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Synthesis of phosphido-bridged dinuclear complexes through sodium reduction of *cis*-$[M\{P(C_6H_{11})_2H\}_2Cl_2]$ (M = Ni or Pd)

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Reduction of *cis*-$[Ni\{P(C_6H_{11})_2H\}_2Cl_2]$ with sodium afforded the dinuclear nickel complex $[\{Ni[\mu\text{-}P(C_6H_{11})_2][P(C_6H_{11})_2H]\}_2]$ which, in turn, reacted with CO producing $[\{Ni[\mu\text{-}P(C_6H_{11})_2](CO)_2\}_2]$. The reduction of *cis*-$[Pd\{P(C_6H_{11})_2H\}_2Cl_2]$ occurred in two steps giving first $[Pd_2\{\mu\text{-}P(C_6H_{11})_2\}Cl\{P(C_6H_{11})_2H\}_3]$, then $[\{Pd[\mu\text{-}P(C_6H_{11})_2][P(C_6H_{11})_2H]\}_2]$. The structure of the chloride complex was determined.

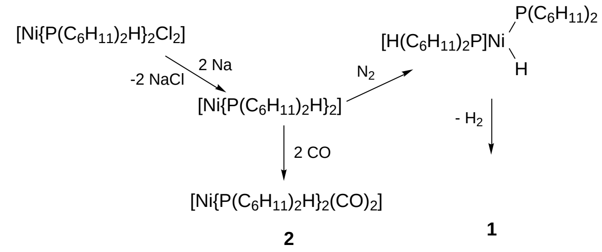
Low-valent transition-metal complexes are the foundations for activating small molecules and for achieving organic syntheses through metal-catalysed reactions. In the framework of our studies on sodium-promoted reduction of metal complexes,[1] we decided to address the divalent metal dicyclohexylphosphino complexes of general formula *cis*-$[M\{P(C_6H_{11})_2H\}_2Cl_2]$ (M = Ni or Pd).

Results and Discussion

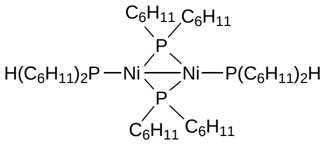
The sodium-promoted reduction of $[Ni\{P(C_6H_{11})_2H\}_2Cl_2]$ in toluene proceeded with evolution of dihydrogen (revealed by GC analyses) and resulted in the synthesis of a brown-red compound the elemental analysis and spectroscopic features of which indicate the formula $[\{Ni[\mu\text{-}P(C_6H_{11})_2][P(C_6H_{11})_2H]\}_2]$ **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 $dm^3\ mol^{-1}\ cm^{-1}$) which is very similar to that of $[\{Ni[\mu\text{-}P(C_6H_{11})_2][P(C_6H_{11})_2Ph]\}_2]$[2] ($\lambda_{max}$ = 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 ^{31}P 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 Ni_2P 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 $[\{Ni[\mu\text{-}P(C_6H_{11})_2][P(C_6H_{11})_2Ph]\}_2]$,[2] $[\{Ni[\mu\text{-}P(SiMe_3)_2](PR_3)\}_2]$ (R = Me, Et or Bu^n),[4] $[\{Ni(\mu\text{-}PBu^t_2)(PR_3)\}_2]$ (R = Me, Et or OMe)[5,6] or $[\{Ni(\mu\text{-}PBu^tH)(PMe_3)\}_2]$.[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(I) complex $[\{Pd(\mu\text{-}PBu^t_2)(PBu^t_2H)\}_2]$[8] can be invoked. In this case the sodium can cleave the two chlorine atoms leading to $Ni[P(C_6H_{11})_2H]_2$ which evolves *via* intramolecular oxidative addition to $[NiH\{P(C_6H_{11})_2\}\{P(C_6H_{11})_2H\}]$. This latter can easily couple giving rise to H_2 and **1**. When the reduction of $[Ni\{P(C_6H_{11})_2H\}_2Cl_2]$ was carried out under atmospheric pressure of carbon monoxide the expected $[Ni\{P(C_6H_{11})_2H\}_2(CO)_2]$ **2** formed according to Scheme 1.

$$2[Ni\{P(C_6H_{11})_2H\}_2Cl_2] + 4\,Na \longrightarrow [\{Ni[\mu\text{-}P(C_6H_{11})_2][P(C_6H_{11})_2H]\}_2] + 4\,NaCl + H_2 \quad (1)$$



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



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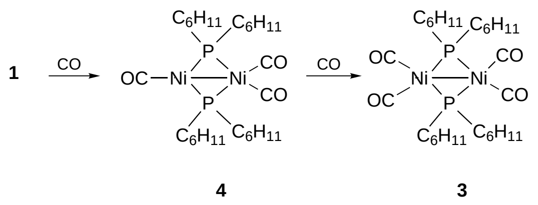
Complex **2** is white and shows in the IR spectrum two bands at 1984 and 1924 cm^{-1} ascribable to the co-ordinated terminal CO groups along with a sharp band at 2294 cm^{-1} ascribable to the co-ordinated $P(C_6H_{11})_2H$. Other spectroscopic features are reported in the Experimental section.

