Hydrogen Abstractions from an Olefinic Di(tertiary phosphine) Promoted by Complexes of Divalent Nickel, Palladium, and Platinum. Chelate η^3-Allyl, η^1-Allyl, and η^1-Alkenyl Complexes and the Crystal and Molecular Structure of a Chelate η^1-Allylpalladium(II) Complex

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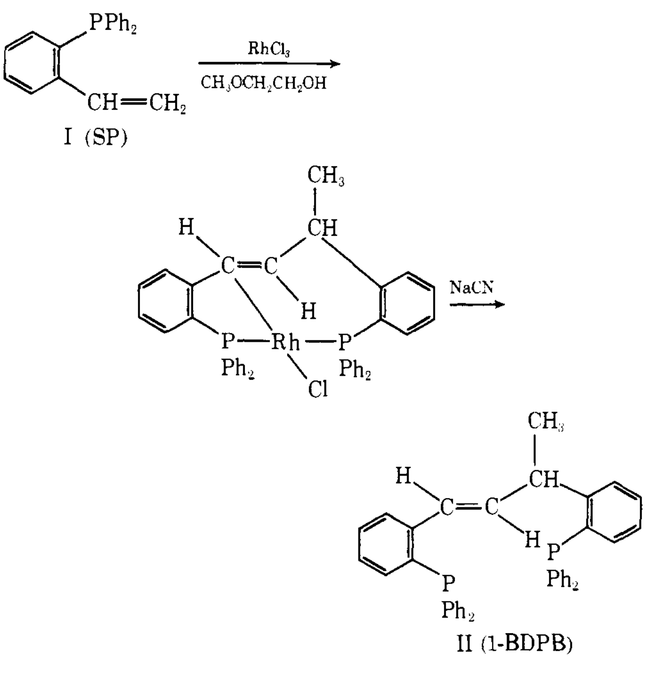
Abstract: The olefinic di(tertiary phosphine) 1,3-bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene, *o*-$Ph_2PC_6H_4$-*t*-$CH{=}CHCH(CH_3)C_6H_4PPh_2$-*o* (1-BDPB) (II), reacts with dichloro complexes of nickel(II), palladium(II) and platinum(II) to give complexes of apparent empirical formula "MCl (1-BDPB)" in which a hydrogen atom has been lost from the tertiary carbon atom of the carbon chain of the ligand. In the case of nickel(II) the product is an approximately 1:1 mixture of isomers of the pseudo-five-coordinate chelate η^3-allyl complex 1-3η-{1,3-bis[(*o*-diphenylphosphino)phenyl]-1-methallyl}chloronickel(II) (III). ^{31}P NMR data suggest that both isomers contain mutually cis-phosphorus atoms. In the case of palladium(II) the product is a chelate η^1-allyl complex $PdCl[o\text{-}Ph_2PC_6H_4CHCH{=}C(CH_3)C_6H_4PPh_2\text{-}o]$ (IV) in which the double bond has migrated from the 1- to the 2-position in the carbon chain. Complex IV crystallizes in the nonstandard monoclinic space group $P2_1/n$, with a = 13.055(5) Å, b = 18.151(7) Å, c = 15.224 (6) Å, β = 112.43 (2)°, and Z = 4. Using data collected by counter methods, the structure has been refined by block diagonal least-squares methods to weighted and unweighted R factors of 0.037 and 0.029, respectively, for the 4436 reflections which are significantly above background. The coordination about the central palladium atom is essentially square planar with the two phosphorus atoms of the tridentate ligand being mutually trans, a feature which can also be inferred from the ^{31}P NMR spectrum. The chlorine atom is trans to the σ-bonded carbon atom (Pd–C, 2.071 (3) Å), the trans-bond weakening influence of which is evident from the long Pd–Cl distance (2.413 (1) Å). NMR data suggest that a platinum complex V which is prepared similarly to IV has a similar structure. The rearrangement is suggested to proceed via an intermediate η^3-allyl species containing cis-phosphorus atoms. A cationic complex of this type can be isolated as its tetrafluoroborate salt VII in the case of palladium by treatment of IV with $AgBF_4$. Reaction of $PtCl(CH_3)(COD)$ (COD = 1,5-cyclooctadiene) with 1-BDPB gives a complex VI which is isomeric with V and is assigned the chelate η^1-alkenyl structure $PtCl[o\text{-}Ph_2PC_6H_4CH{=}CCH(CH_3)C_6H_4PPh_2\text{-}o]$, i.e., a vinylic hydrogen atom has been eliminated from 1-BDPB. The alkenyl unit is retained on reaction of VI with $AgBF_4$ to give a cationic aquo complex VIII, but on treatment with hydrogen chloride, VI rearranges to V. The reaction of 1-BDPB with $Pt(CH_3)_2(COD)$ occurs without loss of a hydrogen atom from the carbon chain to give $Pt(CH_3)_2$(1-BDPB) (IX). In this complex 1-BDPB is coordinated only through the mutually cis-phosphorus atoms, thus giving rise to a ten-membered chelate ring. A tentative explanation is offered for the hydrogen abstraction results based on the likely relative acidities of the eliminated protons.

Recent work in this laboratory has shown that the olefinic ligand (2-vinylphenyl)diphenylphosphine (*o*-styryldiphenylphosphine), *o*-$CH_2{=}CHC_6H_4PPh_2$ (I), abbreviated SP, undergoes reactions with ruthenium- or rhodium-containing precursors in which vinyl groups are coupled in various ways on the metal center.[1-3] The reaction with rhodium trichloride gives the chlororhodium(I) complex of a dimer of SP, 1,3-bis[*o*-(diphenylphosphino)phenyl]-*trans*-1-butene, *o*-$Ph_2PC_6H_4$-*t*-$CH{=}CHCH(CH_3)C_6H_4PPh_2$-*o* (II) (abbreviated 1-BDPB), which is coordinated to the metal via two mutually trans-phosphorus atoms and the double bond.[2] The free ligand 1-BDPB can be readily isolated by treatment of the rhodium(I) complex with excess cyanide ion (Scheme I).

The tendency of the phosphorus atoms of II to occupy trans positions in metal complexes forces the connecting carbon chain into proximity with the metal atom, and this feature suggested that olefinic or aliphatic C–H bonds might readily be cleaved on reaction of 1-BDPB with other d^8 metal ions. We report here the chemistry of 1-BDPB with nickel(II), palladium(II), and platinum(II), together with the single-crystal x-ray structural analysis of a resulting chelate palladium(II)-carbon σ-bonded complex.

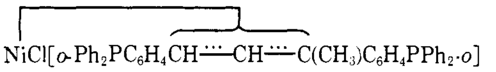
Scheme I



Experimental Section

Preparative, analytical, and spectroscopic procedures have been described previously.[1,3] *o*-Styryldiphenylphosphine (I)[4] was converted into 1,3-bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene, 1-BDPB (II), by heating with rhodium trichloride in 2-methoxyethanol, the resulting complex RhCl(1-BDPB) then being decomposed with sodium cyanide;[2] full details of this preparation will appear shortly. The complexes $NiCl_2(CH_3OCH_2CH_2OCH_3)$, $NiCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$, $PtCl_2(COD)$, $PtCl_2(PhCN)_2$, $PtCl(CH_3)(COD)$, and $Pt(CH_3)_2(COD)$ (COD = 1,5-cyclooctadiene) were made by standard literature methods. Analytical, mass spectrometric, melting point, and selected infrared data are in Table I; ^1H and ^{31}P NMR data are in Table II.

Preparations. 1–3η-{1,3-Bis[(*o*-diphenylphosphino)phenyl]-1-methallyl}chloronickel(II), Isomer Mixture IIIa, IIIb. A mixture of



$NiCl[o\text{-}Ph_2PC_6H_4CH\overset{\cdots}{—}CH\overset{\cdots}{—}C(CH_3)C_6H_4PPh_2\text{-}o]$

1-BDPB (0.20 g, 0.35 mmol) and $NiCl_2(CH_3OCH_2CH_2OCH_3)$ (0.075 g, 0.34 mmol) in 2-methoxyethanol (35 ml) was heated under reflux in a nitrogen atmosphere for 2 h. After removal of the solvent in vacuo, the residue was dissolved in benzene (5 ml). The solution was filtered, treated with *n*-hexane (20 ml) and allowed to stand overnight. The supernatant liquid was decanted and the dark reddish brown microcrystalline product was washed with *n*-hexane and dried at 50° (10^{-3} mm) for 2 h. The yield was 0.086 g (38% based on nickel). The complex can also be prepared from $NiCl_2(PPh_3)_2$ and 1-BDPB under similar conditions.

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-2-buten-1-yl}chloropalladium(II), $PdCl[o\text{-}Ph_2PC_6H_4CHCH{=}C(CH_3)C_6H_4PPh_2\text{-}o]$ (IV). 1-BDPB (0.09 g, 0.16 mmol) and $PdCl_2(PhCN)_2$ (0.06 g, 0.16 mmol) were heated in a mixture of toluene (20 ml) and 2-methoxyethanol (10 ml) under reflux in a nitrogen atmosphere for 2 h. Workup as described above and recrystallization from 1:4 v/v chloroform/*n*-hexane or dichloromethane/*n*-hexane gave 0.083 g (70%) of yellow crystalline product.

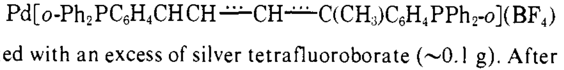
The reaction can also be carried out in pure toluene as solvent and in this case hydrogen chloride evolution is evident ($AgNO_3$ test) even before the reactants are heated.

