme 1. Complex **2** is white and shows in the IR spectrum two bands at 1984 and 1924 cm⁻¹ ascribable to the co-ordinated terminal CO groups along with a sharp band at 2294 cm⁻¹ ascribable to the co-ordinated P(C₆H₁₁)₂H. Other spectroscopic features are reported in the Experimental section.

When a solution of complex **1** was placed under carbon monoxide at room temperature and atmospheric pressure it changed rapidly to yellowish brown and the ³¹P NMR spectrum recorded after 2 h consisted of three sharp singlets at δ 329.9, 290.3 and –29. The spectrum of the same solution after 20 h showed almost complete disappearance of the signal at δ 290.3 and only the two peaks at δ 329.9 and –29 [the latter ascribable to free P(C₆H₁₁)₂H]. The reaction solution afforded, by cooling, pure [{Ni[μ-P(C₆H₁₁)₂](CO)₂}]₂ **3** which when redissolved in toluene gave a singlet at δ 329.9 in the ³¹P NMR spectrum. It is likely that when CO is admitted into a solution containing complex **1** the first product to be formed is the tricarbonyl species [Ni₂{μ-P(C₆H₁₁)₂}(CO)₃]**4** which evolves irreversibly to the tetracarbonyl complex **3** (Scheme 2). The geometry proposed for **4** has been observed in [Ni₂(μ-PBu^t)(CO)₃]⁶ and that of **3** has been found for [Ni(μ-PPh₂)(CO)₂]₂.⁹ Comparison of the IR spectra in solution of the mixture of complexes **3** and **4** with that of pure **3** allowed us to assign to [Ni₂{μ-P(C₆H₁₁)₂}(CO)₃] the bands at 1997, 1959 and 1934 cm⁻¹.

Sodium reduction of [Pd{P(C₆H₁₁)₂H}₂Cl₂] carried out with a Na : Pd ratio >2 : 1 and prolonged for about 6 h resulted in the formation of a complex the elemental analysis and spectro-



Scheme 2 Reaction of complex **1** with CO

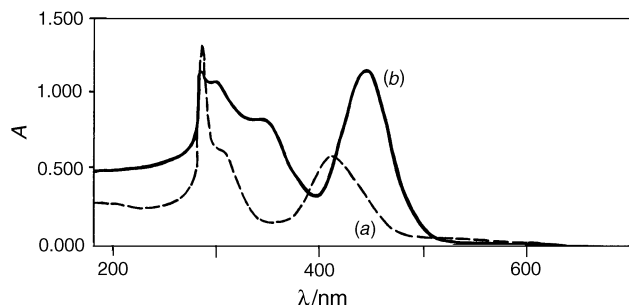


Fig. 1 Electronic absorption spectra of complexes **5** [4.20×10^{-5} mol dm³, (a)] and **6** [5.00×10^{-5} mol dm³, (b)] in toluene

