Inorganica Chimica Acta, 150 (1988) 213–216

Molecular Structure of the Carbon-bound Phosphorus Ylide Complex *trans*-Dichlorobis(benzoyltri-n-butylphosphorane)palladium(II)

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(Received March 24, 1988)

Abstract

The molecular structure of *trans*-$[Pd(PhC(O)CHP(n\text{-}C_4H_9)_3)_2Cl_2]$ has been determined via a single crystal X-ray diffraction study: triclinic, $P\bar{1}$, $a = 8.876(2)$, $b = 10.908(3)$, $c = 11.938(4)$ Å, $\alpha = 97.06(2)^\circ$, $\beta = 102.79(2)^\circ$, $\gamma = 100.51(2)^\circ$, $V = 1092.1(5)$ Å^3, $Z = 1$ and $R(F) = 4.61\%$. The phosphorus ylide molecules are bound to the palladium atom through their methine carbon atoms, the overall coordination geometry about the palladium being square planar. The protons in the *ortho*-positions of the two phenyl groups are poised above and below the palladium atom, suggesting that the complex is a precursor of the *ortho*-metalated complex $[\overline{Pd(\mu\text{-}Cl)(C_6H_4C(O)C}HP(n\text{-}C_4H_9)_3)]_2$ synthesized earlier in our laboratory.

Introduction

Although the potential of keto-stabilized phosphorus ylides of the type $R_3PCR'C(O)R''$ to function as ambidentate ligands has been recognized for quite some time [1, 2], the truly ubiquitous bonding capabilities of these ligands has become apparent quite recently [3–5]. To date, four different bonding modes have been confirmed by single crystal X-ray diffraction studies: O-bonding via the carbonyl oxygen in an axial position in the trigonal bipyramidal complex $[Sn(CH_3)_3(Ph_3PCHC(O)CH_3)Cl]$ [2]; C-bonding via the methine carbon atom, coupled with *ortho*-metalation of a phenyl ring in the dinuclear complex $[\overline{Pt(\mu\text{-}Cl)CH_3C(O)C}HP(C_6H_4)Ph_2]_2$ [3]; metal–metal bridging via the methine carbon atom in the dinuclear complex $[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2Et\}]ClO_4$ [4]; and simple C-bonding via the methine carbon atom in the complex $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(Ph_3PCHC(O)CH_3)]$ [5].

As part of our continuing study of the ligating properties of these fascinating molecules [1, 3, 6–8], we have investigated [8] the possibility of combining C-bonding via the methine carbon atom with *ortho*-metalation of a phenyl ring bound to the carbonyl group, rather than to the phosphorus atom, as was previously observed [3] in the structure noted above. This goal was realized [8] in the synthesis of the complex $[\overline{Pd(\mu\text{-}Cl)(C_6H_4C(O)C}HP(n\text{-}C_4H_9)_3)]_2$, although its structure has not yet been confirmed by a single crystal X-ray diffraction study. Believing that C-coordination via the methine carbon atom was a prerequisite to the *ortho*-metalation reaction, we sought to isolate and structurally characterize the intermediate C-bound complex, *trans*-$[Pd(PhC(O)CHP(n\text{-}C_4H_9)_3)_2Cl_2]$. We now wish to report the success of this venture, including the determination of the molecular structure of the complex via a single crystal X-ray diffraction study.

Experimental

Preparation of Title Complex

Although the complex *trans*-$[Pd(PhC(O)CHP(n\text{-}C_4H_9)_3)_2Cl_2]$ (henceforth *trans*-$[Pd(BBuPY)_2Cl_2]$, where BBuPY represents benzoyl-tri-n-butylphosphorane) had been reported in one of our earlier studies [7], we were skeptical that this was its true identity. The complex *trans*-$[Pt(CH_3C(O)CHPPh_3)_2Cl_2]$ had also been reported in the same paper [7], whereas later work in our laboratory showed [3] the original sample to be an analytically identical 1:2 mixture of *ortho*-metalated $[\overline{Pt(\mu\text{-}Cl)CH_3C(O)C}HP(C_6H_4)Ph_2]_2$ and the $[CH_3C(O)CH_2PPh_3]Cl$ by-product of the *ortho*-metalation reaction.