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-2-buten-1-yl}chloroplatinum(II), $PtCl[o\text{-}Ph_2PC_6H_4CHCH{=}C(CH_3)C_6H_4PPh_2\text{-}o]$ (V). This was prepared similarly to the palladium analogue **IV**, starting either from $PtCl_2(COD)$ (0.044 g, 0.12 mmol) and 1-BDPB (0.07 g, 0.12 mmol) or $PtCl_2(PhCN)_2$ (0.082 g, 0.17 mmol) and 1-BDPB (0.1 g, 0.17 mmol) and heating under reflux in acetone for 20 min. After recrystallization from 1:4 v/v dichloromethane/*n*-hexane, 0.082 g (94%) of the pale yellow, crystalline product was obtained.

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-1-buten-2-yl}chloroplatinum(II), $PtCl[o\text{-}Ph_2PC_6H_4CH{=}CCH(CH_3)C_6H_4PPh_2\text{-}o]$ (VI). A mixture of 1-BDPB (0.17 g, 0.3 mmol) and $PtCl(CH_3)(COD)$ (0.1 g, 0.28 mmol) was heated under reflux in 2-methoxyethanol (35 ml) in a nitrogen atmosphere for 2 h. Workup as described for **IV** and several recrystallizations from 1:3 v/v benzene/*n*-hexane to remove oily impurities gave the colorless crystalline product (0.1 g, 44%).

Isomerization of VI to V. A solution of VI (0.05 g) in dichloromethane (10 ml) was treated with dry hydrogen chloride for 2 min. Solvent was removed in vacuo and the residue heated under reflux with acetone (20 ml) for 15 min. The insoluble product was identified as V by its ^1H NMR and far-ir spectra; the yield was essentially quantitative.

1–3η-{1,3-Bis[(*o*-diphenylphosphino)phenyl]-1-methallyl}palladium(II) Tetrafluoroborate (VII). A solution of IV (0.1 g) in acetone was



$Pd[o\text{-}Ph_2PC_6H_4CHCH\overset{\cdots}{—}CH\overset{\cdots}{—}C(CH_3)C_6H_4PPh_2\text{-}o](BF_4)$

treated with an excess of silver tetrafluoroborate (~0.1 g). After removal of silver chloride by filtration, the product was precipitated as colorless microcrystals by addition of *n*-hexane, and dried in vacuo. The ir spectrum showed a broad absorption at 1640 cm^{-1} and the ^1H NMR spectrum in CD_2Cl_2 showed a broad resonance at δ 3.26 due to water.

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene}dimethylplatinum(II), $Pt(CH_3)_2[o\text{-}Ph_2PC_6H_4\text{-}t\text{-}CH{=}CHCH(CH_3)C_6H_4PPh_2\text{-}o]$ (IX). A mixture of 1-BDPB (0.14 g, 0.24 mmol) and $Pt(CH_3)_2(COD)$ (0.08 g, 0.24 mmol) was heated under reflux in toluene (20 ml) in a nitrogen atmosphere for 30 min. Workup as described for IV and recrystallization from 1:3 toluene/*n*-hexane gave 0.15 g (74%) of the colorless crystalline product in the form of a toluene solvate.

Collection and Reduction of X-Ray Intensity Data. Approximate unit cell dimensions for crystals of IV, grown from dichloromethane/*n*-hexane, were obtained from preliminary Weissenberg (*hk*0, *hk*1 data) and precession (0*kl*, 1*kl*, *h*0*l*, *h*1*l* data) photographs, which showed systematic absences (0*k*0 data, for $k = 2n + 1$) (*h*0*l* data, for $h + l = 2n + 1$) corresponding to space group $P2_1/n$. Space group $P2_1/n$ is a nonstandard setting of space group $P2_1/c$ (C^5_{2h}, No. 14).

The crystal chosen for data collection was transferred to a Picker FACS-1 fully automatic four-circle diffractometer, and was aligned with the crystallographic *c* axis and the instrumental Φ axis approximately coincidental. The unit cell dimensions (together with estimated standard errors) and the crystal orientation matrix were obtained from the least-squares refinement[5] of the 2θ, ω, χ, and Φ values found for 12 carefully centered high angle reflections ($2\theta \geqslant 89°$). Full details of the crystal data are collected in Table III.

Details of data collection and experimental conditions are given in Table IV.

Reflection intensities were reduced to values of $|F_o|$, and each reflection was assigned an individual estimated standard deviation $[\sigma(F_o)]$.[6] For this data set, the instrumental "uncertainty" factor (ρ),[7] was assigned a value of $(0.002)^{1/2}$.

The reflection data were sorted to a convenient order, reflection indices ($hk\bar{l}$, $\bar{h}k\bar{l}$) were transformed to the standard form (hkl, $hk\bar{l}$), equivalent reflections and multiple observations were averaged, and those reflections with $I/\sigma(I) < 3.0$[6] were discarded as being unobserved. The statistical *R* factor[6] (R_s) for the 4436 reflections of the terminal data set was 0.021.

Solution and Refinement of the Structure. The positions of the palladium, phosphorus, and chlorine atoms were determined from an unsharpened three-dimensional Patterson map. The remaining atoms of the molecule were located from successive difference Fourier syntheses. Using data which had been corrected for absorption effects,[8] the structure was refined by block-diagonal least-squares methods (using either 4 × 4 (isotropic) or 3 × 3 and 6 × 6 (anisotropic) matrices) to unweighted and weighted *R* factors of 0.029 (*R*) and 0.037 (R_w), respectively. Atomic scattering factors for the non-hydrogen atoms, which were corrected for the real and imaginary parts of anomalous scattering,[9,10] were taken from the compilation of Cromer and Mann.[11] Hydrogen atom scattering factors were taken from the compilation of Stewart et al.[12] A full description of the course of refinement is given in Table V.

When calculated hydrogen atom coordinates were included in the scattering model, as fixed contributions to F_c, the C–H distance was assumed to be 0.95 Å.[13] The hydrogen atoms were assigned fixed isotropic temperature factors which were 10% greater than the equivalent isotropic temperature factor of the carbon atom to which they were bonded (i.e., $B_H = 1.1B_C$ Å^2). Hydrogen atom coordinates and temperature factors were recalculated prior to each refinement cycle. No attempt was made to include the three methyl hydrogen atoms (bonded to C(31)) in the scattering model.

On the final cycle of least-squares refinement, no individual parameter shift was greater than 0.1 of the corresponding parameter esd (estimated standard deviations were obtained from inversion of the block-diagonal matrices). A final electron-density difference map showed no positive maxima greater than 0.3 e/Å^3. The standard deviation of an observation of unit weight, defined as $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ (where *m* is the number of observations, and *n* (=397) is the number of parameters varied), is 1.20; cf. an expected value of 1.0 for ideal weighting. Comparison of the final $|F_o|$ and $|F_c|$ values showed no evidence of serious extinction effects, and there was no serious dependence of the minimized function on either $|F_o|$ or $\lambda^{-1} \sin\theta$.

The final atomic positional and thermal parameters, together with their estimated standard deviations (where applicable) are listed in Table VI. A listing of observed and calculated structure factor amplitudes [×10 (electrons)] is available (for details regarding the availability of supplementary material, see the paragraph at the end of this paper).

Computer Programs. The data reduction program SETUP3 was written locally for operation on the Univac-1108 computer (Whimp). The sorting (SORTIE), Fourier (ANUFOR), and block-diagonal least-squares refinement (BLKLSQ) programs have been described previously.[14] Absorption corrections were carried out using program

Table I. Analytical, Mass Spectrometric, Melting Point, and Selected Infrared Data[a]

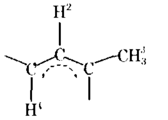
	% C		% H		% Cl		% P		Mol wt				Ir (cm^{-1})		
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	MS	Mp, °C	ν(MCl)	ν(C=C)	δ(=CH)
III	71.7	72.9	5.0	5.0	5.3	5.3	9.2	8.5	669	680	669 (M$^+$) 634 (M – Cl$^+$)	dec > 190	*b*		935 w (?)
IV (i)[c]	65.1	64.8	4.5	4.7	7.7	7.9	8.4	8.0	716	740	716 (M$^+$)	dec > 235	282	*b*	980 m, 892 s[e]
(ii)[d]	66.3	66.3	4.6	4.9	5.9	6.1	8.5	8.5			681 (M – Cl$^+$)				
V (i)[f]	58.9	58.7	4.1	4.5	5.6	6.0	7.6	6.9	806	801	805 (M$^+$)	dec > 240	272	*b*	986 w, 890 s[e]
(ii)[d]	59.6	59.8	4.1	4.2	4.4	4.6	7.7	7.8			770 (M – Cl$^+$)				
VI	59.6	58.7	4.1	4.5	4.4	4.7	7.7	7.8	806	nm	805 (M$^+$) 770 (M – Cl)$^+$	dec > 180	283	1615 vw (?)	942 w (?), 888 s[e]
VII	61.1	59.9	4.5	5.0			7.9	7.5							
IX[g]	64.5	64.7	5.2	5.3			7.3	7.3	802	784	785 (M – CH$_4$)$^+$	dec > 185		*b*	970 s

[a] Molecular weights determined by vapor pressure osmometry in CHCl$_3$ at 37° except where stated, mass spectra recorded at 70 eV, and ir spectra measured as Nujol mulls on CsI windows. Abbreviations: s, strong; m, medium; w, weak; vw, very weak; nm, not measured. [b] Could not be located. [c] Sample recrystallized from CHCl$_3$/*n*-hexane. Calculated analytical figures refer to solvate containing 0.2 mol of CHCl$_3$, mol wt calculated for unsolvated complex. [d] Sample recrystallized from CH$_2$Cl$_2$/CH$_3$OH and dried at 60° (0.01 mm) for 18 h. Calculated analytical figures for IV refer to solvate containing 0.1 mol of CH$_2$Cl$_2$, confirmed by presence of band at δ 5.26 in ^{1}H NMR spectrum. [e] Band probably associated with benzylic C–H. [f] Calculated analytical data refer to solvate containing 0.1 mol of CHCl$_3$. [g] Calculated analytical figures refer to solvate containing 0.5 mol of toluene confirmed by presence of a band at δ 2.3 in the ^{1}H NMR spectrum. Mol wt calculated for unsolvated complex and measured in CH$_2$Cl$_2$ at 25°.