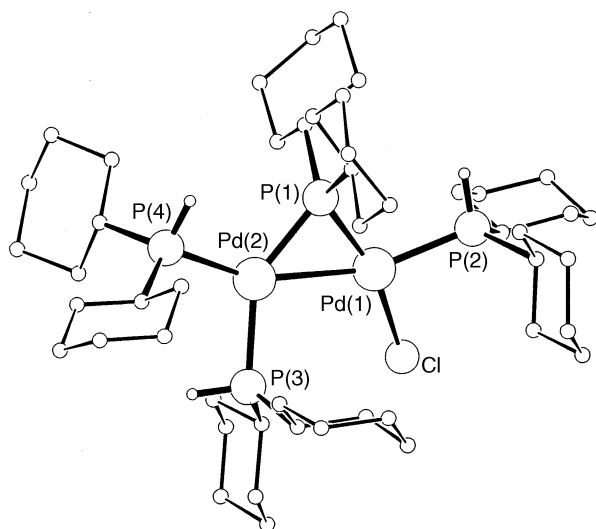


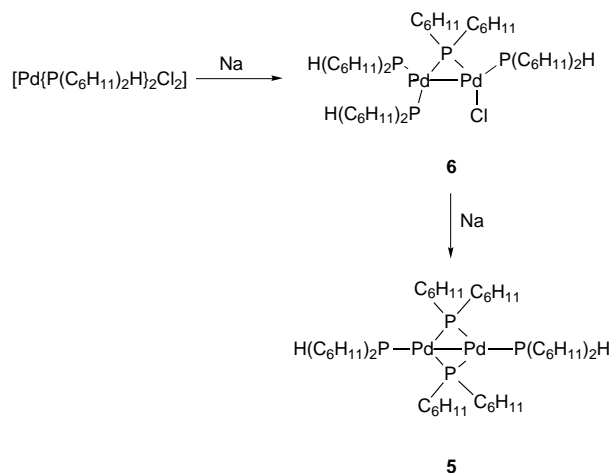
Fig. 2 Molecular structure of complex **6**

scopic features of which indicate the formula $[\{Pd[\mu-P(C_6H_{11})_2]-P(C_6H_{11})_2H\}]_2$ **5**. This was first prepared by Leoni *et al.*¹⁰ by reaction of $P(C_6H_{11})_2H$ with either $[Pd_2\{\mu-P(C_6H_{11})_2\}(\mu-\eta^3-C_3H_5)\{P(C_6H_{11})_2H\}_2]$ or $[Pd(\eta^3-C_3H_5)(cp)]$ (*cp* = cyclopentadienyl anion). Since no electronic absorption data were available on phosphide-bridged palladium(II) complexes we recorded the UV/VIS spectrum of **5** in toluene solution, revealing three bands at 411 (13 300), 297 (sh) and 283 nm (ϵ 30 200 dm³ mol⁻¹ cm⁻¹) (Fig. 1). Care must be taken to prevent the sodium-promoted decomposition of **5** into metallic palladium: when the reaction of $[Pd\{P(C_6H_{11})_2H\}_2Cl_2]$ with a large excess of sodium (Na: Pd \approx 12:1) was kept overnight with stirring a greenish suspension was recovered from which no palladium complex could be isolated.

When the reduction of $[Pd\{P(C_6H_{11})_2H\}_2Cl_2]$ was stopped exactly when the initial suspension became an orange solution, or, alternatively, using a Pd:Na ratio = 2:3, it was possible to recover an orange solid the elemental analysis of which gave a P: Pd: Cl ratio of 4:2:1 and the IR spectrum showed the presence of two absorptions of relative intensity 2:1 in the P–H stretching region at 2298 and 2272 cm⁻¹. Moreover the presence in the ³¹P NMR spectrum of a signal centred at δ 253.4 attributable to a bridging phosphide involved in a three-membered ring allows us to assign to the complex obtained by partial reduction

Table 1 Selected bond distances (Å) and angles (°) for complex **6** with estimated standard deviations in parentheses. All C–H bond distances have been idealized to 0.98 Å

| | | | |
|------------------|----------|------------------|----------|
| Pd(1)–Pd(2) | 2.819(2) | Pd(2)–P(1) | 2.222(5) |
| Pd(1)–Cl | 2.456(5) | Pd(2)–P(3) | 2.319(5) |
| Pd(1)–P(1) | 2.175(5) | Pd(2)–P(4) | 2.339(6) |
| Pd(1)–P(2) | 2.281(5) | | |
| Pd(2)–Pd(1)–Cl | 114.6(1) | Pd(1)–Pd(2)–P(3) | 94.8(1) |
| Pd(2)–Pd(1)–P(1) | 50.9(1) | Pd(1)–Pd(2)–P(4) | 157.6(2) |
| Pd(2)–Pd(1)–P(2) | 155.7(1) | P(1)–Pd(2)–P(3) | 143.0(2) |
| Cl–Pd(1)–P(1) | 162.1(2) | P(1)–Pd(2)–P(4) | 108.3(2) |
| Cl–Pd(1)–P(2) | 89.3(2) | P(3)–Pd(2)–P(4) | 106.8(2) |
| P(1)–Pd(1)–P(2) | 106.4(2) | Pd(1)–P(1)–Pd(2) | 79.7(2) |
| Pd(1)–Pd(2)–P(1) | 49.4(1) | | |



Scheme 3 Reduction of *cis*- $[Pd\{P(C_6H_{11})_2H\}_2Cl_2]$

of $[Pd\{P(C_6H_{11})_2H\}_2Cl_2]$ the formula $[Pd_2\{\mu-P(C_6H_{11})_2\}Cl\{P(C_6H_{11})_2H\}_3]$ **6**.

