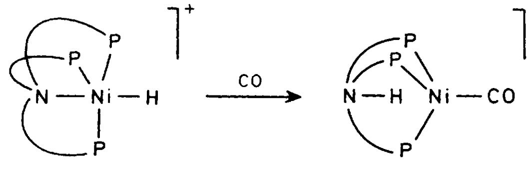
Palladium Complexes with the Tripodal Phosphine Tris-(2-diphenylphosphinoethyl)amine. Synthesis and Structure of Trigonal, Tetrahedral, Trigonal Bipyramidal, and Square Planar Complexes *

Franco Cecconi, Carlo A. Ghilardi, Stefano Midollini, Simonetta Moneti, Annabella Orlandini, and Giancarlo Scapacci
Istituto per lo Studio della Stereochemica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi, 39–50132 Firenze, Italy

The tripod-like ligand $N(CH_2CH_2PPh_2)_3$ (tdpea) forms the palladium(0) trigonal complex $[Pd(tdpea)]\cdot0.5Me_2CO$, (**1**), in which the apical nitrogen atom of the phosphine is unco-ordinated. This unsaturated species undergoes both addition (CO, SO_2) and oxidative-addition reactions (alkyl halides) to form respectively tetrahedral and trigonal bipyramidal complexes. The latter contain quadridentate tdpea. Complex (**1**) reacts with CO_2 or CS_2 in the presence of O_2 to form a square planar carbonate or dithiocarbonate derivative, with oxidation of a terminal PPh_2 group to $OPPh_2$. Crystal data for (**1**) are: a = 10.827(8) Å, α = 108.82(9)°, space group $R3$, and Z = 1. In the molecule the metal atom displays an unprecedented out-of-plane trigonal co-ordination. Crystal data for [Pd(tdpea)Me]I are: a = 10.570(7) Å, α = 106.10(7)°, space group $R3$, and Z = 1. The geometry of the $[Pd(tdpea)Me]^+$ cation is trigonal bipyramidal, with the three-fold crystallographic axis passing through the nitrogen, the palladium, and the carbon atom.

Tripod-like potentially quadridentate phosphines preferentially stabilize trigonal bipyramidal complexes of transition metals. These usually behave as stable and quite inert species. However, the ligand tris(2-diphenylphosphinoethyl)amine (tdpea) shows a remarkable flexibility allowing the formation of derivatives of various geometries, such as trigonal pyramidal, tetrahedral, square planar, trigonal bipyramidal, and octahedral, according to the nature of the metal centre and coligands.[1] Moreover, in spite of the geometry of the ligand, the nitrogen apical atom can easily break off the metal (*e.g.* see Scheme 1):[2] thus the complexes are potentially much more reactive than those of related polydentate phosphines.



Scheme 1.

Although a large variety of complexes of tdpea with nickel have been reported,[1] the reactivity of palladium and platinum toward this ligand has not been tested. In this work we report the results of an investigation of the complexes of palladium with tdpea and contrast the different co-ordinative ability of nickel. A preliminary account of part of this work has been published.[3]

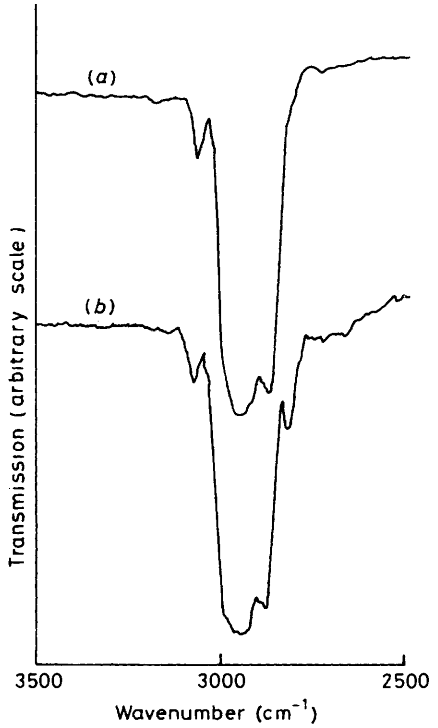


Figure 1. Infrared spectra (Nujol mulls) in the 2 500—3 500 cm^{-1} region of the complexes [Ni(tdpea)] (*a*) and [Pd(tdpea)] (*b*)

Results and Discussion

Well shaped yellow crystals of formula $[Pd(tdpea)]\cdot0.5Me_2CO$ (**1**) have been obtained by an improvement of the synthesis previously described.[4] The complex is air-sensitive but it can be stored without decomposition under an inert atmosphere, in a refrigerator, for about 1 month. The i.r. spectrum of the solid [Pd(tdpea)] (Nujol mull), in the region 3 500—2 500 cm^{-1}, is compared to that of the closely related trigonal pyramidal nickel complex [Ni(tdpea)][5] in Figure 1. The band at 2 820 cm^{-1} in the spectrum of (**1**), attributable to the C–H stretching vibrations of $N-CH_2$, which is obscured by the Nujol band in the spectrum of [Ni(tdpea)], is typical of complexes in which the ligand tdpea acts in a tridentate manner with the nitrogen atom unco-ordinated.[6] So this result may be indicative of a three-co-ordinate geometry in (**1**).