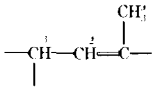
Table II. ^{1}H and ^{31}P NMR Spectra of Complexes Derived from 1-BDPB[a–c]

	Chemical shifts					Coupling constants		
	H$_1$	H$_2$	H$_3$	P$_1$	P$_2$	$J_{\mathrm{H-H}}$	$J_{\mathrm{P-H}}$	$^2J_{\mathrm{P-P}}$
IIIa	5.16 dd (d)[d]	5.48 dd (d)[d]	1.66 d (s)	37.8	35.2	$J_{12} = 11, J_{23} = 0$	$J_{\mathrm{P_1-H_1}} = 6.5, J_{\mathrm{P_2-H_1}} = 0, J_{\mathrm{P_1-H_2}} = 0, J_{\mathrm{P_2-H_2}} = 9,$ $J_{\mathrm{P_1-H_3}} = 12, J_{\mathrm{P_2-H_3}} = 0$	10
IIIb	3.17 dd (d)[d]	6.23 td (d)[d]	1.66 d (s)	40.2	20.6	$J_{12} = 9.5, J_{23} = 0$	$J_{\mathrm{P_1-H_1}} = 1, J_{\mathrm{P_2-H_1}} = 16.5, J_{\mathrm{P_1-H_2}} = 3.5, J_{\mathrm{P_2-H_2}} = 4.5,$ $J_{\mathrm{P_1-H_3}} = 9.5, J_{\mathrm{P_2-H_3}} = 0$	74
IV[e]	5.42 m (m)	5.64 m (m)	1.33 dd (d)	44.0	15.7	$J_{12} = 11, J_{23} = 1.5$	$J_{\mathrm{P-H_1}} = 9, 2; J_{\mathrm{P-H_2}} = 3.5, 0; J_{\mathrm{P-H_3}} = 4,0$	381
V	5.03 m (d)	5.42 m (dd)	1.37 t (d)	38.2	23.0	$J_{12} = 11, J_{23} = 1.5$	$J_{\mathrm{P-H_1}} = 9, 1; J_{\mathrm{P-H_2}} = 2, 0; J_{\mathrm{P-H_3}} = 1.5, 0$[f]	435
VI	6.58 d (s)	—	1.17 d (d)[g]	24.6	1.5	$J_{34} = 7$	$J_{\mathrm{P-H_1}} = 2, 0; J_{\mathrm{P-H_4}} = 2, 0; J_{\mathrm{P-H_3}} = 0$[h]	431
VII	6.50 dd (d)	6.02 d (d)	1.72 dd (s)[i]	36.6	34.4	$J_{12} = 12, J_{23} = 0$	$J_{\mathrm{P-H_1}} = 10, 0; J_{\mathrm{P-H_2}} = 0, 0; J_{\mathrm{P-H_3}} = 6.5, 3.5$	15
VIII	6.47 d (s)	—	1.24 d (d)[j]	24.3	5.9	$J_{34} = 6.5$	$J_{\mathrm{P-H_1}} = 1.5, 0; J_{\mathrm{P-H_4}} = 1.5, 0; J_{\mathrm{P-H_3}} = 0, 0$[k]	369
IX	5.85 m (m)	5.65 m (m)[l]	1.51 d (d)[m]	27.7	20.5	$J_{12} = 15.5, J_{24} = 3.5,$ $J_{34} = 7, J_{23} = 0$	$J_{\mathrm{P-H_2}} = 2$ (sum), remainder zero[n]	12

[a] ^{1}H NMR spectra measured in CDCl$_3$ at 32° except where stated otherwise, δ in ppm downfield of Me$_4$Si. ^{31}P {^{1}H} NMR spectra measured in CH$_2$Cl$_2$ at 34°, δ_{P} in ppm downfield of 85% H$_3$PO$_4$ external reference. *J* is in Hz (±0.5 for H–H and P–H, ±5 for P–P, ±10 for Pt–P). Multiplicities in ^{1}H {^{31}P} spectra are in parentheses. Aromatic resonances are complex multiplets in range δ 6.5–8.1 for all compounds. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; td, triplet of doublets; br, broad. [b] Chain protons are numbered as shown in structures below. [c] ^{31}P nucleus at lower field labeled P$_1$. [d] Assignment of H$_1$ and H$_2$ could be reversed. [e] ^{1}H NMR spectrum measured in CD$_2$Cl$_2$. [f] $J_{\mathrm{Pt-H_1}} = 98, J_{\mathrm{Pt-H_2}} = 0, J_{\mathrm{Pt-H_3}} = 0, J_{\mathrm{Pt-P}} = 3280, 3290$. [g] δ(H$_4$) 3.77 m (q). [h] $J_{\mathrm{Pt-H_1}} = 95, J_{\mathrm{Pt-H_4}} = 71, J_{\mathrm{Pt-P_1}} = 2969, J_{\mathrm{Pt-P_2}} = 2868$. [i] δ(H$_2$O) 3.26 br s. [j] δ(H$_4$) 3.62 br m (1:3:3:1 q). [k] $J_{\mathrm{Pt-H_1}} = 116, J_{\mathrm{Pt-H_4}} = 86, J_{\mathrm{Pt-P_1}} = 2899, J_{\mathrm{Pt-P_2}} = 2793$. [l] H$_1$, H$_2$ show AB pattern with further splittings, which remains unchanged on ^{31}P decoupling; assignment could be reversed. [m] δ(H$_4$) 4.02 m (m), δ(Pt–CH$_3$) 0.08 dd (s), 0.39 dd (s) with 1:4:1 satellites. [n] $J_{\mathrm{Pt-CH_3}} = 71, 68, J_{\mathrm{P-CH_3}} = 8$ and 6.5, 9 and 6.5, respectively. $J_{\mathrm{Pt-P}}$ could not be measured owing to insufficient solubility.



η³-allyl



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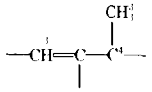
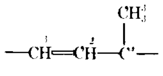


η¹-alkenyl



1-BDPB

Table III. Crystal Data[a]

$a = 13.055\ (5)$ Å[b]	$b = 18.151\ (7)$ Å
$c = 15.224\ (6)$ Å	$\beta = 112.43\ (2)°$
Crystal color: yellow	Formula: $C_{40}H_{33}ClP_2Pd$
Mol wt: 717.5	Cell volume: 3334.3 Å^3
$\rho_{obsd} = 1.42\ (1)$ g cm^{-3}	$\rho_{calcd} = 1.43$ g cm^{-3}
Space group: $P2_1/n$	$Z = 4$
μ (Cu Kα) = 64.58 cm^{-1}	

[a] Cell dimensions were measured at 20 ± 1 °C. [b] Estimated standard deviations (in parentheses) in this and the following tables, and also in the text, refer to the least significant digit(s) in each case.

Table IV. Details of Data Collection

Radiation	Cu Kα
Wavelength	1.5418 Å
Monochromator	Graphite crystal
Tube takeoff angle	3.0°
Crystal to counter distance	28.5 cm
Scan technique	$\theta - 2\theta$ scans
Scan speed	2°/min
Scan width	From 0.85° below the Cu Kα_1 maximum to 0.85° above the Cu Kα_2 maximum of each peak
Scan range	$3° \leqslant 2\theta \leqslant 125°$
Total background counting time[a]	20 s
"Standard" reflection indices[b]	$(680), (00\bar{8}), (\bar{6}80)$
Crystal stability	No decomposition observed
Index range of data collected	$hk\bar{l}, \bar{h}k\bar{l}$
Total number of data collected	5939
Number with $I/\sigma(I) \geqslant 3.0$	4436
p^2	0.002

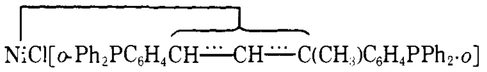
[a] Backgrounds were counted on either "side" of each reflection (10 s each side) at the scan width limits, and were assumed to be linear between these points. [b] The three "standard" reflections were monitored after each 100 measurements throughout the course of data collection.

TOMPAB, a locally modified version (J. D. Bell) of the Brookhaven National Laboratory absorption correction program (the method used to calculate transmission factors is described in ref 15). The figures were produced using ORTEP,[16] and bond lengths and interbond angles, together with their estimated standard deviations, were calculated using ORFFE.[17] All calculations were carried out on the Univac-1108 computer of The Australian National University Computer Centre.

Results and Discussion

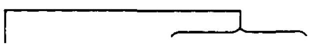
Reaction of stoichiometric amounts of $NiCl_2(CH_3OCH_2CH_2OCH_3)$ and 1-BDPB in refluxing 2-methoxyethanol gives an air-stable, reddish brown solid of apparent formula "NiCl(1-BDPB)" (III) which is soluble in most common organic solvents and is monomeric in chloroform (Table I). In contrast with ligand II and its chlororhodium(I) complex, which show a characteristic methyl doublet in their $^1H\{^{31}P\}$ NMR spectra ($J_{CH\text{-}CH_3} \sim 7$ Hz), III shows two methyl singlets corresponding to three protons and two AB quartets containing two protons to lower field (Table II); in some solvents the methyl resonances coincide. These observations are consistent with the presence of two isomers, IIIa and IIIb, each of which contains the grouping $\text{-CHCHC(CH}_3\text{)-}$; i.e., the ligand has been deprotonated at the tertiary carbon atom and the complex can be written as NiCl(1-BDPB-H). The proportions of IIIa and IIIb vary slightly, depending on the reaction time, but the isomer ratio is generally about 1:1. The presence of isomers is also indicated by the $^{31}P\{^1H\}$ spectrum, which consists of two AB quartets ($^2J_{PP}$ = 10 and 74 Hz, respectively). Although there was no evidence from ^1H NMR spectra for interconversion of IIIa and IIIb between 32 and 80°, attempts to separate them by column chromatography were unsuccessful. Partial separation has been achieved by extracting the mixture with bromopentafluorobenzene, in which IIIb is considerably more soluble than IIIa.