The intense IR band at 2298 cm⁻¹ can be assigned to the stretching of the two P³–H and P⁴–H bonds whereas that at 2272 cm⁻¹ is ascribable to the P²–H stretching. The ³¹P NMR spectrum of a toluene solution of complex **6** consists of four signals centred at δ 253.4, 23.9, 4.0 and –3.4. That at δ 253.4 is a doublet of triplets and belongs to the bridging phosphorus coupled to the P³ atom with a constant of 166 Hz and to the other two phosphorus atoms with a coupling constant of about 45 Hz. The P³ resonance is at δ 23.9 and appears as a broad doublet, the only coupling constant derivable being that to the bridging P¹ atom (166 Hz). The signal at δ 4.0 is a doublet of triplets with ³*J* = 248 and ²*J* = 45 Hz and is attributable to the P⁴ atom. The larger constant is due to coupling to the P² atom, the smaller one to coupling to the other two phosphorus atoms. The signal at δ –3.4 is a doublet of doublets of doublets [*J*(P²P⁴) = 248, *J*(P¹P²) = 45, *J*(P²P³) = 16 Hz] and is ascribable to the P² atom coupled to the other three phosphorus atoms. The structural characterization of this complex was undertaken by X-ray diffraction and the results (Fig. 2) indicate that it contains two palladium atoms bridged by a dicyclohexylphosphido group; one is bonded to two terminal dicyclohexylphosphines and the second to a dicyclohexylphosphine and to a chlorine atom.

Selected bond distances and angles are given in Table 1. The Pd(1)–Pd(2) distance, 2.819(2) Å, is consistent with a metal–metal single bond. It is comparable with that found in the cationic complex $[Pd_2(\mu-PBu^t)_2(PMe_3)_4]BF_4$, 2.834(4) Å,¹¹ in which five ligands surround the two palladium atoms, and longer than that in the neutral $[\{Pd(\mu-PBu^t)_2(PBu^tH)\}_2]$, 2.594(1) Å⁸ or $[\{Pd[\mu-P(C_6H_{11})_2][P(C_6H_{11})_2(OPh)]\}_2]$, 2.620(2) Å.^{3d} This lengthening of the Pd–Pd bond is probably due to the steric hindrance

of the eight cyclohexyl groups almost symmetrically distributed around the Pd- μ -P-Pd core. The Pd-P length is longer in the terminally bound ligands than in the bridging one and, probably due to the different *trans* influences of the phosphine and the chlorine atom, the Pd(2)-P(1) distance is slightly longer than that of Pd(1)-P(1). A complex analogous to **6**, of formula $[\text{Pd}_2\{\mu\text{-P}(\text{C}_6\text{H}_{11})_2\}_2\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_3(\text{CO})]^+$ has been recently proposed as one of the isomerization products of $[\text{Pd}_2\{\mu\text{-P}(\text{C}_6\text{H}_{11})_2\}_2\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_3(\text{CO})]\text{BF}_4$ in $[\text{H}_6]$ acetone solution.¹²

The UV/VIS spectrum of complex **6** is shown in Fig. 1 and reveals bands at 443 (22 100), 344 (15 900), 290 (sh) and 282 nm (ϵ 21 900 dm³ mol⁻¹ cm⁻¹). Complex **6** could be easily reduced to **5** by reaction with a slight excess of sodium in toluene (Scheme 3).

Contrary to the case of nickel, neither $[\{\text{Pd}[\mu\text{-P}(\text{C}_6\text{H}_{11})_2]\}_2\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_2]$ nor $[\text{Pd}_2\{\mu\text{-P}(\text{C}_6\text{H}_{11})_2\}\text{Cl}\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_3]$ reacted with carbon monoxide under ambient conditions.