---

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Selected bond distances (Å) and angles (°)

	(1)	**(2)**
Pd–P	2.299(5)	2.357(4)
Pd–N	2.69(2)	2.23(2)
Pd–C		2.10(3)
P–C(2)	1.83(2)	1.83(2)
P–C(11)	1.82(1)	1.82(1)
P–C(12)	1.84(2)	1.81(1)
N–C(1)	1.46(2)	1.45(2)
C(1)–C(2)	1.50(2)	1.51(2)
P–Pd–P	116.7(1)	119.1(2)
P–Pd–N	79.4(1)	84.6(1)
P–Pd–C		95.4(1)
N–Pd–C		180.0
Pd–P–C(2)	101.6(6)	97.6(6)
Pd–P–C(11)	120.2(4)	117.3(4)
Pd–P–C(12)	126.3(5)	126.0(5)
C(2)–P–C(11)	103.8(8)	104.8(7)
C(2)–P–C(12)	103.8(7)	105.9(7)
C(11)–P–C(12)	98.3(6)	102.8(6)
Pd–N–C(1)	105.2(11)	109.5(9)
C(1)–N–C(1′)	113.4(9)	109.5(9)
N–C(1)–C(2)	112.3(15)	115.0(13)
P–C(2)–C(1)	113.2(12)	107.3(11)

Primed atoms are related to the corresponding unprimed atoms by the three-fold axis.

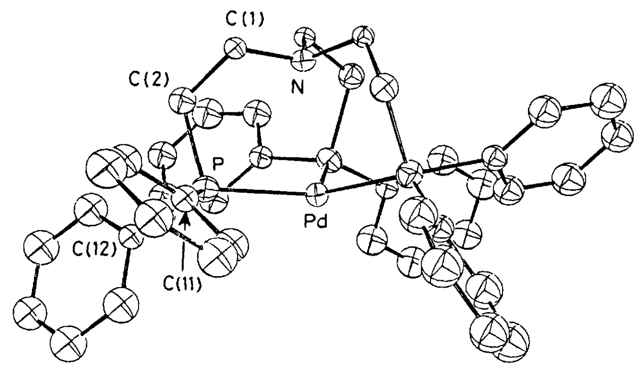


Figure 2. Perspective view of the complex [Pd(tdpea)]. ORTEP drawing with 30% probability ellipsoids

A complete *X*-ray determination established that the molecular structure of (**1**) consists of discrete Pd(tdpea) units with Me_2CO solvating molecules interspersed in the lattice. Figure 2 shows a perspective view of the complex molecule, selected bond distances and angles being given in Table 1. The palladium atom, which lies together with the nitrogen atom on a crystallographic three-fold axis, displays an unprecedented out-of-plane trigonal co-ordination. The metal atom is co-ordinated by the three phosphorus atoms of the ligand, the distance from the central nitrogen atom being 2.69(2) Å. Further evidence for the repulsive interaction between the metal and the nitrogen atom is the deviation (0.42 Å) of the metal from the phosphorus plane in the opposite direction of the nitrogen and the reduced sp^3 character of the nitrogen donor, the C–N–C′ angle being 113.4(9)°. Flattening of the central nitrogen atom has been previously found in tdpea complexes with the nitrogen non-co-ordinated to the metal.[2] Both electronic and steric factors have been generally invoked to justify low co-ordination numbers for d^{10} metal complexes.[7] In this case the difference between the geometry of [Ni(tdpea)] and [Pd(tdpea)] must be attributed only to the electronic factors linked to the nature of the metal. In [Pd(tdpea)], not withstanding the availability of the fourth donor atom, the tripod ligand is forced to distort itself in order to allow the metal a 16e$^-$ configuration.

Oxidative addition and related reactions of [Pd(tdpea)] with small molecules are reported in Scheme 2, the analogous reactions[8–11] of [Ni(tdpea)] being reported in Scheme 3 for comparison.

The compound [Pd(tdpea)] has been found to add small molecules such as P_4,[4] CO, to yield 18e$^-$ tetrahedral derivatives. This behaviour is identical to that of [Ni(tdpea)]. The i.r. spectrum of [Pd(tdpea)(CO)] shows a strong band at 1 930 cm^{-1} (Nujol mull) due to the CO stretching vibration. The presence of the band at 2 820 cm^{-1} attributed to the CH_2–N stretching vibration indicates the non-co-ordination of the nitrogen atom. The ^{31}P-{^{1}H} n.m.r. spectrum of the complex in C_6D_6 solution, with a signal at δ 1.13 p.p.m., shows the equivalence of the three phosphorus atoms of tdpea.