The observed values of $^2J_{PP}$ are much smaller than those found for transplanar nickel(II) complexes, e.g., $NiI_2(t\text{-}Bu_2PH)_2$ (355 Hz)[18] and $\overline{NiCl[o\text{-}Ph_2PC_6H_4C}{=}CH\text{-}C_6H_4PPh_2\text{-}o]$ (326 Hz),[19] but are comparable with those found for five-coordinate trigonal bipyramidal complexes of nickel(II), e.g., $[Ni(CH_3)[P(CH_3)_3]_4]^+$ (51 Hz)[20] and $[Ni[P(OCH_2)_3CC_2H_5]_5]^{2+}$ (119.5 Hz).[21] Thus the P–Ni–P angles in IIIa and IIIb probably lie between 90 and 120°, and molecular models suggest that with this arrangement the tertiary carbon atom cannot approach within σ-bonding distance of the nickel atom; this only becomes possible when the P–Ni–P angle is about 130° or more and then only if the olefinic CH═CH protons adopt a cis configuration. Thus IIIa/IIIb are most reasonably formulated as an isomeric pair of pseudo-five-coordinate η^3-allylic complexes



$$NiCl[o\text{-}Ph_2PC_6H_4CH \overset{\cdots}{—} CH \overset{\cdots}{—} C(CH_3)C_6H_4PPh_2\text{-}o]$$

Molecular models favor a square pyramidal geometry with chlorine occupying the apical position, an arrangement which has been found in the five-coordinate complexes $NiBr[CH_2 \overset{\cdots}{—} C(CH_3) \overset{\cdots}{—} CH_2](dpe)$[22] and $[NiBr(dpe)]_2(CH_2 \overset{\cdots}{—} CH \overset{\cdots}{—} CHCH_2CH_2CH \overset{\cdots}{—} CH \overset{\cdots}{—} CH_2)$[23] (dpe = $Ph_2PCH_2CH_2PPh_2$) by x-ray structural studies. The isomerism probably arises from differing arrangements of substituents on the η^3-allyl group. If we use the terms anti and syn to refer only to the disposition of the terminal hydrogen and methyl substituents with respect to the central hydrogen atom of the allyl group, then four possibilities can be distinguished, denoted by anti-anti, syn-syn, anti-syn, and syn-anti (Figure 1). The interproton coupling constant J_{12} for the allylic protons in IIIa (11.0 Hz) is typical of an anti arrangement for these protons,[24] but the lower value (9.5 Hz) for IIIb is intermediate between the quoted ranges for syn and anti coupling constants, so that a clear-cut assignment is impossible. However, in the complex



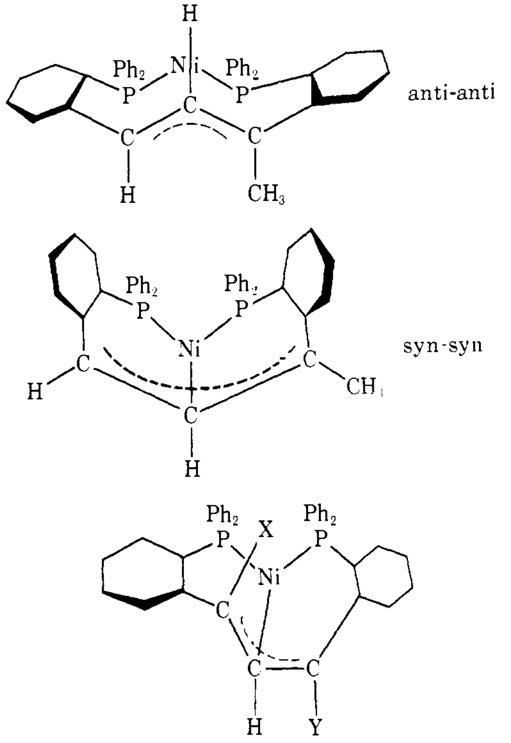
$$RhCl_2[o\text{-}Ph_2PC_6H_4CH \overset{\cdots}{—} CH \overset{\cdots}{—} C(CH_3)C_6H_4PPh_2\text{-}o]$$

obtained from rhodium trichloride and 1-BDPB, the allylic protons are known from a single-crystal x-ray study to be anti, yet J_{12} has the unexpectedly low value of 8.0 Hz.[25] We tentatively suggest that IIIa and IIIb both have anti allylic protons and reject the syn-syn and syn-anti structures (Figure 1). The available evidence does not allow us to say which structure

Table V. Course of Refinement

Set no.	Conditions	No. of cycles	R^a	R_w
1	All atoms isotropic, no hydrogen atoms included, individual weights[b]	6	0.077	0.102
2	At this stage, reflection data were corrected for absorption effects. All atoms isotropic, no hydrogen atoms included, individual weights	6	0.069	0.093
3	All atoms anisotropic,[c] no hydrogen atoms included, individual weights	6	0.042	0.063
4	All non-hydrogen atoms anisotropic, fixed isotropic hydrogen atom contributions included, individual weights	8	0.029	0.037

[a] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$, where $|F_o|$ is the observed, and $|F_c|$ the calculated structure factor. The function minimized throughout least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. [b] Individual weights of the form $w = [\sigma(F_o)]^{-2}$ were used in all refinement cycles. [c] The anisotropic temperature factor takes the form $\{\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]\}$.

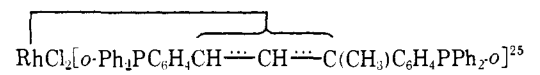


X = H, Y = CH_3 anti-syn
X = CH_3, Y = H syn-anti

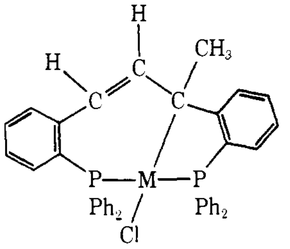
Figure 1. Possible isomers of III (Ni–Cl axis is at right-angles to plane of paper; Cl atom behind Ni has been omitted).

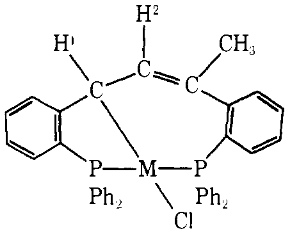
(anti-anti or anti-syn) corresponds to which isomer (IIIa or IIIb).

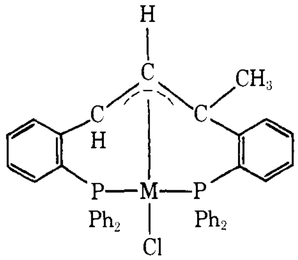
Reaction of the bis(benzonitrile) or 1,5-cyclooctadiene (COD) dichlorometal complexes MCl_2L_2 (M = Pd or Pt; L_2 = 2PhCN or COD) with II in refluxing 2-methoxyethanol gives pale yellow complexes of apparent empirical formula "MCl(ligand)" (M = Pd, IV; M = Pt, V) which are monomeric in chloroform. Their $^1H\{^{31}P\}$ NMR spectra (Table II) resemble those of the nickel complexes IIIa/IIIb (particularly IIIa) in showing an AB quartet (J = 11 Hz) corresponding to two protons and, at higher field, a methyl resonance which is actually a closely spaced doublet (J = 1.5 Hz) owing to coupling with the higher field proton of the AB quartet. These data, taken with the absence of the 7 Hz coupling characteristic of the $CHCH_3$ group, indicate that the ligand has been deprotonated at the tertiary carbon atom. However, the J_{P,CH_3} values for IV and V are noticeably different from those of IIIa and IIIb, and the large magnitudes of $^2J_{PP}$ obtained from the $^{31}P\{^1H\}$ NMR spectra (Table II) are typical of mutually trans-phosphine ligands in planar palladium(II) or platinum(II) complexes.[18,26] The available spectroscopic data are consistent with either of two possible four-coordinate η^1-allyl structures IVa or IVb, or with a five-coordinate η^3-allyl structure IVc. Although molecular models suggest that an arrangement involving trans-phosphorus atoms, together with η^3-allyl bonding to the metal would be severely strained, it is observed in the rhodium(III) complex


$\text{RhCl}_2[o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}\overset{...}{—}\text{CH}\overset{...}{—}\text{C(CH}_3\text{)C}_6\text{H}_4\text{PPh}_2\text{-}o]^{25}$

so that IVc cannot be dismissed solely on steric grounds. We initially favored IVa,[27] but were puzzled by the cis arrangement of the hydrogen atoms on the double bond implied by the vicinal coupling constant of 11 Hz, since in 1-BDPB itself, these hydrogen atoms are trans (J = 17.5 Hz). The single-crystal x-ray study discussed in detail below shows that the palladium(II) complex has the η^1-*cis*-2-buten-1-yl structure IVb, the methyl group being attached to an olefinic carbon atom, not to the aliphatic carbon atom as in 1-BDPB itself. The platinum complex V is probably isostructural with IV, since $J(^{195}Pt\text{–}H_1)$ is 98 Hz, a value which is typical for a proton attached to a carbon atom which is itself bound to platinum.[28] Somewhat surprisingly, no platinum coupling to H_2 was detectable. Another surprising feature, in the light of the known structure, is the observation of $J_{P\,CH_3}$; in five-membered chelate ring systems of the type $\overline{\text{MCH(CH}_3\text{)C}_6\text{H}_4\text{P}}\text{Ph}_2\text{-}o^{3,29,30}$ such coupling has not so far been observed.

