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Synthesis and Characterization of Tertiary Phosphine Pd(0) Complexes

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The synthesis of PdL_n complexes (L = tertiary phosphine; n = 2,3,4) is reported. The coordination number results to be a function of the steric hindrance of the phosphine. Two-coordinate, 14-electron complexes, have been isolated with bulky phosphines (PPr^i_3, P (cyclohexyl)$_3$, PBu^t_2Ph). The behaviour in solution of the PdL_n complexes has been studied by ^{13}C NMR spectroscopy.

Introduction

Palladium complexes are known to catalyze the dimerization and telomerization of butadiene[1]. The catalytic system generally contains PPh_3 to stabilize a Pd(0) species which is catalytically active. We have made a series of tertiary phosphine Pd(0) complexes in order to study the effect of the steric and/or electronic properties of the ligand in the oligomerization reactions of butadiene. Studies in this direction are currently made in our laboratory. Here we report on the preparation and characterization of these complexes.

Results and Discussion

Preparation of the Complexes

$Pd[PPh_3]_4$ has been prepared several years ago[2]. Tolman *et al.*[3] have recentely shown that this complex is completely dissociated in solution into $Pd[PPh_3]_3$ and PPh_3. However whereas three-coordinate complexes of tolyl phosphines[2,3] have been prepared, to the best of our knowledge no general method has yet been given for the preparation of $Pd[PPh_3]_3$. A Pd(0) complex which analyses as $Pd[PPh_3]_3$ has been isolated by Smutny and Chung[4] in the degradation reaction of phenoxyoctadiene to phenol and octatriene.

We have found that $Pd[PPh_3]_3$ may be made in quantitative yields by reacting $[2\text{-}CH_3\text{-}h^3\text{-allylPd}(PPh_3)_2]BF_4$ with a primary amine in presence of one equivalent of PPh_3. The reaction proceeds through a nucleophilic attack of the amine on the coordinated allyl group which is eliminated as N-2-methyl-allylamine (*1*).

$$[2\text{-}CH_3\text{-}h^3\text{-allylPd}(PPh_3)_2]BF_4 + PPh_3 + H_2NR \rightarrow Pd[PPh_3]_3 + [CH_2=\overset{CH_3}{\overset{|}{C}}\text{–}CH_2NH_2R]BF_4 \quad (1)$$

Powell and Shaw have reported[5] that the coordinated allyl group of $(\pi\text{-allylPdCl})_2$ is reductively eliminated by an excess of PPh_3 as $[allylPPh_3]Cl$ with formation of $Pd[PPh_3]_4$. We have found that this reaction may be successfully extended to the preparation of several Pd(0) tertiary phosphine complexes (Table I). The reaction occurs with high yields by adding an excess of phosphine to $(2\text{-methallylPdCl})_2$ suspended in methanol.

The π-allyl complex firstly dissolves and then the Pd(0) complex separates out. Very likely the reaction proceeds through two steps, *i.e.*, formation of the ionic species[6] $[2\text{-methyl-}h^3\text{-allylPd}(PR_3)_2]Cl$ and then nucleophilic attack of the phosphine on the coordinated methallyl group with formation of the Pd(0) complex and of a phosphonium salt* (*2*).

$$[2\text{-}CH_3\text{-}h^3\text{-allylPd}(PR_3)_2]Cl + (x+1)PR_3 \rightarrow Pd[PR_3]_{2+x} + [C_4H_7PR_3]Cl \quad (2)$$

TABLE I. Tertiary Phosphine Pd(O) Complexes.

Ligand (L)	Isolated Complexes
PMe_3	PdL_4
PMe_2Ph	PdL_4
$PMePh_2$	PdL_4
PEt_3	PdL_4, PdL_3
PBu^n_3	PdL_4, PdL_3
PPh_3	PdL_4, PdL_3
PBz_3	PdL_3
PPr^i_3	PdL_3, PdL_2
P(cyclohexyl)$_3$	PdL_2
PBu^t_2Ph	PdL_2

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* PMR analysis of the phosphonium salt has shown that the methallyl group isomerizes to isobutenyl with some phosphines (*e.g.* PPr^i_3). The isomerization should occurr through a Pd–H species which forms through interaction of the Pd(0) complex with methanol.