Experimental

Materials and apparatus

All manipulations were carried out under a pure dinitrogen atmosphere, using freshly distilled and oxygen-free solvents. Dicyclohexylphosphine was obtained from Strem, $[\text{Ni}\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_2\text{Cl}_2]$ ¹³ was synthesized by literature methods, and *cis*- $[\text{Pd}\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_2\text{Cl}_2]$ ¹⁴ was prepared in quantitative yield by reaction of $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ with 2 equivalents dicyclohexylphosphine in toluene at room temperature.

Samples for melting-point determinations were sealed in capillary tubes under nitrogen. Infrared spectra were recorded on a Perkin-Elmer 883 spectrometer, UV/VIS spectra in solution on a Kontron Uvikon 942 spectrophotometer. Elemental analysis were carried out by using a Carlo Erba model EA 1108 elemental analyser. The gas analyses (H_2) were performed using a Carlo Erba gas chromatograph equipped with a Chromosorb 102 column connected to a Varian 4270 integrator. The NMR spectra were recorded on a Varian XL200 spectrometer at 297 K, ³¹P shifts being measured with respect to external 85% H_3PO_4 . The evolution of hydrogen during reduction reactions was assessed by a gas burette (50 cm³) connected to the reaction vessel.

Preparations

Bis(μ -dicyclohexylphosphido)bis(dicyclohexylphosphine)-nickel(i) 1. A suspension of *cis*- $[\text{Ni}\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_2\text{Cl}_2]$ (1.50 g, 2.85 mmol) and sodium sand (0.33 g, 14.2 mmol) in toluene (20 cm³) was stirred at room temperature until a deep red solution was obtained (about 1 h) and then for 3 h. In the course of the reaction a stoichiometric amount (H_2 :Ni = 0.5:1) of dihydrogen was evolved, as revealed by gas chromatographic analysis. The filtered solution was concentrated *in vacuo* to about 3 cm³ and, after addition of hexane (10 cm³), cooled to 20 °C. The dark red crystals which formed on standing (about 48 h) were filtered off, washed with cold hexane and dried *in vacuo* (0.8 g, 62% yield). The compound is air sensitive, soluble in aromatic solvents and in tetrahydrofuran (thf), slightly soluble in hexane and light petroleum (b.p. 30–50 °C). M.p. 166–168 °C (Found: C, 63.4; H, 10.1; Ni, 12.7; P, 13.21. $\text{C}_{48}\text{H}_{90}\text{Ni}_2\text{P}_4$ requires C, 63.5; H, 10.0; Ni, 12.8; P, 13.65%). UV/VIS (toluene, 1.00×10^{-4} mol dm⁻³): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 332 (19 500), 370 (14 700) and 510 (2800). IR (Nujol mull): $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 2236vs, 1173s, 1110s, 1001s, 895s, 853s, 720m and 511m. $\delta(^{31}\text{P}\text{-}\{\text{H}\})$ in $\text{C}_6\text{H}_5\text{Me}$: 16 (t, $J = 31$, 2 P_i) and 118 (t, $J = 31$ Hz, 2 P_{ii}).

Dicarbonylbis(dicyclohexylphosphine)nickel(o) 2. A suspension of $[\text{Ni}\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_2\text{Cl}_2]$ (0.700 g, 1.33 mmol) and sodium (0.5 g, 21.7 mmol) in toluene (30 cm³) was vigorously stirred at room temperature under 1 atm (101 325 Pa) carbon monoxide. As soon as the red suspension turned into a colourless solution

(ca. 4 h) it was filtered and the pale yellow filtrate concentrated to about 4 cm³. Addition of ethanol (20 cm³) and cooling at -30 °C afforded pure $[\text{Ni}\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_2(\text{CO})_2]$ as white crystals which were washed with cold ethanol and dried *in vacuo*. Yield 0.48 g (70%). The compound is quite air stable in the solid state, but sensitive in solution, and is soluble in aromatic solvents. M.p. = 75–76 °C (Found: C, 61.3; H, 9.2; Ni, 11.15; P, 12.0. $\text{C}_{26}\text{H}_{46}\text{NiO}_2\text{P}_2$ requires C, 61.1; H, 9.05; Ni, 11.5; P, 12.1%). UV/VIS (toluene, 2.28×10^{-4} mol dm⁻³): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 294 (5200). IR (Nujol mull): $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 2294s, 1984vs, 1924vs, 1448s, 1375m, 1340m, 1292m, 1262s, 1191m, 1178m, 1105m, 1040m, 1000w, 905w, 893w, 850s, 829s, 811s, 730m, 509s, 466s, 436m and 384s. $\delta(^{31}\text{P}\text{-}\{\text{H}\})$ in $\text{C}_6\text{H}_5\text{Me}$: 17.2 (s).