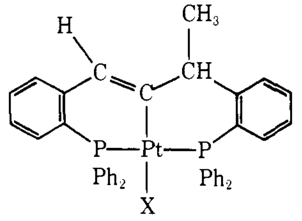

IVa (M = Pd)


IVb (M = Pd)
Vb (M = Pt)

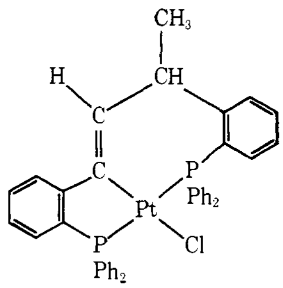

IVc (M = Pd)

Reaction of $PtCl(CH_3)(COD)$ with II gives a complex VI of empirical formula "PtCl(1-BDPB)" which is isomeric but not identical with V. The other product is presumably methane, though no attempt was made to detect it. The $^1H\{^{31}P\}$ NMR spectrum of VI shows a characteristic methyl doublet (J = 7 Hz) as well as two other resonances to lower field, each of which corresponds to one proton. The higher field resonance appears as a quartet owing to coupling with the CH_3 protons and must, therefore, be assigned to a methine proton, whereas the lower field resonance shows no observable coupling to other protons. The value of $^2J_{PP}$ obtained from the $^{31}P\{^1H\}$ NMR spectrum (Table II) is characteristic of mutually trans phosphines, so that the complex is clearly a chelate Pt–C σ-bonded complex similar to V. The available evidence favors the 1-buten-2-yl structure VIa rather than the alternative 1-buten-1-yl structure VIb since, for the latter, observable coupling between the olefinic proton and the methine proton might have been expected. The ^{195}Pt coupling to the olefinic proton (95 Hz) is in good agreement with the value for the coupling to the trans-vinyl proton in the complex *cis*-$PtCl[C(CF_3){=}CH_2](PEt_3)_2$ (92 Hz),[31] but falls below the range quoted for ^{195}Pt coupling to trans-vinyl protons in a series of σ-*trans*-styrylplatinum(II) complexes (119.7–146.4 Hz).[32]

The formation of IVb from the reaction of $PdCl_2(PhCN)_2$ or $PdCl_2(COD)$ with 1-BDPB can be accounted for by assuming that the hydrogen atom on the tertiary carbon atom is abstracted initially to give a cationic η^3-allylic complex VII (Scheme II) in which the phosphorus atoms are probably cis (see below). Return of chloride to the coordination sphere could generate a Pd–C σ-bond at either end of the chain, giving either IVb or IVd, the latter differing from IVa only in that it has a trans arrangement of hydrogen atoms about the double bond. This geometry introduces severe strain into the seven-mem-



VIa (X = Cl)
VIII (X = H_2O)



VIb

bered chelate ring, whereas in IVb, according to the x-ray results, the seven-membered ring is probably less strained than the five-membered ring. We suggest that chelate ring strain is probably the decisive factor in the formation of IVb from VII.

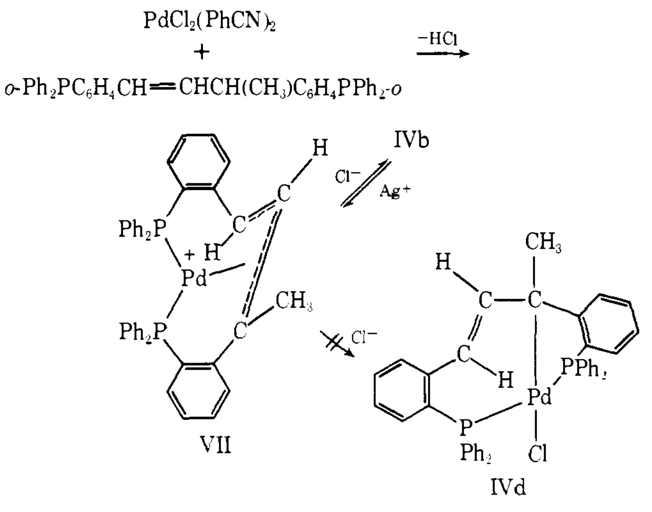
It is worth noting that the hydrogen atom which is lost in the form of HCl on reaction of 1-BDPB with dichloro complexes of nickel, palladium, and platinum is probably the most acidic of the three available, being both benzylic and allylic, whereas the least acidic (or most hydridic) hydrogen atom is eliminated in the form of methane on reaction of $PtCl(CH_3)(COD)$ with 1-BDPB. It may of course be an oversimplification to assume that the methine hydrogen is abstracted first in the reaction of 1-BDPB with the dichloro complexes, particularly as we find that VIa is quantitatively isomerized to Vb by treatment with hydrogen chloride in dichloromethane and by reaction of the product with hot acetone. However, the reaction of $PtCl_2(PhCN)_2$ with 1-BDPB in the presence of diisopropylethylamine gave Vb as the only isolable organometallic product; there was no sign of the σ-alkenyl VIa, so that our assumption is probably valid.

The nature of the intermediate in the HCl-catalyzed isomerization of VIa to Vb could not be established owing to its instability and the complexity of its ^1H NMR spectrum. The obvious possibilities are (i) cleavage of the Pt-C σ-bond in VIa to give $PtCl_2$(1-BDPB), which could then lose its methine hydrogen atom as in Scheme II, or (ii) addition of HCl to the C=C bond and its subsequent elimination. In the latter case, irrespective of the direction of addition, it is difficult to see how Vb can arise, and in view of the known susceptibility of planar platinum(II) alkyls and alkenyls to acid cleavage,[32-34] the first alternative seems preferable.

The postulate of an intermediate η^3-allylic complex VII as a precursor to IVb seems reasonable in view of the nickel chemistry described above, and receives support from the isolation of the cation as a tetrafluoroborate salt by treatment of IVb with $AgBF_4$ in acetone. Although the interproton coupling constant J_{12} of 11 Hz does not distinguish between a η^3-butenyl and a η^1-*cis*-2-buten-1-yl structure for VII, the $^{31}P\{^1H\}$ NMR spectrum of the cation shows an AB quartet with $^2J_{PP}$ = 15 Hz, which shows the phosphorus atoms to be mutually cis, not trans as in IVb. This provides good evidence for the η^3-allylic formulation, with planar coordination about palladium. The complex is analogous to $[Pd(CH_2\text{⋯}C(CH_3)\text{⋯}(CH_2)(dpe)]PF_6$, for which $^2J_{PP}$ has been estimated as 12 Hz.[35] Since the isolated salt contains firmly bound water, as shown by ir and NMR spectra, we cannot exclude the possibility that the complex is a five-coordinate η^3-allyl like the nickel complexes, with water occupying the fifth coordination site, but in view of the reluctance of palladium(II) relative to nickel(II) to form five-coordinate complexes,[36] this seems unlikely.

Attempts to isolate the platinum analogue of VII were unsuccessful, though it is presumably the precursor to Vb.

Scheme II



Treatment of Vb with $AgBF_4$ gave silver chloride and a solution which deposited platinum too rapidly for reliable spectroscopic data to be obtained. Treatment of the isomeric σ-alkenyl VIa with $AgBF_4$ gave a more stable solution, but the cationic complex decomposed on attempted isolation. However, the $^{31}P\{^1H\}$ NMR spectrum of the solution shows that the complex present has mutually trans-phosphorus atoms (Table II), and since the $^1H\{^{31}P\}$ NMR spectrum is very similar to that of VIa, it seems likely that the complex is simply the cationic aquo-complex VIII derived from VIa by replacement of chloride.

In view of the ease with which methane is eliminated in the reaction of $PtCl(CH_3)(COD)$ with 1-BDPB, we investigated the reaction of $Pt(CH_3)_2(COD)$ with the same ligand, expecting to isolate the σ-methyl analogue of VIa. In refluxing toluene the product is a colorless solid of empirical formula $Pt(CH_3)_2$(1-BDPB) which is monomeric in dichloromethane. The $^1H\{^{31}P\}$ NMR spectrum shows the presence of two inequivalent methyl groups with ^{195}Pt satellites in addition to resonances attributable to the protons of structurally unchanged 1-BDPB; the latter are not observably coupled either to ^{31}P or ^{195}Pt and their chemical shifts are similar to those of the free ligand, suggesting that the double bond is not coordinated. The ^{31}P chemical shifts and the small value of $^2J_{PP}$ (12 Hz) indicate coordination of both phosphorus atoms in a cis configuration. These data are compatible with structure IX in which 1-BDPB behaves as a cis bidentate 2P-bonded ligand. Although the resulting ten-membered chelate ring might have been expected to impart instability to the compound, the complex shows no tendency to eliminate methane on heating either in high-boiling solvents or in the solid state in vacuo to just below its decomposition point. This may be due to the reluctance to form a Pt-C σ-bond in a position trans to another trans-bond weakening Pt-C σ-bond, though it may be noted that the chelate ligand *o*-diphenylphosphino-*trans*-stilbene, o-$Ph_2PC_6H_4$-t-$CH{=}CHC_6H_4PPh_2$-o, eliminates one of its olefinic protons on reaction with $Pt(CH_3)_2(COD)$ to give the chelate σ-alkenyl $\overline{Pt(CH_3)(o\text{-}Ph_2PC_6H_4}C{=}CHC_6H_4PPh_2$-$o$).[19] A likely transition state or intermediate in this reaction is a complex $Pt(CH_3)_2(o\text{-}Ph_2PC_6H_4\text{-}t\text{-}CH{=}CHC_6H_4PPh_2\text{-}o)$ in which the phosphorus atoms are mutually trans and the double bond is close to, and possibly coordinated to, the platinum atom. Molecular models suggest that the double bond is forced closer to the metal in the case of the stilbene ligand than for 1-BDPB, thus presumably favoring elimination of an olefinic proton.