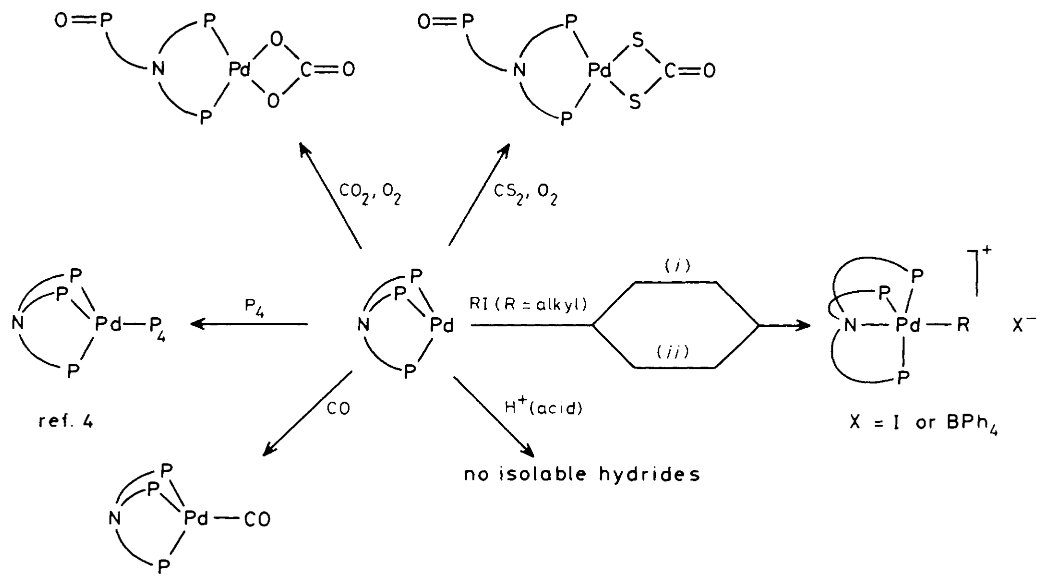
The compound (**1**) reacts at room temperature with alkyl halides such as RI (R = Me, Et, Pr, Bu, or CH_2Ph) to form palladium(II) alkyl derivatives. The complexes are indefinitely stable at room temperature under a nitrogen atmosphere. They are soluble in polar organic solvents such as methylene chloride and acetonitrile in which they behave as 1 : 1 electrolytes. The ^{31}P-{^{1}H} n.m.r. spectra (see Experimental section) indicate the equivalence of the three phosphorus atoms of tdpea. The ^{1}H n.m.r. spectra show that the protons attached to the carbon linked to the metal are displaced to higher field according to previously reported results.[12] The five-co-ordinate geometry of these derivatives has been definitively ascertained by an *X*-ray crystal structure determination of [Pd(tdpea)Me]I (**2**).

The molecular structure of (**2**) consists of discrete [Pd(tdpea)-Me]$^+$ cations and I$^-$ anions. Figure 3 shows a perspective view of the complex cation, selected bond distances and angles being given in Table 1. Upon co-ordination of the methyl group the Pd(tdpea) fragment undergoes dramatic changes. The Pd–N separation decreases from 2.69(2) to 2.23(2) Å, the N–Pd–P angle going from 79.4(1) to 84.6(1)° with a consequent decrease in the displacement of the metal from the phosphorus plane from 0.42 to 0.22 Å. Moreover the nitrogen atom becomes pure sp^3, the C–N–C′ angle being 109.5(9)°. The geometry of [Pd(tdpea)Me]$^+$ is therefore trigonal bipyramidal, the crystallographic three-fold axis passing through the nitrogen, the palladium, and the carbon atom. Also the iodine anion which is 3.59 Å from the methyl carbon lies on the three-fold axis.

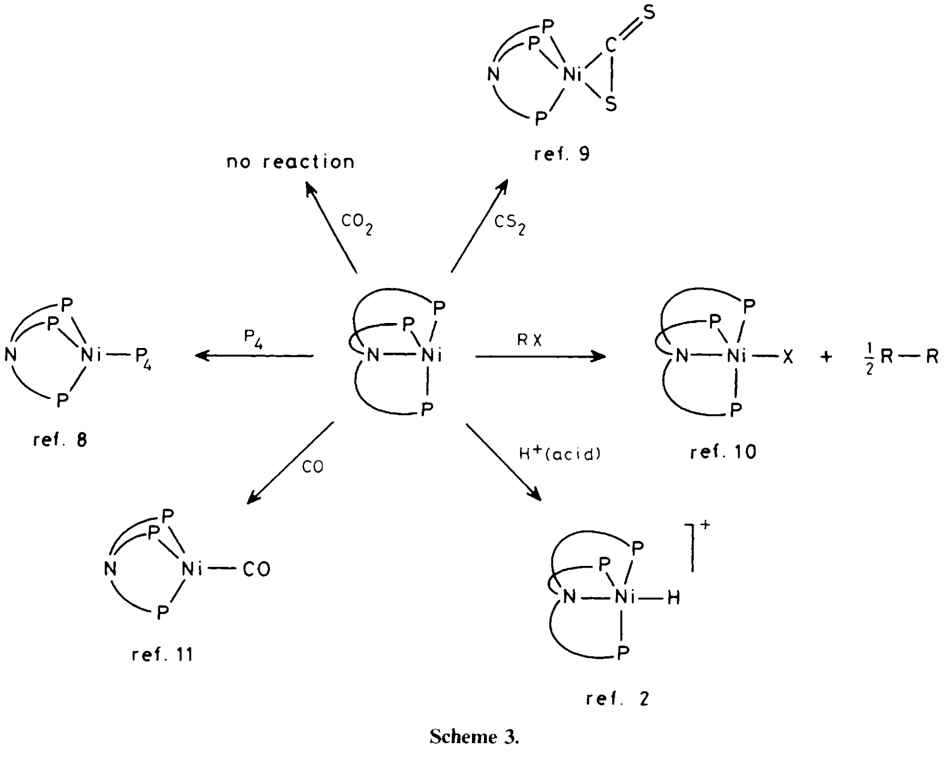
The bond distances within the co-ordination polyhedra of (**1**) and (**2**) appear normal, the shortening of the Pd–P bond distances in (**1**) with respect to (**2**) [2.299(5) *vs.* 2.357(4) Å] being mainly attributable to the different co-ordination number.