Tetracarbonylbis(μ -dicyclohexylphosphido)nickel(i) 3. Carbon monoxide was bubbled with stirring into a toluene solution (0.30 g, 0.33 mmol, in 6 cm³) of $[\{\text{Ni}[\mu\text{-P}(\text{C}_6\text{H}_{11})_2]\}_2\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_2]$ at room temperature causing a change to red-brown. Concentration, addition of ethanol and cooling to -20 °C afforded dark red-brown crystals which were filtered off and characterized as $[\{\text{Ni}[\mu\text{-P}(\text{C}_6\text{H}_{11})_2]\}_2(\text{CO})_2]_2$ (0.13 g, 63% yield). $\delta(^{31}\text{P}\text{-}\{\text{H}\})$ in $\text{C}_6\text{H}_5\text{Me}$: 329.9 (s).

Bis(μ -dicyclohexylphosphido)bis(dicyclohexylphosphine) palladium(i) 5. A suspension of *cis*- $[\text{Pd}\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_2\text{Cl}_2]$ (1.6 g, 2.79 mmol) and sodium sand (0.5 g, 21.7 mmol) in toluene (30 cm³) was stirred at room temperature until a red-brown solution was obtained (about 6 h). The metallic sodium in excess was filtered out and the solution concentrated *in vacuo* to about 5 cm³ and cooled to -30 °C. The dark red crystals formed on standing overnight were filtered off, washed with cold hexane and dried *in vacuo*. Yield 0.60 g (43%). The compound is air sensitive, soluble in aromatic solvents and in thf, slightly soluble in hexane. M.p. = 151 °C (Found: P, 11.9; Pd, 20.85. Calc. for $\text{C}_{48}\text{H}_{90}\text{Pd}_2\text{P}_4$: P, 12.35; Pd, 21.15%). UV/VIS (toluene, 4.20×10^{-5} mol dm⁻³): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 411 (13 300), 297 (sh) and 283 (30 200). IR (Nujol mull): $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 2249vs, 1447vs, 1338s, 1291m, 1260m, 1170vs, 1119s, 1108vs, 1069w, 1042m, 1022m, 1000vs, 923s, 905s, 894vs, 852vs, 825vs, 812vs, 784w, 719s, 512s, 454m, 441s, 393s, 363s and 299w. $\delta(^{31}\text{P}\text{-}\{\text{H}\})$ in $\text{C}_6\text{H}_5\text{Me}$: 10.8 (t, $J = 39$, 2 P_i) and 234.6 (t, $J = 39$ Hz, 2 P_{ii}) [lit.,¹⁰ 14.2 (t) and 238.0 (t) with $J(\text{P-P})$ 39 Hz, in C_6D_6].