Discussion of the Structure

The crystal structure of IV, as defined by the unit cell pa-

Table VI. Fractional Atomic Positional and Thermal Parameters for $[\mathrm{PdCl}\{o\text{-}(C_6H_5)_2PC_6H_4C(CH_3){=}CHCHC_6H_4P(C_6H_5)_2\text{-}o\}]$

(a) Refined Positional and Anisotropic Thermal Parameters

ATOM	X/A	Y/B	Z/C	BETA11	BETA22	BETA33	BETA12	BETA13	BETA23
PD	0.00414(2)	0.05873(1)	0.24175(1)	0.00394(1)	0.00169(1)	0.00348(1)	-0.00006(1)	0.00165(1)	0.00007(1)
CL	-0.01361(6)	0.18942(4)	0.26133(7)	0.00624(6)	0.00189(2)	0.00677(6)	0.00051(3)	0.00270(5)	0.00018(3)
P(1)	0.19173(6)	0.07094(4)	0.26467(6)	0.00387(5)	0.00167(2)	0.00350(4)	0.00002(3)	0.00146(4)	-0.00009(2)
P(2)	-0.16977(6)	0.03327(4)	0.23047(6)	0.00427(5)	0.00223(2)	0.00405(4)	-0.00027(3)	0.00208(4)	-0.00009(3)
C(1)	0.0171(2)	-0.0540(2)	0.2278(2)	0.0049(2)	0.0019(1)	0.0038(2)	0.0001(1)	0.0018(2)	0.0001(1)
C(2)	0.0366(2)	-0.0625(2)	0.1390(2)	0.0050(2)	0.0019(1)	0.0040(2)	-0.0005(1)	0.0015(2)	-0.0002(1)
C(3)	0.1348(2)	-0.0688(2)	0.1307(2)	0.0052(2)	0.0018(1)	0.0036(2)	-0.0001(1)	0.0018(2)	-0.0003(1)
C(31)	0.1433(3)	-0.0733(2)	0.0343(3)	0.0077(3)	0.0037(1)	0.0039(2)	0.0004(2)	0.0030(2)	0.0001(1)
C(111)	0.2747(2)	-0.0131(2)	0.2834(2)	0.0046(2)	0.0019(1)	0.0040(2)	0.0001(1)	0.0020(2)	0.0000(1)
C(112)	0.2410(2)	-0.0705(2)	0.2161(2)	0.0046(2)	0.0021(1)	0.0042(2)	-0.0001(1)	0.0020(2)	-0.0001(1)
C(113)	0.3115(3)	-0.1306(2)	0.2287(3)	0.0068(3)	0.0022(1)	0.0057(2)	0.0005(1)	0.0021(2)	-0.0008(1)
C(114)	0.4110(3)	-0.1352(2)	0.3052(3)	0.0072(3)	0.0028(1)	0.0070(3)	0.0019(2)	0.0012(2)	-0.0005(1)
C(115)	0.4438(3)	-0.0794(2)	0.3715(3)	0.0062(3)	0.0031(1)	0.0058(2)	0.0015(1)	0.0003(2)	-0.0002(1)
C(116)	0.3755(3)	-0.0185(2)	0.3597(3)	0.0053(2)	0.0025(1)	0.0049(2)	0.0005(1)	0.0010(2)	-0.0005(1)
C(121)	0.2264(3)	0.1175(2)	0.1740(2)	0.0061(3)	0.0021(1)	0.0049(2)	-0.0005(1)	0.0028(2)	-0.0002(1)
C(122)	0.3250(3)	0.1033(2)	0.1622(3)	0.0097(4)	0.0032(1)	0.0091(3)	0.0003(2)	0.0062(3)	0.0009(2)
C(123)	0.3533(4)	0.1432(2)	0.0976(4)	0.0126(5)	0.0043(2)	0.0109(4)	-0.0008(2)	0.0093(4)	0.0002(2)
C(124)	0.2841(4)	0.1963(3)	0.0436(3)	0.0153(5)	0.0054(2)	0.0076(3)	-0.0016(3)	0.0072(4)	0.0013(2)
C(125)	0.1660(4)	0.2093(3)	0.0524(4)	0.0122(5)	0.0060(2)	0.0060(3)	0.0005(3)	0.0042(3)	0.0036(2)
C(126)	0.1560(3)	0.1702(2)	0.1177(3)	0.0078(3)	0.0040(1)	0.0061(3)	0.0005(2)	0.0030(2)	0.0011(2)
C(131)	0.2610(3)	0.1256(2)	0.3711(2)	0.0049(2)	0.0023(1)	0.0044(2)	0.0008(1)	0.0006(2)	-0.0007(1)
C(132)	0.3329(3)	0.1830(2)	0.3743(3)	0.0069(3)	0.0027(1)	0.0074(3)	-0.0003(2)	-0.0003(2)	-0.0010(2)
C(133)	0.3734(4)	0.2263(2)	0.4551(4)	0.0102(4)	0.0032(1)	0.0101(4)	0.0010(2)	-0.0030(3)	-0.0024(2)
C(134)	0.3473(4)	0.2146(3)	0.5297(3)	0.0119(5)	0.0049(2)	0.0083(3)	0.0041(2)	-0.0041(3)	-0.0039(2)
C(135)	0.2794(4)	0.1571(3)	0.5297(3)	0.0117(4)	0.0072(2)	0.0047(3)	0.0052(3)	0.0009(3)	-0.0012(2)
C(136)	0.2337(3)	0.1124(2)	0.4481(3)	0.0080(3)	0.0046(2)	0.0043(2)	0.0018(2)	0.0016(2)	-0.0008(1)
C(211)	-0.1785(3)	-0.0661(2)	0.2256(2)	0.0055(2)	0.0022(1)	0.0041(2)	-0.0007(1)	0.0021(2)	-0.0011(1)
C(212)	-0.0820(3)	-0.0992(2)	0.2254(2)	0.0064(3)	0.0021(1)	0.0039(2)	-0.0002(1)	0.0024(2)	0.0001(1)
C(213)	-0.0769(3)	-0.1760(2)	0.2236(3)	0.0094(3)	0.0022(1)	0.0077(3)	-0.0011(2)	0.0048(3)	0.0002(1)
C(214)	-0.1676(3)	-0.2171(2)	0.2196(3)	0.0107(4)	0.0023(1)	0.0076(3)	-0.0012(2)	0.0047(3)	0.0001(1)
C(215)	-0.2630(3)	-0.1847(2)	0.2189(3)	0.0087(3)	0.0031(1)	0.0061(2)	-0.0018(2)	0.0029(2)	0.0006(1)
C(216)	-0.2693(3)	-0.1086(2)	0.2222(3)	0.0067(3)	0.0030(1)	0.0058(2)	-0.0008(1)	0.0028(2)	0.0005(1)
C(221)	-0.2815(2)	0.0694(2)	0.1268(2)	0.0038(2)	0.0028(1)	0.0045(2)	-0.0003(1)	0.0019(2)	0.0000(1)
C(222)	-0.3411(3)	0.0258(2)	0.0497(3)	0.0063(3)	0.0032(1)	0.0052(2)	-0.0007(1)	0.0018(2)	0.0000(1)
C(223)	-0.4170(3)	0.0585(2)	-0.0328(3)	0.0067(3)	0.0048(2)	0.0052(2)	-0.0013(2)	0.0008(2)	0.0000(2)
C(224)	-0.4343(3)	0.1327(2)	-0.0379(3)	0.0052(3)	0.0050(2)	0.0070(3)	-0.0003(2)	0.0013(2)	0.0017(2)
C(225)	-0.3766(3)	0.1763(2)	0.0391(3)	0.0062(3)	0.0034(1)	0.0094(3)	0.0005(2)	0.0027(3)	0.0012(2)
C(226)	-0.2994(3)	0.1449(2)	0.1210(3)	0.0058(3)	0.0031(1)	0.0059(2)	0.0001(1)	0.0020(2)	-0.0001(1)
C(231)	-0.2020(3)	0.0614(2)	0.3317(3)	0.0068(3)	0.0025(1)	0.0050(2)	-0.0001(1)	0.0035(2)	0.0001(1)
C(232)	-0.3090(3)	0.0643(2)	0.3284(3)	0.0082(3)	0.0042(2)	0.0071(3)	-0.0006(2)	0.0047(3)	-0.0006(2)
C(233)	-0.3278(4)	0.0842(3)	0.4102(4)	0.0122(4)	0.0060(2)	0.0096(4)	-0.0001(2)	0.0085(4)	-0.0003(2)
C(234)	-0.2414(4)	0.1002(2)	0.4925(3)	0.0163(6)	0.0044(2)	0.0073(3)	-0.0006(2)	0.0079(4)	-0.0006(2)
C(235)	-0.1366(4)	0.0981(3)	0.4959(3)	0.0141(5)	0.0066(2)	0.0053(3)	-0.0017(3)	0.0046(3)	-0.0017(2)
C(236)	-0.1156(3)	0.0795(2)	0.4156(3)	0.0091(4)	0.0054(2)	0.0048(2)	-0.0009(2)	0.0032(2)	-0.0006(2)

(b) Fixed Hydrogen Atom Coordinates and Isotropic Thermal Parameters[a]

ATOM	X/A	Y/B	Z/C	B(A**2)	ATOM	X/A	Y/B	Z/C	B(A**2)
H(1)	0.015	-0.073	0.283	3.1	H(136)	0.184	0.073	0.447	5.3
H(2)	-0.027	-0.064	0.082	3.2	H(213)	-0.011	-0.203	0.225	5.0
H(113)	0.290	-0.169	0.183	4.2	H(214)	-0.164	-0.269	0.217	5.3
H(114)	0.467	-0.177	0.312	5.3	H(215)	-0.324	-0.214	0.216	5.1
H(115)	0.512	-0.083	0.425	5.0	H(216)	-0.335	-0.086	0.222	4.5
H(116)	0.398	0.020	0.405	4.0	H(222)	-0.331	-0.026	0.053	4.5
H(122)	0.373	0.066	0.199	5.6	H(223)	-0.457	0.029	-0.086	5.6
H(123)	0.421	0.134	0.091	6.9	H(224)	-0.486	0.154	-0.094	5.8
H(124)	0.304	0.224	0.003	7.4	H(225)	-0.389	0.228	0.036	5.8
H(125)	0.137	0.246	0.013	7.8	H(226)	-0.260	0.115	0.174	4.5
H(126)	0.087	0.180	0.123	5.3	H(232)	-0.370	0.053	0.271	5.4
H(132)	0.354	0.192	0.322	5.6	H(233)	-0.401	0.086	0.408	6.8
H(133)	0.422	0.266	0.457	8.2	H(234)	-0.235	0.113	0.548	6.9
H(134)	0.376	0.246	0.583	9.1	H(235)	-0.077	0.110	0.554	7.5
H(135)	0.263	0.147	0.584	7.8	H(236)	-0.042	0.079	0.419	5.8

[a] The hydrogen atoms are numbered according to the carbon atoms to which they are bonded.

rameters, space group symmetry operations, and atom coordinates of Table VI, consists of discrete monomeric molecular units which have neither crystallographic nor virtual symmetry higher than C_1. A perspective view of the molecule, and the atom numbering scheme, is shown by the stereopairs of Figure 2; the thermal ellipsoids have been drawn to include 50% of the probability distribution, and, for clarity, the hydrogen atoms have been omitted. Principal bond lengths and interbond angles, together with their estimated standard deviations, are listed in Table VII, while bond lengths and interbond angles within the six phenyl rings are given in Table VIII. As atom-atom correlations have been neglected, both in the least-squares refinement process and the subsequent calculation of geometrical estimated standard deviations, the tabulated esd's will almost certainly be underestimated. The results of weighted least-squares planes calculations[37] are collected in Table IX.