The bond distances in the [Pd(tdpea)Me]$^+$ cation are comparable, allowing for the different radius, with those reported for the closely related complex [Ni(tdpea)Me]$^+$.[13] It is noteworthy that, while the palladium alkyl derivative is strictly isostructural with the nickel analogue, the palladium(0) complex differs substantially from the nickel(0) one which exhibits a trigonal pyramidal geometry.

Actually the great geometrical flexibility of the tdpea ligand allows various geometries as well as different co-ordination numbers. The case of [Pd(tdpea)] provides further evidence of the peculiar co-ordination ability of the tdpea ligand. On the other hand some molecular orbital (m.o.) calculations carried out on the d^{10} tdpea fragment by monitoring the geometrical deformation through a combined variation of the N–M–P and M–N parameters showed a very small barrier (7—8 kcal mol^{-1}, *ca.* 29—33 kJ mol^{-1}) of interconversion between the two limit geometries (Scheme 4).[2]

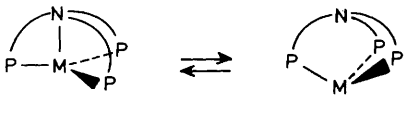


Scheme 2. (*i*) R = Me or Et; (*ii*) R = Pr^n, Bu^n, or CH_2Ph, in the presence of $NaBPh_4$



Scheme 3.

Concerning the molecular packing in the lattice of compound (**2**), the stacking of the I$^-$ anions, the tdpea nitrogen, and the CH_3 group along the three-fold axis, with contact distances of 3.59 and 4.29 Å for I ••• CH_3 and I ••• N respectively, suggests some residual electrostatic interaction between the iodine and the alkyl group. The hypothesis that such a configuration derives directly from the polar transition state, involved in the nucleophilic attack on alkyl halide by the metal complex according to a S_N2 mechanism (Scheme 5), is quite stimulating. Further investigations to elucidate the mechanism of these oxidative additions are currently underway.



Scheme 4.

The reactivity of [Pd(tdpea)] towards organic halides appears quite different with respect to that of [Ni(tdpea)]. The latter has been reported to react with alkyl and aryl halides with a one-equivalent process to form invariably nickel paramagnetic halide complexes.[10] The derivative $[Ni(tdpea)Me]BPh_4$, which has been prepared by reaction of

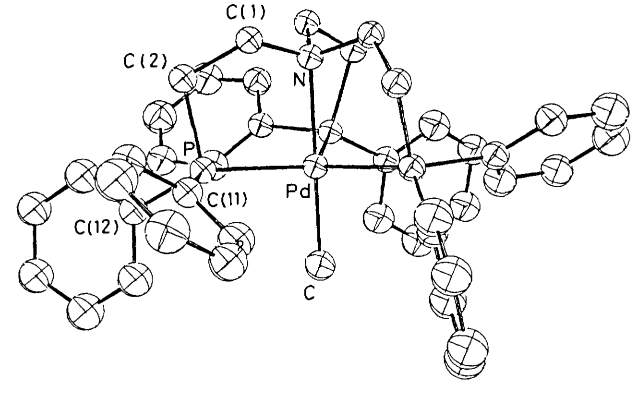
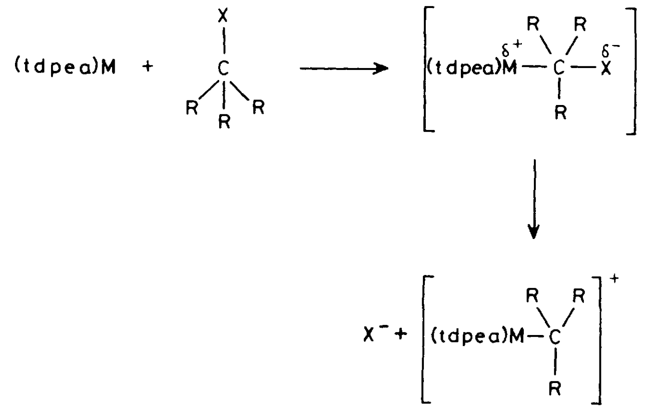


Figure 3. Perspective view of the complex $[\mathrm{Pd(tdpea)(Me)}]^+$. ORTEP drawing with 30% probability ellipsoids



Scheme 5.

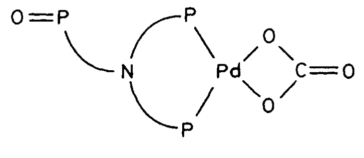
$[\mathrm{Ni(tdpea)Cl}]\mathrm{BPh}_4$ with MgMeCl[13] can be also formed by oxidative-addition reaction of $[\mathrm{HgMe}]\mathrm{NO}_3$ to [Ni(tdpea)][14] [equation (1)].

$$[(\mathrm{tdpea})\mathrm{Ni}] + [\mathrm{HgMe}]^+ \longrightarrow [(\mathrm{tdpea})\mathrm{NiHgMe}]^+ \longrightarrow [(\mathrm{tdpea})\mathrm{NiMe}]^+ + \mathrm{Hg} \quad (1)$$

Thus the different products of the reaction of compound (**1**) with alkyl halides with respect to that of [Ni(tdpea)] must be attributed to a different mechanism, the different nature of the metals appearing to be the real driving force in several reaction processes. The tdpea alkyl derivatives of palladium, in contrast to the related nickel compounds,[15] do not react with CO at atmospheric pressure, so confirming the higher stability of the Pd–C bond compared with the Ni–C one.