TABLE II. ^{13}C NMR Data of Pd(0) Tertiary Phosphine Complexes.[a]

Compound	T(° C)	Solvent	α-C	β-C	γ-C	δ-C	1-C	o-C	m-C	p-C
PMe_3[b]			14.3(*d*,13.6)							
$Pd[PMe_3]_4$	+30	toluene	25.5(*d*,4)							
	−68	toluene	25.6(*t*,14)							
PMe_2Ph[c]			14.7(*d*,14.6)				143.5(*d*,15.6)	130.7(*d*,17.5)	128.5(*d*,5.8)	128.0
$Pd[PMe_2Ph]_4$	+30	THF	22.0(*d*,4)				148.2(*d*,7)	130.2(*d*,17)	127.8(*d*,7)	126.9
	−80	CH_2Cl_2[d]	21.1(*t*,14)				147.4(13)	129.2(*t*,17)	127.1(8)	126.1
$PMePh_2$[c]			12.7(*d*,15.4)				141.5(*d*,14.1)	132.6(*d*,18.8)	128.8(*d*,6.4)	128.7
$Pd[PMePh_2]_4$	+30	CH_2Cl_2	18.7(*d*,5)				144.1(*d*,8)	132.1(*d*,16)	127.9(*d*,8)	127.7
	−65	CH_2Cl_2	18.4(20)				143.7(18)	131.1(20)	127.1(16)	127.1(16)
PEt_3[c]			19.5(*d*,14.0)	10.3(*d*,13.8)						
$Pd[PEt_3]_4$	+30	THF	22.6(7)	9.4(*d*,5)						
$Pd[PEt_3]_3$	+30	THF	23.4(7)	9.5(9)						
PBu^n_3[c]			29.3(*d*,13.8)	28.6(*d*,14.8)	25.4(*d*,11.1)	14.7				
$Pd[PBu^n_3]_4$	+30	toluene	31.4(8)	28.8(9)	25.3(15)	14.2				
$Pd[PBu^n_3]_3$	+30	toluene	32.4(5)	28.9(6)	25.4(8)	14.3(5)				
PPh_3[e]							138.3(*d*,12)	134.4(*d*,20)	129.2(*d*,7)	129.3
$Pd[PPh_3]_3$	+30	THF					139.7(*d*,18)	134.1(*d*,16)	128.0(*d*,9)	128.2
PBz_3	+30	CH_2Cl_2	34.7(*d*,20)				138.3(*d*,6)	129.5(*d*,6)	128.7	126.1(*d*,2)
$Pd[PBz_3]_3$	+30	THF	37.2(5)				137.9(3)	130.5(4)	128.2(4)	125.9(3)
PPr^i_3	+30	neat	22.1(*d*,19)	21.2(*d*,14)						
$Pd[Pr^i_3]_3$	+30	benzene	23.7(3)	21.6(7)						
$Pd[Pr^i_3]_2$	+30	benzene	24.7(*t*,9)	21.7(9)						
P(cyclohexyl)$_3$	+30	benzene	32.2(*d*,19)	31.6(*d*,13)	28.0(*d*,9)	26.9				
$Pd[P(cyclohexyl)_3]_2$	+30	toluene	34.9(*t*,11)	32.4(*t*,7)	28.1(*t*,10)	27.2(4)				
PBu^t_2Ph	+30	THF	31.9(*d*,23)	30.4(*d*,16)			137.6(*d*,24)	136.9(*d*,23)	127.8(*d*,9)	129.2(5)
$Pd[PBu^t_2Ph]_2$	+30	THF	34.7(*t*,7)	31.1(*t*,13)			f	f	127.3(*t*,10)	129.4(3)

[a] Shifts (ppm, ±0.2) are reported positive downfield with respect to $SiMe_4$. The coupling constants to phosphorus (Hz, ±1) when observed are given in parenthesis (*d*, doublet; *t*, triplet); for triplet peaks the separation between outer lines is reported; when no fine structure was observed, the peak width at half height is given in parenthesis. [b] W. McFarlane, *Proc. Roy. Soc., A, 306,* 185 (1968). [c] B.E. Mann, *J.C.S. Perkin II,* 30 (1973). [d] At room temperature the compound decomposes in CH_2Cl_2, thus, it has been dissolved at −80° C. [e] O.A. Gansow, B.Y. Kimura, *Chem. Comm.,* 1621 (1970); T. Bundgaard, H.J. Jakobsen, *Acta Chem. Scand., 26,* 2548 (1972). [f] Two resonances at 137.2(*t*,16) and 138.3(*t*,22) for 1-C and *o*-C, but the assignment is dubious.