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 ^{31}P 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 $P(C_6H_{11})_2H$]. The reaction solution afforded, by cooling, pure $[\{Ni[\mu\text{-}P(C_6H_{11})_2](CO)_2\}_2]$[2] **3** which when redissolved in toluene gave a singlet at δ 329.9 in the ^{31}P 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 $[Ni_2\{\mu\text{-}P(C_6H_{11})_2\}_2(CO)_3]$ **4** which evolves irreversibly to the tetracarbonyl complex **3** (Scheme 2). The geometry proposed for **4** has been observed in $[Ni_2(\mu\text{-}PBu^t_2)_2(CO)_3]$[6] and that of **3** has been found for $[\{Ni(\mu\text{-}PPh_2)(CO)_2\}_2]$.[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 $[Ni_2\{\mu\text{-}P(C_6H_{11})_2\}_2(CO)_3]$ the bands at 1997, 1959 and 1934 cm^{-1}.

Sodium reduction of $[Pd\{P(C_6H_{11})_2H\}_2Cl_2]$ 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

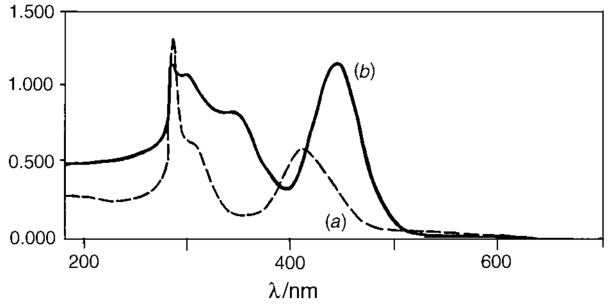


Fig. 1 Electronic absorption spectra of complexes **5** [4.20 × 10^{-5} mol dm^3, (a)] and **6** [5.00 × 10^{-5} mol dm^3, (b)] in toluene

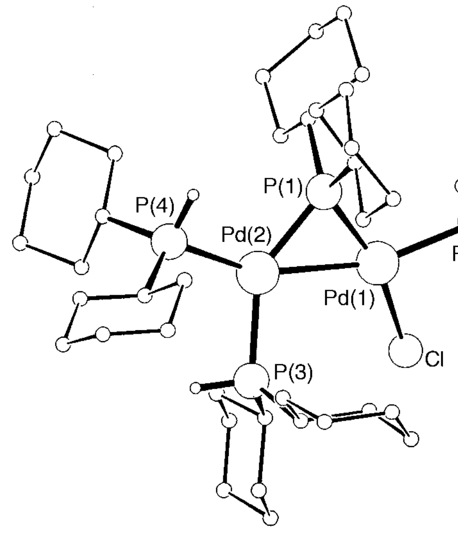


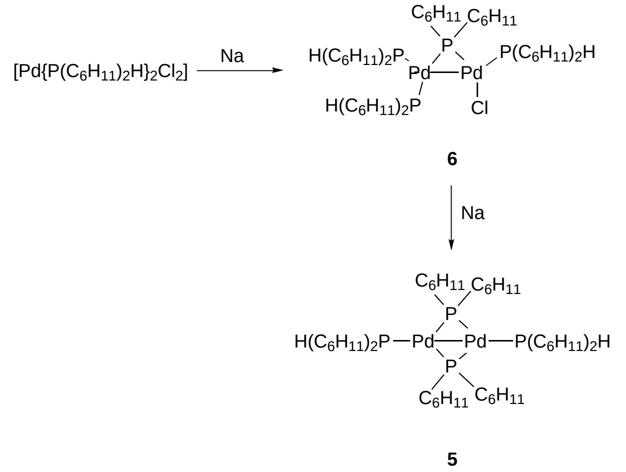
Fig. 2 Molecular structure of complex **6**

scopic features of which indicate the formula $[\{Pd[\mu\text{-}P(C_6H_{11})_2][P(C_6H_{11})_2H]\}_2]$ **5**. This was first prepared by Leoni *et. al.*[10] by reaction of $P(C_6H_{11})_2H$ with either $[Pd_2\{\mu\text{-}P(C_6H_{11})_2\}(\mu\text{-}\eta^3\text{-}C_3H_5)\{P(C_6H_{11})_2H\}_2]$ or $[Pd(\eta^3\text{-}C_3H_5)(cp)]$ (cp = cyclopentadienyl anion). Since no electronic absorption data were available on phosphide-bridged palladium(I) 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 dm^3 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 $[Pd\{P(C_6H_{11})_2H\}Cl_2]$ with a large excess of sodium (Na : Pd ≈ 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 ^{31}P 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 of $[Pd\{P(C_6H_{11})_2H\}_2Cl_2]$ the formula $[Pd_2\{\mu\text{-}P(C_6H_{11})_2\}Cl\{P(C_6H_{11})_2H\}_3]$ **6**.