Accordingly, the original sample [7] of $[Pd(BBuPY)_2Cl_2]$ was thoroughly washed with water to remove the (presumed) $[PhC(O)CH_2P(n\text{-}C_4H_9)_3]Cl$ impurity. This proved to be unnecessary, since the water washing did not alter the analytical results. *Anal.* Calc. for $[Pd(C_6H_5C(O)CHP(n\text{-}C_4H_9)_3)_2Cl_2]$: C, 58.72; H, 8.13; P, 7.57. Found (originally [7]): C, 58.95; H, 8.45; P, 7.48. Found (after water washing): C, 58.91; H, 8.51; P, 7.52%. Apparently, the shorter reflux time in acetonitrile employed in the earlier study (15 min [7], *versus* 30 min in our more recent work [8]) permitted the isolation of the non-*ortho*-metalated intermediate.

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Elemental Analysis

Elemental microanalyses were carried out by Guelph Chemical Laboratories, Ltd., Guelph, Ont., Canada.

X-ray Crystallography

Crystals of [Pd(BBuPY)$_2$Cl$_2$] suitable for X-ray diffraction were obtained by slow evaporation of an acetone solution. The deep yellow crystal was attached to a glass fiber with epoxy cement. All samples examined diffracted diffusely limiting data collection to a 45° maximum in 2θ. A hemisphere of data ($\pm h$, $\pm k$, $+l$) was collected on a Nicolet R3m/μ automated diffractometer, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at ambient temperatures. Pertinent crystallographic parameters are summarized in Table I.

Preliminary photographic characterization revealed no symmetry higher than triclinic and was confirmed by TRACER (del = 1.0). The centrosymmetric alternative, $P\bar{1}$, was suggested by E-statistics and confirmed by the chemically sensible and computationally stable results of refinement.

The structure was solved intuitively with the Pd atom at the origin. One of the butyl groups, C(13–16), is disordered over two sites with some atoms superimposed. The atoms labeled D(14) and D(16) are the minor occupancy (refined 34%) sites; C(13) and C(15) are common to both orientations. All nonhydrogen atoms, except for those of the disordered butyl group, were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized updated, isotropic contributions. All computations and sources of scattering factors used the SHELXTL (5.1) program library [10].

An ORTEP plot of the structure of the [Pd(BBuPY)$_2$Cl$_2$] complex is shown in Fig. 1. Atomic coordinates are given in Table II. Important bond distances and angles are shown in Tables III and IV.

Discussion

As anticipated, the coordination environment about the palladium atom is square planar, with a *trans*-arrangement of the coordinated methine carbon atoms. It should be noted that the protons in the *ortho*-positions of the two phenyl groups are poised 2.98 Å above and below the palladium atom, in an ideal position to undergo *ortho*-metalation.

TABLE I. Crystal and Intensity Data Collection Summary for *trans*-[Pd(PhC(O)CHP(n-C$_4$H$_9$)$_3$)$_2$Cl$_2$]

Molecular formula	PdCl$_2$P$_2$O$_2$C$_{40}$H$_{66}$
Molecular weight	818.2
a (Å)	8.876(2)
b (Å)	10.908(3)
c (Å)	11.938(4)
α (°)	97.06(2)
β (°)	102.79(2)
γ (°)	100.51(2)
V (Å^3)	1092.1(5)
Crystal system	triclinic
Space group	$P\bar{1}$
ρ (calc.) (g/cm^3)	1.244
Z	1
Diffractometer	Nicolet R3m/μ
Radiation	Mo Kα (graphite monochromated)
Absorption coefficient μ(Mo Kα) (cm^{-1})	6.4
Temperature (°C)	24 ± 2
Scan speed (°/min)	5.0–20.0
Scan type	$\theta - 2\theta$
Scan limits (°)	$4 \leqslant 2\theta \leqslant 45$
Standards monitored (x standards every y reflections), x/y	3/197
Reflections collected	$\pm h, \pm k, +l$
No. reflections collected	3023
Unique reflections ($F_o \geqslant 5\sigma(F_o)$)	2856 (R_{int} = 1.9%)
Unique reflections used	2444
Weighting factor g, $w^1 = \sigma^2(F_o) + g(F_o^2)$	0.001
$R(F)$ (%)	4.61
$R(F_w)$ (%)	4.97
GOF	1.344
Highest peak on final difference map (e/Å^3)	0.43
N_o/N_v	12.6