The three-coordinate complexes $Pd[PBu^n_3]_3$ and $Pd[PEt_3]_3$, and the two coordinate complex $Pd[PPr^i_3]_2$ are prepared analytically pure by pumping in high vacuum $Pd[PBu^n_3]_4$, $Pd[PEt_3]_4$, and $Pd[PPr^i_3]_3$ respectively.

For the preparation of $Pd[P(cyclohexyl)_3]_2$ and $Pd[PBu^t_2Ph]_2$ the excess of phosphine which is used in the reaction scheme (*2*) may be avoided if the methallyl-Pd chloride complex is reacted with the phosphine in presence of sodium methoxide as the nucleophile.

Other preparation methods of the $P(cyclohexyl)_3$ and PBu^t_2Ph complexes have been recentely reported[7,8], however our method appears to give better yields.

Characterization of the Complexes

We have studied the behaviour in solution of the PdL_n complexes by ^{13}C NMR spectroscopy** (Table II). A preliminary account has been published[9].

The PdL_4 complexes may dissociate in solution according to equilibrium (*3*).

$$PdL_4 \rightleftarrows PdL_3 + L \qquad (3)$$

Tolman and coworkers have found that arylphosphine complexes of Ni,Pd,Pt are three-coordinate in solution at 25° C[3]. Analogously $Pt[PEt_3]_4$ [11]and $Ni[PEt_3]_4$[10,12] are dissociated in solution whereas no dissociation occurs for $Ni[PMe_3]_4$[10]. It appears that dissociation of tetracoordinate complexes is essentially dominated by steric rather than electronic effects, the dissociation being favoured for complexes containing phosphorous ligands of large cone angle[13].

The ^{13}C chemical shifts of $Pd[PMePh_2]_4$ do not change appreciably by lowering the temperature. However a change in the fine structure is observed for CH_3, C–1 and *ortho* carbon atoms which are broad singlets at –65° C whereas they are doublets at room temperature. This may be due to phosphine exchange which has been slowed down at low temperature[14].

A mixture of the complex and free ligand shows separate signals for the coordinate and free phosphine at –65° C, whereas at room temperature only one set of signals is observed which corresponds to the appropriately weighted averages of the chemical shifts of the coordinated and free ligand. This correspondence is particularly significative for the methyl carbon atom considering that for this carbon atom there is a deshielding of 6.1 ppm through effect of coordination. The low temperature spectra of the complex, both in presence and absence of an excess of ligand, demonstrate that the $PMePh_2$ complex exists as a four-coordinate species. At room temperature the four-coordinate species may still be the predominant complex as shown by the cryoscopic molecular weight determination (Table III), however the degree of dissociation, which accounts for the coordinated phosphine exchange, cannot be estimated from the data available at present since the chemical shifts of the three-coodinate complex is unknown. This is consistent with Clark's conclusion for ^1H NMR studies that dissociation is negligible[16].

TABLE III. Molecular Weights of Some Pd(O) Complexes.[a]

Complex	Calcd.	Found	%Theory
$Pd[PMe_2Ph]_4$	658	637	97
$Pd[PMePh_2]_4$	967	906	93
$Pd[PBz_3]_3$	1019	893	87
$Pd[PPh_3]_3$	893	783[b]	87
$Pd[P(cyclohexyl)_3]_2$	667	579	87

[a] Cryoscopic determination under N_2. [b] Ref. 25.