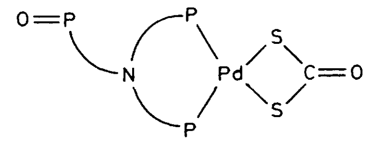
Whereas the complex [Ni(tdpea)] readily reacts with H^+ to form the five-co-ordinated hydride $[\mathrm{Ni(tdpea)H}]^+$.[2,16] the reaction of [Pd(tdpea)] with acids does not afford any identifiable species. Further we were unable to prepare the $[\mathrm{Pd(tdpea)H}]^+$ complex, also by different methods (*i.e.* reactions with NaBH_4). This fact appears rather surprising because the related platinum species $[\mathrm{Pt(tdpea)H}]^+$ is very stable and it can easily be prepared.[17] Moreover the gaseous products from thermolysis, determined by gas chromatographic analysis, of [Pt(tdpea)Et]I at 250 °C were CH_4, $\mathrm{C}_2\mathrm{H}_4$, and $\mathrm{C}_2\mathrm{H}_6$, suggesting initial β elimination.

Solutions of [Pd(tdpea)], under a nitrogen atmosphere, react with CO_2 to form pale yellow crystals in very low yield (*ca.* 5%). The i.r. spectrum of this compound shows bands at 1 665 and 1 640 and at 1 180 and 1 120 cm⁻¹ attributable to the C=O stretching of co-ordinated carbonate and to a phosphine oxide group respectively.[18] The $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum of the complex in $\mathrm{CD}_2\mathrm{Cl}_2$ solution shows signals at δ 20.6 (2 P) and 31.2 (1 P) p.p.m. attributable to two PPh_2 co-ordinated to the metal and to an unco-ordinated $\mathrm{Ph}_2\mathrm{P{=}O}$ group respectively. Preliminary *X*-ray results* confirmed a square planar co-ordination, as shown below. Concerning the formation of the complex, since we have found the yield to increase considerably by adding non-degassed solvents to the reaction solution,† we propose reaction (2), analogous to that previously reported for $[\mathrm{Pt(PPh}_3)_2(\mathrm{CO}_3)]$.[19]



$$[(\mathrm{tdpea})\mathrm{Pd}] + \mathrm{CO}_2 + \mathrm{O}_2 \longrightarrow \mathrm{O{=}PPh_2N(PPh_2)_2Pd(CO_3)} \quad (2)$$

When [Pd(tdpea)] is reacted with CS_2 an orange oil is obtained which after standing in air for a long time (1 d) affords crystals of formula $[\mathrm{Pd(tdpeaO)(CS_2O)}]$. The i.r. spectrum, besides signals at 1 180 and 1 120 cm⁻¹ attributable to a $\mathrm{PPh}_2{=}\mathrm{O}$ group, shows signals at 1 620 and 1 700 cm⁻¹ characteristic of a co-ordinated dithiocarbonate group.[20] The $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum with signals at δ 13.6 (2 P) and 29.1 (1 P) p.p.m. is similar to that of the carbonate, indicating that the structure contains bidentate dithiocarbonate.



The different behaviour of the systems $[\mathrm{Pd(tdpea)}] + \mathrm{CO}_2 + \mathrm{O}_2$ and $[\mathrm{Pd(tdpea)}] + \mathrm{CS}_2 + \mathrm{O}_2$ is consistent with the initial formation of $[\mathrm{Pd(tdpea)(O_2)}]$ and $[\mathrm{Pd(tdpea)(CS_2)}]$ respectively. Thus in the first case a large amount of oxygen favours the complete oxidation of tdpea to the trisphosphine oxide, in the second prolonged exposure is necessary to oxidize the co-ordinated CS_2. The latter process is well known for tripodal CS_2 complexes.[21]

Experimental

The solvents were dried and degassed before use. All operations were performed under nitrogen. The alkyl halides were commercially available. The solid complexes were collected on a sintered-glass frit and washed successively with ethanol and light petroleum (b.p. 40—70 °C) before being dried in a stream of nitrogen. I.r. spectra were recorded on a Perkin-Elmer 457

---

* Unit-cell dimensions: $a = 27.008(16)$, $b = 18.915(12)$, $c = 9.546(6)$ Å, $\beta = 95.91(4)°$, space group $P2_1/a$.

† Prolonged exposure of the reaction solution to air does not improve the yield of the carbonate but results in complete decomposition probably because an excess of oxygen causes the complete oxidation of the ligand.

spectrophotometer, n.m.r. spectra on Varian VXR-300 (^{1}H) and CFT-20 (^{31}P) spectrometers. Chemical shifts are quoted with respect to $SiMe_4$ (^{1}H) or phosphoric acid (^{31}P). The chemical shifts and some coupling constants were assigned on the basis of homonuclear decoupling experiments. G.c. analyses were performed on a Shimadzu GC-8A chromatograph equipped with a thermal conductivity detector and a Carbosiene S-II stainless-steel column (Supelco).