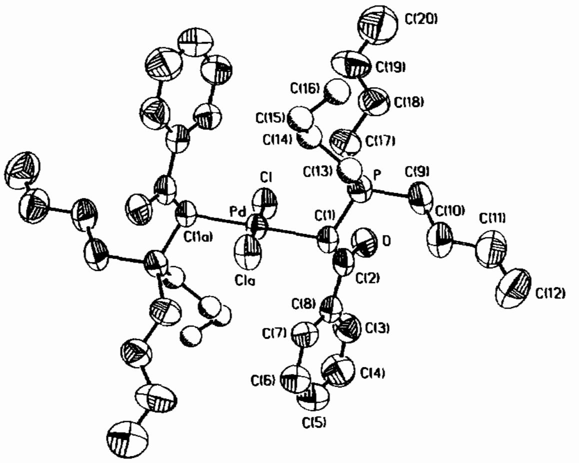


Fig. 1. Molecular structure and labeling scheme for [Pd(BBuPY)$_2$Cl$_2$]. Hydrogen atoms have been deleted. Thermal ellipsoids are shown at the 50% probability level. The C(13–16) butyl group is disordered. The major orientation is shown as arbitrary size spheres.

TABLE II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 $\times$ 10^3) for [Pd(BBuPY)$_2$Cl$_2$]

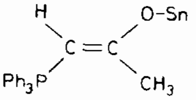
	x	y	z	U^a
Pd	0	0	0	61(1)*
Cl	2184(2)	1228(1)	−389(1)	87(1)*
P	−1933(2)	2225(1)	−574(1)	77(1)*
O	1056(5)	3577(3)	1035(3)	91(2)*
C(1)	−833(6)	1629(4)	600(4)	69(2)*
C(2)	503(6)	2607(5)	1355(5)	74(2)*
C(3)	2401(5)	3343(3)	3277(4)	106(3)*
C(4)	3075	3205	4414	136(4)*
C(5)	2545	2106	4828	133(4)*
C(6)	1342	1144	4105	116(4)*
C(7)	668	1282	2968	91(3)*
C(8)	1198	2382	2554	78(2)*
C(9)	−2380(8)	3718(6)	−82(6)	102(3)*
C(10)	−3134(8)	3708(6)	929(6)	109(3)*
C(11)	−3340(10)	5028(8)	1388(7)	135(4)*
C(12)	−4117(12)	5052(10)	2315(8)	173(6)*
C(13)	−3802(8)	1105(6)	−1166(6)	100(2)
C(14)	−3783(14)	132(11)	−2129(10)	113(5)
D(14)	−4897(28)	1081(23)	−2281(20)	133(10)
C(15)	−5565(18)	−848(17)	−2624(14)	227(6)
C(16)	−6389(19)	−175(16)	−3122(14)	177(7)
D(16)	−5874(46)	−1396(39)	−3648(38)	165(18)
C(17)	−898(7)	2467(6)	−1701(5)	96(3)*
C(18)	−1586(9)	3155(6)	−2639(5)	110(3)*
C(19)	−790(11)	3021(9)	−3686(6)	148(5)*
C(20)	−1326(16)	3717(12)	−4571(9)	225(8)*

^{a}Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III. Bond Lengths (Å) for [Pd(BBuPY)$_2$Cl$_2$]

Pd–Cl	2.317(1)
Pd–C(1)	2.149(5)
P–C(1)	1.786(5)
P–C(9)	1.805(7)
P–C(13)	1.809(6)
P–C(17)	1.808(7)
O–C(2)	1.225(7)
C(1)–C(2)	1.478(6)
C(2)–C(8)	1.497(7)
C(9)–C(10)	1.504(12)
C(10)–C(11)	1.534(11)
C(11)–C(12)	1.428(15)
C(13)–C(14)	1.471(14)
C(13)–D(14)	1.458(23)
C(14)–D(14)	1.556(30)
C(14)–C(15)	1.676(18)
D(14)–C(16)	1.747(24)
C(15)–C(16)	1.240(25)
C(15)–D(16)	1.241(45)
C(16)–D(16)	1.588(49)
C(17)–C(18)	1.504(10)
C(18)–C(19)	1.571(12)
C(19)–C(20)	1.423(15)