Chloro(μ -dicyclohexylphosphido)tris(dicyclohexylphosphine)-dipalladium(i) 6. A suspension of *cis*- $[\text{Pd}\{\text{P}(\text{C}_6\text{H}_{11})_2\text{H}\}_2\text{Cl}_2]$ (1.21 g, 2.11 mmol) and sodium sand (73 mg, 3.17 mmol) in toluene (30 cm³) was stirred at 0 °C (ice-bath) until a red-orange solution was obtained (about 5 h). The stirring was prolonged for about 1 h at room temperature. The filtered solution was concentrated *in vacuo* to about 5 cm³ and cooled to -30 °C. The orange crystals formed on standing (about 7 d) were filtered off, washed with cold hexane and dried *in vacuo* (0.47 g, 43% yield). The compound is air stable in the solid state but sensitive in solution, soluble in aromatic solvents and in thf, slightly soluble in hexane. Decomposition at 231 °C (Found: Cl, 3.45; P, 12.05; Pd, 19.95. $\text{C}_{48}\text{H}_{91}\text{ClP}_4\text{Pd}_2$ requires: Cl, 3.4; P, 11.9; Pd, 20.45%). UV/VIS (toluene, 5.00×10^{-5} mol dm⁻³): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 443 (22 100), 344 (15 900), 290 (sh) and 282 (21 900). IR (Nujol mull): $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 2298s, 2272s, 1376m, 1340m, 1292m, 1264s, 1179s, 1170s, 1103s, 1043m, 1002s, 929m, 915s, 894s, 852vs, 808vs, 728s, 511m, 471s, 440m and 385s. $\delta(^{31}\text{P}\text{-}\{\text{H}\})$ in $\text{C}_6\text{H}_5\text{Me}$: 253.4 [dt, $J(\text{P}^1\text{P}^3) = 166$, $J(\text{P}^1\text{P}^2) = J(\text{P}^1\text{P}^4) = 45$ Hz, P_{1i}], 23.9 (br d, $J = 166$, P³), 4.0 [dt, $J(\text{P}^2\text{P}^4) = 248$, $J(\text{P}^3\text{P}^4) = J(\text{P}^2\text{P}^4) = 45$, P⁴] and -3.4 [ddd, $J(\text{P}^2\text{P}^1) = 45$, $J(\text{P}^4\text{P}^2) = 248$, $J(\text{P}^3\text{P}^2) = 16$ Hz, P²].

Reduction of complex 6 with sodium. A toluene solution of complex **6** (300 mg in 8 cm³) was treated with sodium sand (55 mg) and stirred at room temperature. After 3 h the originally

Table 2 Crystal data and parameters of data collection and refinement for **6**

| | |
|---|--|
| Formula | C ₄₈ H ₉₁ ClP ₄ Pd ₂ |
| M _r | 1040.41 |
| Crystal system | Triclinic |
| Space group | P $\bar{1}$ (no. 2) |
| a/Å | 11.000(9) |
| b/Å | 13.715(9) |
| c/Å | 17.916(9) |
| α /° | 84.91(5) |
| β /° | 76.27(7) |
| γ /° | 76.45(6) |
| U/Å ³ | 2551(3) |
| Z | 2 |
| F(000) | 1096 |
| D _c /g cm ⁻³ | 1.354 |
| λ (Mo-K α)/Å | 0.710 73 |
| μ (Mo-K α)/cm ⁻¹ | 9.02 |
| Scan type | ω |
| Absorption correction | Numerical |
| Transmission (maximum, minimum) | 0.94–0.90 |
| Measured reflections | 12 709 |
| Independent reflections | 7759 |
| Observed reflections [$I > 1.0\sigma(I)$] | 3229 |
| Refined parameters | 256 |
| R ^a | 0.092 |
| R' ^b | 0.066 |

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b R' = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

orange solution turned deep red. After filtration, crystallization from toluene–hexane afforded pure **5**.

Crystallography

Compound **6** crystallizes in the form of orange coloured rods. Owing to the small size of the crystals, a redundant data set was collected. The intensity data were collected with an Enraf-Nonius CAD4 diffractometer, equipped with a graphite monochromator. On a specimen of dimensions 0.17 × 0.09 × 0.08 mm with well developed and readily indexable faces, 12 709 reflections were collected at –70 °C in the range 3.0 < θ < 24.0° over the whole diffraction sphere (–12 < h < 12, –15 < k < 15, –20 < l < 20) which resulted in 7759 unique data after merging and 3229 observed data with $I > 1.0\sigma(I)$. Crystallographic data are summarized in Table 2. The structure was solved by direct methods¹⁵ and refined on F with the MOLEN system.¹⁶ In the full-matrix least-squares refinement only the Pd, Cl and P atoms were assigned anisotropic displacement parameters to avoid an unsatisfactory ratio between observations and variables. Carbon atoms were refined isotropically, and hydrogen atoms placed in idealized positions [C–H 0.98 Å, $B(H)$ = 1.3 $B(C)$] and allowed to ride on their C atoms. Refinement con-

verged with 256 parameters using a statistical weighting scheme $w = 1/[\sigma^2(F_o)]$ at values of $R = 0.092$ and $R' = 0.066$ with a goodness of fit of 1.239.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/399.

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