$Pd[PMe_2Ph]_4$ and $Pd[PMe_3]_4$ were shown to behave similarly by the same arguments given above for $Pd[PMePh_2]_4$, *i.e.*, ^{13}C chemical shifts do not change by lowering the temperature, the only change being the fine structure of the signals. Additional evidences for $Pd[PMe_2Ph]_4$ are that at low temperature (–80° C) a mixture of PdL_4 and L shows separate signals, whereas at room temperature one set of weighted average signals are observed and that the cryoscopic molecular weight determination also shows that the complex does not dissociate appreciably in solution.

$Pd[PBu^n_3]_4$ and $Pd[PEt_3]_4$ are extensively dissociated in solution to the three-coordinate species. The evidences are the following.

The tetrakis-complexes are white crystalline solids at –20° C. They melt at room temperature to give yellow oils which smell strongly of phosphine and lose quantitavely one molecule of phosphine in high vacuum to afford analytically pure three-coordinate complexes. Moreover at room temperature the observed ^{13}C chemical shifts are the weighted averages of those of the three-coordinate complexes and free phosphine. On lowering the temperature the signals become broad. Extensive crystallization of the samples at –68° C prevented us from obtaining the limiting spectra.

With PPh_3, PBu^n_3 and PEt_3 as the ligands both tetrakis and three-coordinate complexes can be made. PBz_3 and PPr^i_3 are anomalous in this respect. In the preparative reaction even by using a large excess of ligand only three-coordinate complexes are obtained.

The ^{13}C chemical shifts of $Pd[PBz_3]_3$ do not change by lowering the temperature. The room temperature spectrum of a mixture of the complex and the ligand shows one set of signals. The observed chemical shifts correspond to the weighted averages of those of Pd

** A study of the electronic spectra at variable concentration of both the complexes, and the complexes and ligands has been attempted, but reproducible results were not obtained owing to the extreme reactivity of the PdL_n complexes towards traces of oxygen. Dr. B. E. Mann (Sheffield University) is currently making a ^{31}P NMR study on these complexes.[15]

$[PBz_3]_3$ and tribenzylphosphine. At –20° C separate signals are observed for the three-coordinate complex and the free ligand.

Equilibrium (*3*) may readily account for the exchange of coordinated and free phosphine. However the lack of a line shape analysis of the ^{13}C spectra at variable concentration of the ligand does not allow to rule out equilibrium (*4*).

$$PdL_3 \rightleftarrows PdL_2 + L \qquad (4)$$

If equilibrium (*4*) occurs, according to the ^{13}C spectra and the molecular weight determination, the concentration of PdL_2 should only be kinetically significant. Interestingly the ^1H NMR spectrum of $Pd[PBz_3]_3$ does not show phosphorus–hydrogen coupling for the methylene group (toluene-d^8, 2.59δ) at +30° C. At –46° C the peak is largely broad ($\nu_{1/2}$ = 10 Hz). This is very likely due to phosphine exchange[14]. The traces of free phosphine exchanging with the coordinated one may come from equilibrium (*4*) or may be present as an impurity in the compound. Probably ^{31}P NMR studies will clarify this point.

There are some indications that equilibrium (*4*) is operative for $Pd[PPr^i_3]_3$. The ^{13}C chemical shifts at room temperature are weighted averages of those of $Pd[PPr^i_3]_2$ and PPr^i_3. The limiting ^{13}C spectrum of $Pd[PPr^i_3]_3$ was not obtained at –68° C which was the lowest temperature reached before large crystallization of the sample occured in the NMR tube. The observation that $Pd[PPr^i_3]_3$ loses one molecule of phosphine under vacuum is another indication that the three-coordinate complex exists as such only in the solid state. A molecular weight determination could not be attempted owing to the extreme sensitivity to oxygen of the complex.

Differently from PPr^i_3 for which both three-coordinate and two-coordinate complexes can be made, only two-coordinate complexes have been isolated with P(cyclohexyl)$_3$ and PBu^t_2Ph. It is pertinent to note that the literature offers only a few examples of two-coordinate d^{10} complexes[7,8,17], which appear not to follow the 16–18 electron rule formulated by Tolman[18]. The ^{13}C and ^1H NMR spectra of the PdL_2 complexes are consistent with a linear coordination of the metal. The ^1H NMR spectrum of the methyl protons of $Pd[PPr^i_3]_2$ [toluene-d^8, –38° C, 1.20δ (quartet, $|^3J(H–H)| = {}^1/_2|^3J(P–H) + {}^5J(P–H)| = 6.5$ Hz)] and of $Pd[PBu^t_2Ph]_2$ [toluene-d^8, 1.45δ (triplet, $|^3J(P–H) + {}^5J(P–H)| = 13.0$ Hz)] are consistent with a large value of $^2J(P–P)$ which is expected for two mutually *trans* phosphines[19]. Accordingly the triplet observed in the ^{13}C spectra (X part of an ABX spectrum) of the PdL_2 complexes is the pattern generally observed for two mutually *trans* tertiary phosphines[20].