Preparations.—$[Pd(tdpea)]\cdot 0.5Me_2CO$ (**1**). By adding a large excess of $NaBH_4$ in boiling ethanol (20 cm^3) to an acetone (20 cm^3) and ethanol (20 cm^3) solution containing $K_2[PdCl_4]$ (0.65 g, 2 mmol) and tdpea (1.31 g, 2 mmol), crystals of $[Pd(tdpea)]\cdot 0.5Me_2CO$ precipitated {Found: C, 66.0; H, 5.85; N, 1.70. Calc. for $[Pd(tdpea)]\cdot 0.5Me_2CO$: C, 66.2; H, 5.75; N, 1.75%}.

$[Pd(tdpea)(CO)]$. Carbon monoxide was bubbled through a solution of $[Pd(tdpea)]\cdot 0.5Me_2CO$ (0.82 g, 1 mmol) in benzene (50 cm^3). Concentration of the solution, under CO, led to the precipitation of white crystals of $[Pd(tdpea)(CO)]$. The complex must be stored under an atmosphere of CO {Found: C, 64.2; H, 5.25; N, 1.80. Calc. for $[Pd(tdpea)(CO)]$: C, 65.6; H, 5.35; N, 1.80%}. I.r. (Nujol mull): $\nu(NCH_2)$ 2 820; $\nu(CO)$ 1 930 cm^{-1}. ^{31}P-{^{1}H} N.m.r. (C_6D_6): δ 1.13 p.p.m.

$[Pd(tdpea)R]I$ (R = Me *or* Et). An excess of the appropriate alkyl halide was added to a solution of $[Pd(tdpea)]\cdot 0.5Me_2CO$ (0.82 g, 1 mmol) in tetrahydrofuran (thf) (30 cm^3) at room temperature. After a few minutes yellow crystals of $[Pd(tdpea)R]I$ precipitated {Found: C, 57.15; H, 5.05; N, 1.60. Calc. for $[Pd(tdpea)Me]I$: C, 57.25; H, 5.05; N, 1.55%. N.m.r. (CD_2Cl_2): ^{1}H, δ 1.65 [q, $^3J(HP) = 8.2$ Hz]; ^{31}P-{^{1}H}, δ 8.97 p.p.m. Found: C, 59.45; H, 5.25; N, 1.70. Calc. for $[Pd(tdpea)Et]I$: C, 57.7; H, 5.15; N, 1.55%. N.m.r. (CD_2Cl_2):* ^{1}H, δ 1.08 [pseudo-octet, $^4J(HP) = 3.8$, $^3J(HH) = 7$, CH_3], 2.7 [pseudo-septuplet, $^3J(HP) = 6.9$ Hz, CH_2]; ^{31}P-{^{1}H} δ 8.96 p.p.m.}.

$[Pd(tdpea)R]BPh_4\cdot C_4H_8O$ (R = Pr, Bu, *or* CH_2Ph). These complexes were prepared by an analogous method except that $NaBPh_4$ (0.36 g, 1 mmol) in ethanol (30 cm^3) was added to precipitate the crystals {Found: C, 72.9; H, 6.70; N, 1.00. Calc. for $[Pd(tdpea)(Pr)]BPh_4\cdot C_4H_8O$: C, 73.4; H, 6.50; N, 1.15%. N.m.r. ($C^aH_3C^bH_2C^cH_2Pd$) (CD_2Cl_2): ^{1}H, δ 0.77 [t, $^3J(HH) = 7.1$ Hz, CH_3], 1.54 (m, C^bH_2), and 2.62 [m, $^3J(HP) = 6.6$ Hz, C^cH_2]; ^{31}P-{^{1}H}, δ 8.49 p.p.m. Found: C, 74.35; H, 6.70; N, 1.05. Calc. for $[Pd(tdpea)(Bu)]BPh_4\cdot C_4H_8O$: C, 73.55; H, 6.60; N, 1.15%. N.m.r. ($C^aH_3C^bH_2C^cH_2C^dH_2Pd$) ($CD_2Cl_2$): ^{1}H, δ 0.63 [t, $^3J(HH) = 7.3$ Hz, CH_3], 1.18 (m, C^bH_2), 1.47 (m, C^cH_2), and 2.65 (m, C^dH_2); ^{31}P-{^{1}H} δ 8.51 p.p.m. Found: C, 75.75; H, 6.35; N, 1.00. Calc. for $[Pd(tdpea)(CH_2Ph)]BPh_4\cdot C_4H_8O$: C, 74.4; H, 6.25; N, 1.10%. N.m.r. (CH_2Pd) (CD_2Cl_2): ^{1}H, δ 3.65 [q, $^3J(HP) = 6.6$ Hz]; ^{31}P-{^{1}H}, δ 8.23 p.p.m.}.

$[Pd(tdpeaO)(CO_3)]$. Carbon dioxide was bubbled for *ca.* 10 min through a solution of $[Pd(tdpea)]\cdot Me_2CO$ (0.82 g, 1 mmol) in Me_2CO (50 cm^3). After addition of ethanol (20 cm^3), yellow crystals of $[Pd(tdpeaO)(CO_3)]$ separated {Found: C, 60.9; H, 5.45; N, 1.60. Calc. for $[Pd(tdpeaO)(CO_3)]$: C, 61.75; H, 5.05; N, 1.65%}. I.r.(Nujol mull): $\nu(CO)$ 1 665 and 1 640, $\nu(PO)$ 1 180 and 1 120 cm^{-1}. ^{31}P-{^{1}H} N.m.r. (CD_2Cl_2): δ 20.6 (2 P) and 31.2 (1 P) p.p.m.