The coordination at the central palladium atom is essentially square planar, with the phosphorus atoms of the tridentate o-$(C_6H_5)_2PC_6H_4CHCH{=}C(CH_3)C_6H_4P(C_6H_5)_2$-$o$ ligand

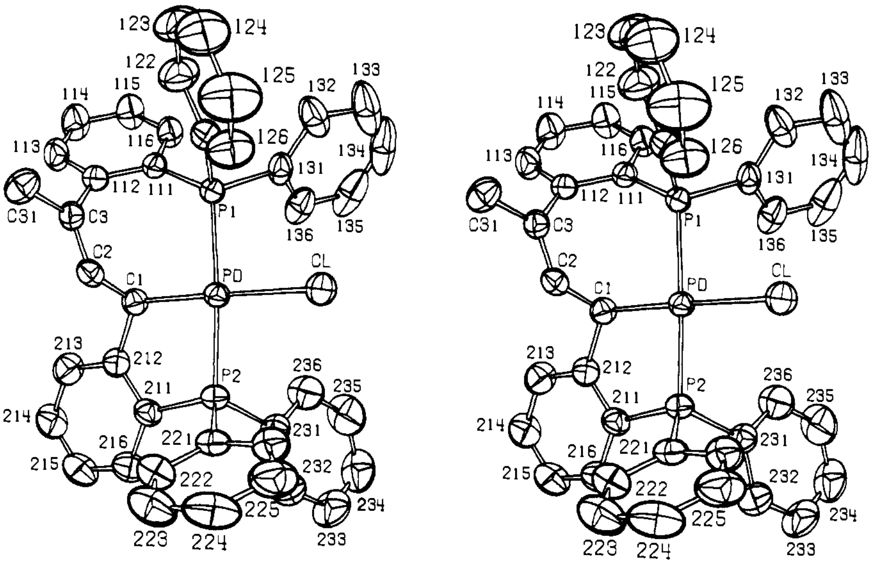


Figure 2. A perspective view of one molecule of IV. (The symbol C has been omitted from all phenyl ring carbon atoms.)

Table VII. Principal Bond Lengths and Interbond Angles

(a) Bond Distances, Å					
Atoms	Distance	Atoms	Distance	Atoms	Distance
Pd–Cl	2.413 (1)	Pd–P(1)	2.349 (1)	Pd–P(2)	2.258 (1)
Pd–C (1)	2.071 (3)	P(1)–C(111)	1.830 (3)	P(1)–C(121)	1.817 (4)
P(1)–C(131)	1.819 (3)	P(2)–C(211)	1.808 (3)	P(2)–C(221)	1.814 (3)
P(2)–C(231)	1.818 (4)	C(111)–C(112)	1.408 (4)	C(112)–C(3)	1.495 (3)
C(3)–C(31)	1.516 (6)	C(3)–C(2)	1.340 (5)	C(2)–C(1)	1.477 (5)
C(1)–C(212)	1.521 (5)	C(212)–C(211)	1.396 (5)		

(b) Interbond Angles, degrees					
Atoms	Angle	Atoms	Angle	Atoms	Angle
Cl–Pd–P(1)	91.87 (3)	Cl–Pd–P(2)	93.98 (2)	Cl–Pd–C(1)	178.0 (1)
P(1)–Pd–P(2)	172.58 (3)	P(1)–Pd–C(1)	89.29 (9)	P(2)–Pd–C(1)	84.77 (9)
Pd–P(1)–C(111)	117.8 (1)	Pd–P(1)–C(121)	118.6 (1)	Pd–P(1)–C(131)	108.6 (1)
C(111)–P(1)–C(121)	101.6 (2)	C(111)–Pd–C(131)	104.6 (1)	C(121)–P(1)–C(131)	103.9 (2)
Pd–P(2)–C(211)	104.7 (1)	Pd–P(2)–C(221)	116.3 (1)	Pd–P(2)–C(231)	115.4 (1)
C(211)–Pd–C(221)	107.9 (1)	C(211)–Pd–C(231)	106.5 (2)	C(221)–Pd–C(231)	105.5 (2)
P(1)–C(111)–C(112)	120.0 (2)	P(1)–C(111)–C(116)	120.3 (2)	C(112)–C(111)–C(116)	119.4 (3)
C(111)–C(112)–C(113)	118.1 (3)	C(111)–C(112)–C(3)	123.1 (3)	C(113)–C(112)–C(3)	118.7 (3)
C(112)–C(3)–C(2)	121.6 (3)	C(112)–C(3)–C(31)	117.0 (3)	C(31)–C(3)–C(2)	121.4 (3)
C(3)–C(2)–C(1)	126.9 (3)	C(2)–C(1)–C(212)	111.3 (2)	C(2)–C(1)–Pd	104.3 (2)
Pd–C(1)–C(212)	115.7 (2)	C(1)–C(212)–C(213)	119.5 (3)	C(1)–C(212)–C(211)	121.8 (3)
C(213)–C(212)–C(211)	118.7 (3)	C(212)–C(211)–C(216)	121.0 (3)	C(212)–C(211)–P(2)	112.8 (2)
C(216)–C(211)–P(2)	126.2 (3)				

Table VIII. Bond Distances and Interbond Angles within the Six Phenyl Rings

(a) Bond Distances, Å						
Atoms	$m = 1, n = 1$	$m = 1, n = 2$	$m = 1, n = 3$	$m = 2, n = 1$	$m = 2, n = 2$	$m = 2, n = 3$
P(*m*)–C(*mn*1)	1.830 (3)	1.817 (4)	1.819 (3)	1.808 (3)	1.814 (3)	1.818 (4)
C(*mn*1)–C(*mn*2)	1.408 (4)	1.390 (6)	1.390 (5)	1.396 (5)	1.382 (5)	1.380 (6)
C(*mn*2)–C(*mn*3)	1.392 (5)	1.380 (8)	1.384 (6)	1.395 (5)	1.401 (5)	1.404 (8)
C(*mn*3)–C(*mn*4)	1.377 (5)	1.362 (6)	1.322 (9)	1.382 (6)	1.363 (6)	1.360 (6)
C(*mn*4)–C(*mn*5)	1.378 (5)	1.358 (9)	1.368 (7)	1.374 (6)	1.376 (6)	1.350 (8)
C(*mn*5)–C(*mn*6)	1.389 (5)	1.394 (8)	1.411 (6)	1.386 (5)	1.389 (5)	1.393 (8)
C(*mn*6)–C(*mn*1)	1.387 (4)	1.376 (5)	1.370 (6)	1.398 (5)	1.388 (5)	1.383 (5)

(b) Interbond Angles, degrees						
Atoms	$m = 1, n = 1$	$m = 1, n = 2$	$m = 1, n = 3$	$m = 2, n = 1$	$m = 2, n = 2$	$m = 2, n = 3$
P(*m*)–C(*mn*1)–C(*mn*2)	120.0 (2)	121.6 (3)	122.6 (3)	112.8 (2)	122.5 (2)	122.6 (3)
P(*m*)–C(*mn*1)–C(*mn*6)	120.3 (2)	119.7 (3)	117.6 (3)	126.2 (3)	118.3 (2)	118.6 (3)
C(*mn*2)–C(*mn*1)–C(*mn*6)	119.4 (3)	118.7 (4)	119.6 (3)	121.0 (3)	118.9 (3)	118.8 (4)
C(*mn*1)–C(*mn*2)–C(*mn*3)	118.1 (3)	120.5 (4)	118.7 (5)	118.7 (3)	119.7 (3)	119.7 (4)
C(*mn*2)–C(*mn*3)–C(*mn*4)	121.7 (3)	120.4 (5)	122.4 (4)	119.6 (4)	121.0 (3)	120.5 (5)
C(*mn*3)–C(*mn*4)–C(*mn*5)	120.3 (3)	119.8 (5)	120.0 (4)	121.8 (3)	119.6 (3)	121.1 (5)
C(*mn*4)–C(*mn*5)–C(*mn*6)	119.0 (3)	120.9 (4)	119.7 (5)	119.5 (4)	120.1 (4)	120.6 (4)
C(*mn*5)–C(*mn*6)–C(*mn*1)	121.4 (3)	119.7 (4)	119.4 (4)	119.3 (4)	120.7 (3)	120.3 (4)