A X-ray structure determination of Pd[P(cyclohexyl)$_3$]$_2$ and $Pd[PBu^t_2Ph]_2$ has been done in our laboratory[21]. The X-ray structure determination of Pd $[PBu^t_2Ph]_2$ has also been reported, independently and with comparable results, by Otsuka and coworkers[8]. It appears that the coordination of the metal in the two complexes is not rigorously linear, the P–Pd–P angle being 158.4° and 175.7° in the P(cyclohexyl)$_3$ and in the PBu^t_2Ph complex respectively. Moreover, the two phenyl rings of $Pd[PBu^t_2Ph]_2$ are practically coplanar with the P–Pd–P group. With this geometry, a distance of 2.73 Å of one *ortho* hydrogen atom from the metal can be calculated. Variable temperature ^1H NMR experiments have shown that there is hindered rotation of the phenyl ring around the P–C bond. At low temperatures (–60° C) two signals are observed for the *ortho* hydrogen atoms at 9.07 and 7.52δ. The low field resonance owing to the large deshielding[22] is assigned to the proton close to the metal. At room temperature the aromatic *ortho* protons give an average signal at 8.32δ (7.52δ in the free phosphine).

The X-ray structure and the ^1H NMR spectrum do not exclude a kind of bonding interaction between the aromatic *ortho* hydrogens and the metal in the PBu^t_2Ph complex. This may cause the slightly different geometry in the two PdL_2 complexes. However before drawing final conclusions on what should be the "normal" geometry of the P–Pd–P group in the PdL_2 complexes other X-ray structural determinations of two-coordinate complexes are necessary.

In conclusion we have shown that the sterical hindrance of the phosphine has a remarkable effect on the coordination number of the metal.

The order of the phosphines according to their preferences in forming Pd(0) complexes of low coordination number is the following:

$PMe_3 \sim PMe_2Ph \sim PMePh_2 < PPh_3 \sim PEt_3 \sim PBu^n_3 < PBz_3 < PPr^i_3 <$ P(cyclohexyl)$_3$ $\sim PBu^t_2Ph$. This order correlates well with that of the increasing steric hindrance of the phosphines. Bulky ligands such as PPr^i_3, P(cyclohexyl)$_3$ and PBu^t_2Ph allow the separation of the coordinatively unsatureted 14 electron complexes. Preliminary results of our laboratory have shown that the size of the coordinate phosphine, as one would expect, has a remarkable influence in some telomerization reactions of butadiene[23].

Experimental

All the PdL_n complexes are air sensitive, particularly those in which trialkylphosphines are coordinated. Preparation and handling of the complexes has been carried out in an inert atmosphere of nitrogen purified by passage through Alfa Inorganics De Ox catalyst. Solvents were carefully degassed before use.

^1H NMR spectra were run on a Varian HA-100 spectrometer. The ^{13}C NMR spectra were recorded on a Bruker HFX-90 spectrometer operating at 22.62 MHz with a wide band proton decoupling and were

accumulated with a Fabritek 1074 computer. The measurements were done with 10 mm o.d. tubes which were sealed under vacuum. The solutions (0.3 *M*) were made by distilling the solvents through the vacuum line into the tubes which contained the Pd(0) complexes. The assignment of the ^{13}C resonances of the complexes was readily made by comparison with the spectra of the free ligands.

The molecular weights were determined cryoscopically under nitrogen in benzene solutions about 0.05 *M*.

Melting points were determined in evacuated, sealed capillaries. Elemental analyses were performed by F. Pascher, Mikroanalytisches Laboratorium, Bonn.