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*-$[Pd\{P(C_6H_{11})_2H\}_2Cl_2]$

The intense IR band at 2298 cm^{-1} can be assigned to the stretching of the two P^3–H and P^4–H bonds whereas that at 2272 cm^{-1} is ascribable to the P^2–H stretching. The ^{31}P 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 P^3 atom with a constant of 166 Hz and to the other two phosphorus atoms with a coupling constant of about 45 Hz. The P^3 resonance is at δ 23.9 and appears as a broad doublet, the only coupling constant derivable being that to the bridging P^1 atom (166 Hz). The signal at δ 4.0 is a doublet of triplets with $^3J = 248$ and $^2J = 45$ Hz and is attributable to the P^4 atom. The larger constant is due to coupling to the P^2 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 [$J(P^2P^4) = 248$, $J(P^1P^2) = 45$, $J(P^2P^3) = 16$ Hz] and is ascribable to the P^2 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 $[Pd_2(\mu\text{-}PBu^t_2)(PMe_3)_4]BF_4$, 2.834(4) Å,[11] in which five ligands surround the two palladium atoms, and longer than that in the neutral $[\{Pd(\mu\text{-}PBu^t_2)(PBu^t_2H)\}_2]$, 2.594(1) Å[8] or $[\{Pd[\mu\text{-}P(C_6H_{11})_2][P(C_6H_{11})_2(OPh)]\}_2]$, 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 $[Pd_2\{\mu\text{-}P(C_6H_{11})_2\}\{P(C_6H_{11})_2H\}_3(CO)]^+$ has been recently proposed as one of the isomerization products of $[Pd_2(\mu\text{-}PBu^t_2)\{P(C_6H_{11})_2H\}_3(CO)]BF_4$ in $[^2H_6]$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 $dm^3 mol^{-1} cm^{-1}$). 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 $[\{Pd[\mu\text{-}P(C_6H_{11})_2][P(C_6H_{11})_2H]\}_2]$ nor $[Pd_2\{\mu\text{-}P(C_6H_{11})_2\}Cl\{P(C_6H_{11})_2H\}_3]$ 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, *cis*-$[Ni\{P(C_6H_{11})_2H\}_2Cl_2]$[13] was synthesized by literature methods, and *cis*-$[Pd\{P(C_6H_{11})_2H\}_2Cl_2]$[14] was prepared in quantitative yield by reaction of $[Pd(PhCN)_2Cl_2]$ 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, ^{31}P 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 cm^3) connected to the reaction vessel.

Preparations

Bis(μ-dicyclohexylphosphido)bis[(dicyclohexylphosphine)-nickel(I)] 1. A suspension of *cis*-$[Ni\{P(C_6H_{11})_2H\}_2Cl_2]$ (1.50 g, 2.85 mmol) and sodium sand (0.33 g, 14.2 mmol) in toluene (20 cm^3) 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 cm^3 and, after addition of hexane (10 cm^3), 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. $C_{48}H_{90}Ni_2P_4$ requires C, 63.5; H, 10.0; Ni, 12.8; P, 13.65%). UV/VIS (toluene, 1.00 × 10^{-4} mol dm^{-3}): λ_{max}/nm (ε/$dm^3 mol^{-1} cm^{-1}$) 332 (19 500), 370 (14 700) and 510 (2800). IR (Nujol mull): $\tilde{\nu}_{max}/cm^{-1}$ 2236vs, 1173s, 1110s, 1001s, 895s, 853s, 720m and 511m. δ(^{31}P-{H}) in C_6H_5Me: 16 (t, *J* = 31, 2 P_t) and 118 (t, *J* = 31 Hz, 2 P_μ).