$[Pd(tdpeaO)(CS_2O)]$. This complex was prepared by a method analogous to that used for the carbonate derivative but with bubbling of carbon disulphide vapour instead of carbon dioxide {Found: C, 58.0; H, 5.20; N, 1.60. Calc. for $[Pd(tdpeaO)(CS_2O)]$: C, 59.5; H, 4.90; N, 1.60%}. I.r.(Nujol mull): $\nu(CO)$ 1 700 and 1 620, $\nu(PO)$ 1 180 and 1 120 cm^{-1}. ^{31}P-{^{1}H} N.m.r. (CD_2Cl_2): δ 13.6 (2 P) and 29.1 (1 P) p.p.m.

Table 2. Crystal data and data collection details *

Complex	(**1**)	(**2**)
Formula	$C_{43.5}H_{45}NOP_3Pd$	$C_{43}H_{45}INP_3Pd$
M	782.17	902.07
a/Å	10.827(8)	10.570(7)
α/°	108.82(9)	106.10(7)
U/Å^3	999.9	1 006.7
D_c/g cm^{-3}	1.310	1.488
F(000)	408	454
Crystal habit	Rhombohedral	Hexagonal prism
Dimensions/mm	0.15 × 0.15 × 0.15	0.15 × 0.15 × 0.075
μ(Mo-K_α)/cm^{-1}	6.05	13.60
Scan speed/° s^{-1}	0.08	0.05
Max. deviation of standards (intensity)/%	20	3
2θ limits/°	5—40	5—50
Total data	702	1 308
Data used [$I \geqslant 3\sigma(I)$]	574	883

* Details common to both compounds: $Z = 1$; space group $R3$; colour, yellow; scan method, ω—2θ; background time, half scan time; scan width, $0.7 + 0.3\tan\theta$; standards, 3 every 120; final parameters, 55; temperature, 22 °C.

X-Ray Crystallography.—Collection and reduction of intensity data. Intensity data for both compounds were collected on a Philips PW 1100 automatic diffractometer, using Mo-K_α monochromatized radiation ($\lambda = 0.7107$ Å). Details are given in Table 2. Unit-cell parameters were determined from a least-squares refinement of the setting angles of 20 carefully centred reflections. The intensities were rescaled on the basis of three standard reflections, which were monitored during the collection. While no particular trend was noticed for the crystal of (**2**), compound (**1**) appeared extremely air-sensitive and some decay (20%) was noticed throughout the collection. After correction for the background, the intensities were assigned a standard deviation σ, calculated with an instability factor k of 0.03 for both compounds.[22] All data were corrected for Lorentz polarization effects. An X-ray absorption correction was applied to compound (**2**),[23] but not for compound (**1**), owing to the equidimensional shape of the crystal as well as to the small linear absorption coefficient.

Solution and refinement of the structure. All the calculations were performed by using SHELX 76[23] and ORTEP[24] programs on a SEL 32/77 computer. Atomic scattering factors for all non-hydrogen atoms were taken from ref. 25 and those for hydrogen atoms from ref. 26. An anomalous dispersion correction was applied to the calculated structure factor amplitudes.[27] The function minimized during the refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The structure of each compound was solved by the heavy-atom method. Successive Fourier syntheses enabled location of all non-hydrogen atoms. Full-matrix least-squares refinements were carried out with anisotropic thermal motion for palladium, phosphorus, and nitrogen atoms. Throughout the refinement the phenyl rings were treated as rigid bodies of D_{6h} symmetry. The hydrogen atoms were introduced in their calculated geometrical positions, but were not refined.

From a ΔF Fourier map of compound (**1**), a disordered solvent acetone molecule, lying on a three-fold axis, was detected. In both compounds, owing to the chirality of the space group $R3$, two possible enantiomeric structures must be considered: the x,y,z and the inverted $\bar{x},\bar{y},\bar{z}$ one. For compound (**1**) refinement of the two possibilities gave R, R' of 0.054,0.051 and 0.056,0.053 respectively; for compound (**2**) the two refinements gave R, R' of 0.050,0.051 and 0.055,0.056 respectively. An analysis of the standard deviations confirmed

---

* In the previous communication[3] the signals of CH_3CH_2 in the ^{1}H n.m.r. spectrum were not correctly assigned due to the poor resolution of the spectrum recorded at 80 MHz.