PBu^t_2Ph was prepared according to Mann, Shaw and Slade[19]. All the other phosphines were commercially available (Strem) and were used without further purification except PBu^n_3 which was redistilled.

$Pd[PMe_3]_4$

2-methallylPdCl (1.64g, 8.3 mmol) was suspended in methanol (20 ml). The reaction vessel was connected to the vacuum line and kept at –75° C while the phosphine (5g, 65.7 mmol) was distilled into it. The mixture was left to warm up to room temperature. A yellow-orange solution was obtained, the color faded after 1 hr and white crystals began to precipitate. The mixture was stirred overnight and then cooled from 0° C to –75° C. The white solid was filtered cooling the filter with dry ice and washed with precooled methanol (100 ml). The white crystalline material was transferred into a round bottom flask and dried in high vacuum at –75, –50° C and for a few minutes at room temperature (2.52 g, 73% yield). During the drying, even at the low temperatures, some decomposition occurred. A reddish color was observed in some parts of the bulk material which turned yellow at room temperature.

Owing to the extreme air sensitivity of the compound a recrystallization was not attempted. ^1H NMR: toluene-d^8, 30° C, 1.15δ, doublet, J_{P-H} 2 Hz. *Anal.* Calcd. for $PdP_4C_{12}H_{36}$: C,35.09;H,8.82;P,30.16;Pd, 25.91. Found: C,34.97;H,8.78;P,29.63;Pd,25.84.

$Pd[PMe_2Ph]_4$

PMe_2Ph (1.40 g, 10.1 mmol) dissolved in methanol (10 ml) was added to 2-methallylPdCl (0.394 g, 2 mmol) suspended in methanol (30 ml). A red solution formed. After 1.5 hr the mixture was cooled at –75° C. Yellow crystals of the complex separated out which were washed with cold methanol (0.75 g, 56% yield). The compound may be recrystallized from methanol. M.p. 65–67° C. ^1H NMR, toluene-d^8, 30° C, 1.30δ (doublet, J_{P-H} 2 Hz, $-CH_3$); 7.30δ (multiplet, *ortho* protons); 7.00δ (multiplet, *meta* and *para* protons). *Anal.* Calcd. for $PdP_4C_{32}H_{44}$: C,58.32;H,6.72;P, 18.80;Pd,16.14. Found: C,58.48;H,7.04;P,18.73;Pd, 16.09.

$Pd[PMePh_2]_4$

The preparation of this complex was analogous to that of $Pd[PMe_2Ph]_4$. The crude product, which separated out at room temperature from the reaction mixture (95% yield), was recrystallized from a toluene–methanol mixture (~ 1:2) to afford yellow crystals. M.p. 134–136° C (lit. 80–83° C)[24]. ^1H NMR: toluene-d^8, 30° C, 1.55δ (doublet, J_{P-H} 1.4 Hz, $-CH_3$); 7.3δ (multiplet, *ortho* protons); 6.9δ (multiplet, *meta* and *para* protons). *Anal.* Calcd. for $PdP_4C_{52}H_{52}$: C, 68.84;H,5.77;P,13.65;Pd,11.72. Found: C,68.81;H, 5.85;P,13.96;Pd,11.96.

$Pd[PEt_3]_4$

PEt_3 (16 ml, 108 mmol) was added at –80° C to 2-methallylPdCl (3.0 g, 15.2 mmol) suspended in methanol (40 ml). The mixture was warmed up to room temperature; after dissolution of the π-allyl complex a yellow oil began to separate out. The mixture was kept stirring overnight and then cooled at –25° C for 1 hr. The yellow oil solidified together with a white crystalline material. The methanol was siphoned out. The solid residue after several washings with cold methanol was dried under high vacuum (10^{-6} mm Hg) at –25° C for 3 hr. The crude Pd(0) complex was dissolved in pentane (25–30 ml). PdL_4 crystallized from the filtered pentane solution to which phosphine was added (3–4 ml) as white crystals by cooling down slowly to –80° C. The crystals, after washing with pentane at –80° C, were dried in high vacuum keeping the temperature around –50° C (7.45 g, 84% yield). At room temperature $Pd[PEt_3]_4$ melts to give a yellow oil. ^1H NMR: benzene, 30° C, 1.2δ (2 overlapping triplets, J_{P-H} 14 Hz, J_{H-H} 7 Hz, $-CH_3$) 1.6δ (complex multiplet, $-CH_2$). *Anal.* Calcd. for $PdP_4C_{24}H_{60}$: C,49.78;H,10.43;P,21.31;Pd,18.37. Found: C,48.75; H,10.51;P,21.38;Pd,19.01.