It is instructive to compare the structure of the [Pd(BBuPY)$_2$Cl$_2$] complex with those of the four phosphorus ylide metal complexes mentioned in the 'Introduction' (see Table V). The O-bound tin(IV) complex is best represented by the idealized structure



as evidenced by its relatively short (methine)C$\overset{\cdots}{-}$C(carbonyl) bond and its relatively long C—O bond. None of the five complexes give evidence of significant P$\overset{\cdots}{-}$C multiple bonding, when their P$\overset{\cdots}{-}$C bond lengths are compared with that in Ph$_3$PCH$_2$ (1.66 Å [9], with an estimated bond order of 1.3 [11]) and the average P–C single bond distance of 1.81 Å [2].

Finally, it should be noted that yet another reaction mode has been observed [12] for keto-stabilized ylides of the type under discussion, albeit with concomitant major alteration in the ylide framework. Nickel(0) complexes have been found [12] to react with α-keto ylides of phosphorus and arsenic, yielding a variety of new nickel complexes wherein phenyl group migration from the ylide has taken place. Depending on the nature of the nickel(0) complexes applied, the phenyl group either migrates to the nickel, forming a nickel–phenyl bond, or to a hydrocarbon ligand, thus forming the corresponding C–C-linked hydrocarbon product.

TABLE IV. Bond Angles (°) for [Pd(BBuPY)$_2$Cl$_2$]

Cl–Pd–C(1)	92.7(1)
Cl–Pd–Cl(A)	180.0(1)
C(1)–Pd–Cl(A)	87.3(1)
C(1)–Pd–C(1A)	180.0(1)
C(1)–P–C(9)	111.8(3)
C(1)–P–C(13)	107.5(3)
C(9)–P–C(13)	107.1(3)
C(1)–P–C(17)	112.7(3)
C(9)–P–C(17)	107.2(3)
C(13)–P–C(17)	110.4(3)
Pd–C(1)–P	112.2(2)
Pd–C(1)–C(2)	110.1(4)
P–C(1)–C(2)	112.3(4)
O–C(2)–C(1)	122.7(5)
O–C(2)–C(8)	119.5(4)
C(1)–C(2)–C(8)	117.8(4)
C(2)–C(8)–C(3)	117.1(2)
C(2)–C(8)–C(7)	122.9(2)
P–C(9)–C(10)	114.1(5)
C(9)–C(10)–C(11)	111.9(6)
C(10)–C(11)–C(12)	113.8(8)
P–C(13)–C(14)	113.9(6)
P–C(13)–D(14)	125.1(11)
C(13)–C(14)–C(15)	110.3(10)
C(14)–C(15)–C(16)	102.9(14)
C(14)–C(15)–D(16)	115.6(23)
P–C(17)–C(18)	117.4(5)
C(17)–C(18)–C(19)	111.0(7)
C(18)–C(19)–C(20)	113.6(9)

TABLE V. Comparisons of Selected Bond Lengths (Å) Among Metal Complexes of Phosphorus Ylides

Complex	P$\overset{\cdots}{-}$C(methine)	(methine)C$\overset{\cdots}{-}$C(carbonyl)	C$\overset{\cdots}{-}$O	Reference
[Sn(CH$_3$)$_3$(Ph$_3$PCHC(O)CH$_3$)Cl] [a]	1.75	1.36	1.27	2
[Pd(Cl(η^3-2-MeC$_3$H$_4$)(Ph$_3$PCHC(O)CH$_3$)] [b]	1.769(3)	1.452(5)	1.228(4)	5
[Pd(PhC(O)CHP(n-C$_4$H$_9$)$_3$)$_2$Cl$_2$] [b]	1.786(5)	1.478(6)	1.225(7)	this work
[Pt(μ-Cl)CH$_3$C(O)CHP(C$_6$H$_4$)Ph$_2$]$_2$ [c]	1.762(13)	1.547(22)	1.228(21)	3
[{Au(PPh$_3$)}$_2${μ-C(PPh$_3$)CO$_2$Et}]$^+$ [d]	1.763(10)	1.464(14)	1.211(13)	4

[a] O-bound ylide. [b] C-bound ylide. [c] C-bound ylide, with *ortho*-metalation. [d] Methine carbon bridges two gold atoms.

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