Dicarbonylbis(dicyclohexylphosphine)nickel(0) 2. A suspension of $[Ni\{P(C_6H_{11})_2H\}_2Cl_2]$ (0.700 g, 1.33 mmol) and sodium (0.5 g, 21.7 mmol) in toluene (30 cm^3) 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 cm^3. Addition of ethanol (20 cm^3) and cooling at −30 °C afforded pure $[Ni\{P(C_6H_{11})_2H\}_2(CO)_2]$ 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. $C_{26}H_{46}NiO_2P_2$ requires C, 61.1; H, 9.05; Ni, 11.5; P, 12.1%). UV/VIS (toluene, 2.28 × 10^{-4} mol dm^{-3}): λ_{max}/nm (ε/$dm^3 mol^{-1} cm^{-1}$) 294 (5200). IR (Nujol mull): $\tilde{\nu}_{max}/cm^{-1}$ 2294s, 1984vs, 1924vs, 1448s, 1375m, 1340m, 1292m, 1262s, 1191m, 1178m, 1105m, 1040m, 1000w, 905w, 893w, 850s, 829s, 811s, 730m, 509s, 466s, 436m and 384s. δ(^{31}P-{H}) in C_6H_5Me: 17.2 (s).

Tetracarbonylbis(μ-dicyclohexylphosphido)dinickel(I) 3. Carbon monoxide was bubbled with stirring into a toluene solution (0.30 g, 0.33 mmol, in 6 cm^3) of $[\{Ni[\mu\text{-}P(C_6H_{11})_2][P(C_6H_{11})_2H]\}_2]$ 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 $[\{Ni[\mu\text{-}P(C_6H_{11})_2](CO)_2\}_2]$[2] (0.13 g, 63% yield). δ(^{31}P-{H}) in C_6H_5Me: 329.9 (s).

Bis(μ-dicyclohexylphosphido)bis[(dicyclohexylphosphine) palladium(I)] 5. A suspension of *cis*-$[Pd\{P(C_6H_{11})_2H\}_2Cl_2]$ (1.6 g, 2.79 mmol) and sodium sand (0.5 g, 21.7 mmol) in toluene (30 cm^3) 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 cm^3 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 $C_{48}H_{90}P_4Pd_2$: P, 12.35; Pd, 21.15%). UV/VIS (toluene, 4.20 × 10^{-5} mol dm^{-3}): λ_{max}/nm = (ε/$dm^3 mol^{-1} cm^{-1}$ 411 (13 300), 297 (sh) and 283 (30 200). IR (Nujol mull): $\tilde{\nu}_{max}/cm^{-1}$ 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. δ(^{31}P-{H}) in C_6H_5Me: 10.8 (t, *J* = 39, 2 P_t) and 234.6 (t, *J* = 39 Hz, 2 P_μ) [lit.,[10] 14.2 (t) and 238.0 (t) with *J*(P–P) 39 Hz, in C_6D_6].

Chloro(μ-dicyclohexylphosphido)tris(dicyclohexylphosphine)-dipalladium(I) 6. A suspension of *cis*-$[Pd\{P(C_6H_{11})_2H\}_2Cl_2]$ (1.21 g, 2.11 mmol) and sodium sand (73 mg, 3.17 mmol) in toluene (30 cm^3) 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 cm^3 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. $C_{48}H_{91}ClP_4Pd_2$ requires: Cl, 3.4; P, 11.9; Pd, 20.45%). UV/VIS (toluene, 5.00 × 10^{-5} mol dm^{-3}): λ_{max}/nm (ε/$dm^3 mol^{-1} cm^{-1}$ 443 (22 100), 344 (15 900), 290 (sh) and 282 (21 900). IR (Nujol mull): $\tilde{\nu}_{max}/cm^{-1}$ 2298s, 2272s, 1376m, 1340m, 1292m, 1264s, 1179s, 1103s, 1043m, 1002s, 929m, 915s, 894s, 852vs, 808vs, 728s, 511m, 471s, 440m and 385s. δ(^{31}P-{H}) in C_6H_5Me: 253.4 [dt, $J(P^1P^3) = 166$, $J(P^1P^2) = J(P^1P^4) = 45$ Hz, P^1_μ], 23.9 (br d, *J* = 166, P^3), 4.0 [dt, $J(P^2P^4) = 248$, $J(P^3P^4) = J(P^2P^4) = 45$, P^4] and −3.4 [ddd, $J(P^2P^1) = 45$, $J(P^4P^2) = 248$, $J(P^3P^2) = 16$ Hz, P^2].

Reduction of complex 6 with sodium. A toluene solution of complex **6** (300 mg in 8 cm^3) 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	$C_{48}H_{91}ClP_4Pd_2$
M_r	1040.41
Crystal system	Triclinic
Space group	$P1$ (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-Kα)/Å	0.710 73
μ(Mo-Kα)/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] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

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 $3.0 < \theta < 24.0°$ 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 methods[15] 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 converged 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.

Acknowledgements

Professor G. Pampaloni is gratefully acknowledged for magnetic susceptibility measurements. We thank Consiglio Nazionale delle Ricerche and Ministero dell'Università e della Ricerca Scientifica e Technologica for financial support.

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Received 28*th October* 1996; *Paper* 6/07334D