$Pd[PEt_3]_3$

At room temperature $Pd[PEt_3]_4$ loses quantitatively one molecule of phosphine in high vacuum to afford the three-coordinate complex as a yellow oil, analytically pure. ^1H NMR: benzene, 30° C, 1.2δ (broad peak, $-CH_3$), 1.5δ (triplet, $-CH_2$). *Anal.* Calcd. for $PdP_3C_{18}H_{45}$: C,46.91;H,9.83;P,20.16;Pd,23.09. Found: C,45.75;H,9.88;P,19.48;Pd,23.36.

$Pd[PBu^n_3]_4$ and $Pd[PBu^n_3]_3$

These were prepared analogously to the PEt_3 complexes with comparable yields.

$Pd[PBu^n_3]_4$

^1H NMR: benzene, 30° C, 0.98δ (broad, $-CH_3$), 1.56δ (broad, $-CH_2$). *Anal.* Calcd. for $PdP_4C_{48}H_{108}$: C,62.96;H,11.87;P,13.53;Pd,11.62. Found: C,62.87;H, 11.73;P,13.72;Pd,11.63.

Pd[PBu$^n_3$]$_3$

^{1}H NMR: benzene, 30° C, 1.05δ (broad, –CH_3), 1.65δ (broad, –CH_2). *Anal.* Calcd. for $PdP_3C_{36}H_{81}$: C,60.61;H,11.43;P,13.02;Pd,14.91. Found: C,60.54;H, 11.45;P,13.44;Pd,14.55.

Pd[PPh$_3$]$_3$

A methylene chloride (60 ml) solution of PPh_3 (1.0 g, 3.8 mmol) was added to a stirred solution of [2-methallylPd(PPh_3)$_2$]BF_4 (3.15 g, 4 mmol) and then benzylamine (2.6 ml, 24 mmol) was added. The mixture was stirred for 1 hr at room temperature. The methylene chloride was evaporated. The yellow residue was washed with heptane and then extracted with warm toluene (50 ml). Upon cooling yellow crystals were obtained (2.7 g, 67% yield). The complex, as shown from the elemental analysis and the ^{1}H NMR spectrum, crystallizes with one molecule of toluene. The preparation method described above gives better yields than the one previously published[25]. M.p. 190–203° C (dec.). ^{1}H NMR: benzene-d^6, 30° C, 6.8δ (complex pattern, *meta* and *para* protons), 7.4δ (complex pattern, *ortho* protons). *Anal.* Calcd. for $PdP_3C_{61}H_{53}$: C,74.35; H,5.41;P,9.42;Pd,10.79. Found: C,74.55;H,5.32;P, 9.45;Pd,11.23.

Pd[P(benzyl)$_3$]$_3$

2-methallylPdCl (1.0 g, 5 mmol) was suspended in methanol (75 ml). P(benzyl)$_3$ (9.0 g, 30 mmol) dissolved in toluene (50 ml) was added. Upon addition of the phosphine the methallyl complex dissolved and then a yellow solid separated out. The mixture was stirred overnight. The yellow solid was filtered and, after drying under vacuum, was extracted with 50 ml of toluene. Heptane (10 ml) was added to the filtered yellow solution. Crystallization afforded the compound as yellow microcrystals (3.8 g, 73% yield). M.p. 156–175° C (dec.). ^{1}H NMR: toluene-d^8, 30° C, 2.59δ (singlet, –CH_2), 6.9–7.1δ (aromatic protons). *Anal.* Calcd. for $PdP_3C_{63}H_{63}$: C,74.22;H,6.22;P,9.11; Pd,10.43. Found: C,74.70;H,6.41;P,8.82;Pd,10.02.