Table 3. Positional parameters (× 10^4) for [Pd(tdpea)]·$0.5Me_2CO$

Atom	*x*	*y*	*z*
Pd	0	0	0
P	458(6)	−942(6)	1 620(6)
N	2 405(20)	2 405(20)	2 405(20)
C(1)	2 877(19)	1 891(19)	3 473(18)
C(2)	1 592(19)	754(18)	3 412(19)
C(11)	1 594(16)	−1 874(13)	1 633(12)
C(21)	2 518(16)	−1 791(13)	2 934(12)
C(31)	3 376(16)	−2 513(13)	2 895(12)
C(41)	3 309(16)	−3 317(13)	1 554(12)
C(51)	2 384(16)	−3 399(13)	253(12)
C(61)	1 527(16)	−2 678(13)	293(12)
C(12)	−938(17)	−2 170(16)	1 901(14)
C(22)	−1 685(17)	−3 687(16)	919(14)
C(32)	−2 801(17)	−4 653(16)	1 040(14)
C(42)	−3 169(17)	−4 101(16)	2 144(14)
C(52)	−2 422(17)	−2 583(16)	3 126(14)
C(62)	−1 307(17)	−1 618(16)	3 005(14)
C(3)*	6 506(110)	6 506(110)	6 506(110)
C(4)*	6 467(73)	7 344(68)	6 248(72)

* Of the solvent molecule.

Table 4. Positional parameters (× 10^4) for [Pd(tdpea)Me]I

Atom	*x*	*y*	*z*
Pd	0	0	0
I	5 340(2)	5 340(2)	5 340(2)
P	264(4)	−1 244(4)	1 530(4)
N	1 829(16)	1 829(16)	1 829(16)
C	−1 722(26)	−1 722(26)	−1 722(26)
C(1)	2 417(16)	1 337(15)	2 918(16)
C(2)	1 327(18)	306(18)	3 202(18)
C(11)	1 376(13)	−2 278(12)	1 393(10)
C(21)	2 209(13)	−2 420(12)	2 584(10)
C(31)	3 077(13)	−3 189(12)	2 445(10)
C(41)	3 113(13)	−3 815(12)	1 114(10)
C(51)	2 280(13)	−3 673(12)	−78(10)
C(61)	1 412(13)	−2 905(12)	62(10)
C(12)	−1 161(15)	−2 351(14)	1 852(11)
C(22)	−2 112(15)	−3 634(14)	730(11)
C(32)	−3 230(15)	−4 541(14)	909(11)
C(42)	−3 396(15)	−4 166(14)	2 208(11)
C(52)	−2 445(15)	−2 883(14)	3 330(11)
C(62)	−1 328(15)	−1 975(14)	3 151(11)

that the structures corresponding to the lower values of *R* were the correct ones. Final positional parameters for both compounds are given in Tables 3 and 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Acknowledgements

We are grateful to Mr. F. Nuzzi for elemental analyses and to Mr. P. Innocenti for technical assistance.

References

1 L. Sacconi and F. Mani, in 'Transition Metal Chemistry,' eds. G. A. Melson and B. N. Figgis, Marcel Dekker, New York, 1982, vol. 8.
2 F. Cecconi, C. A. Ghilardi, P. Innocenti, C. Mealli, S. Midollini, and A. Orlandini, *Inorg. Chem.*, 1984, **23**, 922.
3 C. A. Ghilardi, S. Midollini, S. Moneti, and A. Orlandini, *J. Chem. Soc., Chem. Commun.*, 1986, 1771.
4 P. Dapporto, L. Sacconi, P. Stoppioni, and F. Zanobini, *Inorg. Chem.*, 1981, **20**, 3834.
5 C. Mealli and L. Sacconi, *J. Chem. Soc., Chem. Commun.*, 1973, 886.
6 C. Bianchini, A. Meli, and G. Scapacci, *Organometallics*, 1983, **2**, 1834.
7 S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Am. Chem. Soc.*, 1976, **98**, 5850 and refs. therein.
8 P. Dapporto, S. Midollini, and L. Sacconi, *Angew. Chem.*, 1979, **91**, 510.
9 C. Bianchini, C. A. Ghilardi, A. Meli, and A. Orlandini, *J. Organomet. Chem.*, 1984, **270**, 251.
10 A. Biliotti, R. Morassi, and P. Stoppioni, *J. Organomet. Chem.*, 1982, **236**, 119.
11 C. A. Ghilardi, A. Sabatini, and L. Sacconi, *Inorg. Chem.*, 1976, **15**, 2763.
12 G. M. Whitesides and J. F. Gaasch, *J. Organomet. Chem.*, 1971, **33**, 241.
13 C. Benelli, P. Dapporto, P. Innocenti, L. Sacconi, and P. Stoppioni, *Inorg. Chem.*, 1977, **16**, 1669.
14 S. Midollini, unpublished work.
15 P. Dapporto, L. Sacconi, and P. Stoppioni, *Inorg. Chem.*, 1978, **17**, 718.
16 L. Sacconi, A. Orlandini, and S. Midollini, *Inorg. Chem.*, 1974, **13**, 2850.
17 S. Midollini and S. Moneti, unpublished work.
18 C. Bianchini, C. Mealli, A. Meli, and M. Sabat, *Inorg. Chem.*, 1984, **23**, 273.
19 C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc. A*, 1968, 561.
20 C. Bianchini, A. Meli, and A. Orlandini, *Inorg. Chem.*, 1982, **21**, 4166.
21 C. Bianchini and A. Meli, *J. Chem. Soc., Chem. Commun.*, 1983, 157.
22 P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1976, **6**, 197.
23 G. M. Sheldrick, SHELX System of Computing Programs, University of Cambridge, 1976.
24 C. K. Johnson, ORTEP, Report ORNL (U.S.) ORNL-5138, Oak Ridge National Laboratory, Tennessee.
25 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 99.
26 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
27 Ref. 25, p. 149.

Received 1st February 1988; *Paper* 8/00492G