Table IX. Selected Least-Squares Planes

(a) Best Weighted Least-Squares Planes

Plane	Atoms defining plane	Equation[a]
1	Pd, Cl, P(1), P(2)	$0.0906X + 0.1195Y - 0.9887Z + 3.3698 = 0$
2	C(1), C(2), C(3)	$0.0786X + 0.9941Y - 0.0744Z + 1.2996 = 0$
3	Phenyl ring C(111)–C(116)	$0.7113X + 0.4572Y - 0.5339Z + 0.8593 = 0$
4	Phenyl ring C(211)–C(216)	$0.0202X + 0.0304Y - 0.9993Z + 3.2792 = 0$

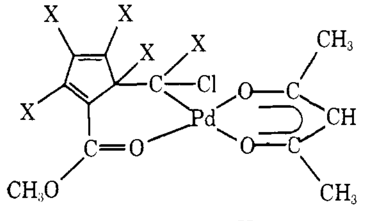
(b) Deviations (Å) of Atoms from Planes

Atoms	Plane 1	Atoms	Plane 2	Atoms	Plane 3	Atoms	Plane 4
Pd	0.0115 (2)	C(1)	0.000 (3)	C(111)	0.001 (3)	C(211)	−0.003 (3)
Cl	−0.0088 (9)	C(2)	0.000 (3)	C(112)	−0.004 (3)	C(212)	0.006 (3)
P(1)	−0.0711 (8)	C(3)	0.000 (3)	C(113)	0.005 (4)	C(213)	−0.008 (4)
P(2)	−0.0866 (8)	Pd	2.0002 (2)	C(114)	0.000 (4)	C(214)	0.001 (4)
C(1)	−0.017 (3)	Cl	4.3107 (7)	C(115)	−0.005 (4)	C(215)	0.004 (4)
C(2)	1.271 (3)	P(1)	2.3786 (7)	C(116)	0.004 (4)	C(216)	−0.003 (4)
C(3)	1.493 (3)	P(2)	1.3793 (8)	Pd	−1.4301 (2)	Pd	−0.1152 (2)
C(31)	2.885 (4)	C(31)	0.072 (4)	P(1)	0.1461 (8)	P(2)	−0.0152 (8)
C(111)	−0.426 (3)	C(111)	0.918 (3)	C(1)	−2.084 (3)	C(1)	0.024 (3)
C(112)	0.382 (3)	C(112)	−0.050 (3)	C(2)	−0.938 (3)	C(2)	1.284 (3)
C(211)	−0.242 (3)	C(211)	−0.416 (3)	C(3)	0.018 (3)	C(111)	−0.674 (3)
C(212)	−0.197 (3)	C(212)	−0.914 (3)	C(31)	1.182 (3)	C(112)	0.240 (3)

[a] The plane equations $LX + MY + NZ + D = 0$ refer to orthogonal coordinates where: $X = 13.0549x + 0.0y - 5.8093z$; $Y = 0.0x + 18.1507y + 0.0z$; $Z = 0.0x + 0.0y + 14.0718z$.

occupying trans coordination sites. The two remaining sites are occupied by the coordinated chlorine atom and the σ-bonded carbon atom of the tridentate ligand. The seven-membered chelate ring is in the half-boat conformation with the atoms Pd, P(1), and C(111) all lying on the same side of the plane defined by C(1), C(2), C(3), and C(112). The atoms C(1) and C(112) are in a cis configuration about the double bond [C(2)-C(3)].

There is evidence of severe steric strain in the molecule, and, in particular, the four atoms of the "coordination" plane (i.e., Pd, Cl, P(1), P(2)) deviate significantly from planarity, the maximum deviation being −0.0866(8) Å at P(2). The σ-bonded carbon atom, C(1), is −0.017(3) Å from this plane. In addition, within the five-atom chelate ring, the angles C(1)-Pd-P(2) (84.79 (9)°), Pd-P(2)-C(211) (104.7 (1)°), and P(2)-C(211)-C(212) (112.8 (2)°) are severely distorted from their strain-free values of 90, 116, and 120°, respectively. In contrast, there is very little strain in the seven-atom chelate ring, and the internal angles at Pd, P(1), C(111), C(112), C(3), and C(1) are very close to their expected values.



XI ($X = CO_2CH_3$)

The Pd-C σ-bond distance (Pd-C(1), 2.071 (3) Å) is in reasonable agreement with previous values, i.e., 2.16 (5) Å in $PdBr(C_7H_8OCH_3)py_2$[38] (py = pyridine; $C_7H_8OCH_3$ = 5-methoxy-3-nortricyclenyl), 2.05 (2) Å in $Pd_2Cl_2(C_7H_8Ph)_2$ (C_7H_8Ph = *endo*-3-phenyl-2-norbornenyl),[39] 2.025 (12) Å in the complex $C_5(CH_3)_5CH(p\text{-tolyl})CH_2Pd(acac)$,[40] and 2.038 (14) Å in complex XI.[41] The present value is significantly longer than the corresponding bond lengths for two σ-aryl-palladium(II) complexes, i.e., 1.994 (15) Å in $PdCl(o\text{-}C_6H_4N{=}NC_6H_5)(PEt_3)_2$[42] and 1.981 (7) Å in $Pd[o\text{-}C_6H_4CH_2N(CH_3)_2](OC_6H_4CH{=}NC_6H_5)$,[43] even after allowance has been made for the differing σ-bond radii of sp^2 (0.74 Å) and sp^3 (0.77 Å) hybridized carbon atoms. It could be suggested that chelate ring strain in our complex is partly responsible for this difference. However, the value of 1.30 Å for the σ-bond covalent radius of Pd(II) in a planar environment obtained from the present structure is in excellent agreement with the value of 1.31 (1) Å derived from the structures of $(NH_4)_2PdCl_4$[44] or K_2PdCl_4.[45] Since Pd(II) and Pt(II) probably have equal covalent radii in their planar derivatives,[45,46] the excellent agreement of our value for Pd-C(sp^3) with those for Pt-C(sp^3) in simple alkylplatinum(II) complexes, e.g., 2.081 (6) Å for *trans*-$PtCl(CH_3)(PMePh_2)_2$[47] and 2.079 (14) Å for *trans*-$PtCl(CH_2SiMe_3)(PMe_2Ph)_2$[48] is particularly gratifying and suggests that chelate ring strain is not an important factor in determining the present Pd-C bond length.

The Pd-Cl distance of 2.413 (1) Å is significantly longer than the corresponding distances in K_2PdCl_4 (2.313 (2) Å, Cl trans to Cl)[45] and $PdCl_2(PMe_2Ph)_2$ (2.362 (3) Å, Cl trans to P)[49] and provides additional evidence for the well-known trans-bond weakening influence of a σ-bonded carbon atom.[50] A similar effect on palladium(II)-halogen bond lengths is evident from the structures of $PdBr(C_7H_8OCH_3)py_2$[38] and $Pd_2Cl_2(C_7H_8Ph)_2$.[39] The present Pd-Cl distance is also in excellent agreement with Pt-Cl distances trans to Pt-C σ-bonds, e.g., 2.412 (2) Å for $PtCl(CH_3)(PMePh_2)_2$[47] and 2.415 (5) Å for $PtCl(CH_2SiMe_3)(PMe_2Ph)_2$.[48]

The Pd-P distances (Pd-P(1), 2.349 (1); Pd-P(2), 2.258 (1) Å) are significantly different ($\Delta = 0.091$ Å, $\Delta/\sigma - 90$), and both are considerably shorter than the sum of covalent radii for simple σ-bonds (ca. 2.41 Å). The longer bond length [Pd-P(1)] is in excellent agreement with the corresponding distance of 2.333 (7) Å found in *trans*-$PdI_2(PMe_2Ph)_2$ (P trans to P),[51] whereas the shorter bond length [Pd-P(2)] agrees well with that found in *cis*-$PdCl_2(PMe_2Ph)_2$ (2.260 (2) Å, P cis to P).[49] The shortening of the Pd-P(2) bond may be a consequence of steric strain in the five-membered chelate ring (see above).

Within the tridentate ligand, the C(2)-C(3) bond length of 1.340 (5) Å agrees well with the value of 1.335 (5) Å expected for an olefinic linkage,[52] and the remaining distances (i.e., C(112)-C(3), C(3)-C(31), C(2)-C(1), and C(1)-C(212)) are all close to the expected value of 1.50 Å for σ-bonds between sp^2 and sp^3 hybridized carbon atoms. Apart from the unusually low value of the angle Pd-P(2)-C(211) (see above), the geometry at the phosphorus atoms and within the phenyl rings is normal.

There are no unusually short inter- or intramolecular contacts.

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Supplementary Material Available: A listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Large Zero Field Splitting and Subcritical Antiferromagnetic Interactions in $[Ni(C_5H_5NO)_6](ClO_4)_2$

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Abstract: The single-crystal paramagnetic susceptibilities of $[Ni(C_5H_5NO)_6](ClO_4)_2$ have been measured between 1.5 and 20 K and indicate a rather large zero field splitting. The data cannot be fit without the inclusion of a significant antiferromagnetic interaction which, however, is of the subcritical kind and which, of itself, cannot lead to long range spin ordering. The resulting parameters are $g_{\parallel} = 2.32 \pm 0.02$, $g_{\perp} = 2.33 \pm 0.02$, and $D/k = 6.26 \pm 0.05$ K, with a molecular field constant $zJ/k = -1.5 \pm 0.3$ K.

The nickel(II) ion is a sensitive probe of crystalline field distortions in transition metal complexes.[1] The g value is often isotropic with a value of 2.2–2.3 so, contrary to the case of cobalt, which exhibits widely variable g-value anisotropy,[2] this is not the source of the diagnostic procedure. But, zero field splittings of the ground state may occur, and these vary widely from compound to compound. What is interesting about nickel is that the zero field splittings are typically of the order of a few Kelvins, and thus are easily measured by either susceptibility or specific heat measurements at low temperatures.

The electronic structure of the nickel ion in octahedral fields has been reviewed.[3] A ${}^3A_{2g}$ ground state is found. Since nickel