Pd[PPr$^i_3$]$_3$

To 2-methallylPdCl (2.02 g, 10.25 mmol) suspended in methanol (38 ml) and cooled at –70° C PPr^i_3 (10 g, 62.5 mmol) was added. The mixture was left to warm up at room temperature and left stirring overnight. The solution was then cooled at 0° C for 2 hr while stirring. A copious white precipitate of the complex formed, which was quickly filtered and washed with cold methanol (–60°, –70° C). The white solid was dried in high vacuum at –20° C (3.78 g; 63% yield). The crude product was crystallized from pentane (30 ml) in presence of phosphine (0.6 ml) by cooling slowly down to –75° C. White crystals formed, the pentane was siphoned off and then the crystals were washed with cold pentane (–75° C) and finally dried at –30° C in high vacuum. M.p. 41–43° C. The compound is extremely air sensitive and must be handled with extreme care. ^{1}H NMR: toluene-d^8, 30° C, 1.20δ (broad, –CH_3), 1.70δ (multiplet, –CH). *Anal.* Calcd. for $PdP_3C_{27}H_{63}$: C,55.24; H,10.80;P,15.82;Pd,18.12. Found: C,54.17;H,10.66; P,15.65;Pd,18.35.

Pd[PPr$^i_3$]$_2$

Pd[PPr$^i_3$]$_3$ was melted in high vacuum (10^{-6} mm Hg) and kept at 50° C for 3 hr. One molecule of phosphine was quantitatively lost. The two-coordinate complex as it came from the preparation was a yellow oil at room temperature. Crystallization of the oil (1.7 g) from methanol (10 ml) afforded white crystals which melted at room temperature. The compound is extremely air sensitive. ^{1}H NMR: toluene-d^8, –38° C, 1.20δ (quartet, –CH_3), 1.70δ (broad, –CH). *Anal.* Calcd. for $PdP_2C_{18}H_{42}$: C,50.64;H,9.90;P,14.51; Pd,24.92. Found: C,50.37;H,9.73;P,14.42;Pd,25.05.

Pd[P(cyclohexyl)$_3$]$_2$

2-methallylPdCl (1.03 g, 5.2 mmol) was suspended in 30 ml of methanol. Sodium methoxide (4 ml, 1.54 *M* methanol solution) was added. The methallyl complex dissolved; methanol was then added (70 ml) and then the phosphine (4.39 g, 15.6 mmol) dissolved in toluene (35 ml). After a few minutes a white solid started to separate out. The mixture was stirred for 24 hr. The white solid was filtered and washed with methanol. After drying in high vacuum the solid was extracted with warm toluene. White crystals were obtained upon cooling at –15° C, further crystals were obtained by diluting the mother liquor with methanol (2.78 g, 80%). M.p. 180–183° C (dec.). ^{1}H NMR: toluene-d^8, 30° C, 1.2–2.2δ (featureless resonance). *Anal.* Calcd. for $PdP_2C_{36}H_{66}$: C,64.80;H,9.96;P,9.28; Pd,15.94. Found: C,64.72;H,10.08;P,9.37;Pd,16.07.

Pd[PBu$^t_2$Ph]$_2$

Sodium methoxide (2 ml, 1.54 *M* solution) was added to 2-methallylPdCl (0.49 g, 2.5 mmol) suspended in methanol (20 ml). After dissolution of the allyl complex the phosphine was added (2.18 g, 9.81 mmol). After a few minutes a yellow solid started to separate out. The mixture was stirred overnight at room temperature. The yellow solid was filtered and washed with methanol. After drying in vacuum it was extracted with toluene (20 ml). To the filtered yellow solution methanol was added (12 ml). Pale yellow crystals were obtained upon cooling at –15° C; additional crystals were obtained by diluting the mother liquid with methanol (1.03 g, 74% yield). M.p. 161–162° C (dec.). ^{1}H NMR: toluene-d^8, 30° C, 1.45δ (triplet, –CH_3), 7.1δ (*meta* and *para* protons), 8.32δ (*ortho* protons). *Anal.* Calcd. for $PdP_2C_{28}H_{46}$: C,61.03;H,8.40;P,11.24;Pd, 19.31.
Found: C,61.11;H,8.36;P,11.03;Pd,19.47.

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