Journal of Organometallic Chemistry, 290 (1985) 125–131
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CATIONIC PALLADIUM(II) COMPLEXES INVOLVING UNPRECEDENTED *O*-COORDINATION OF ACETYLMETHYLENETRIPHENYLPHOSPHORANE

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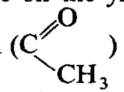
(Received January 30th, 1985)

Summary

Cationic pentafluorophenyl palladium(II) complexes of the type $[Pd(C_6F_5)L_2(APPY)]ClO_4$ ($L = PPh_3$, PBu^n_3; L_2 = bipy and APPY = $Ph_3PCHCOCH_3$, acetylmethylenetriphenylphosphorane) have been prepared by addition of APPY to the perchlorato complexes $[Pd(OClO_3)(C_6F_5)L_2]$; the APPY ligand is *O*-coordinated, which is unprecedented in keto-stabilized ylide complexes of palladium.

The neutral complex $Pd(C_6F_5)(Cl)(tht)(APPY)$ has been made by addition of APPY to the binuclear complex $Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2$ (tht = tetrahydrothiophene); in which the APPY ligand shows the normal *C*-coordination.

Introduction

In phosphorus ylides, $R^3P^+{-}^-C(R^1)(R^2)$ [1,2], the negative charge on the ylidic carbon may be delocalized over suitable substituents. For R^1 = acetyl  $\left(C\begin{matrix}{}^{\nearrow}O\\ {}_{\searrow}CH_3\end{matrix}\right)$ and $R^2 = H$, the stabilization of the phosphorus ylide produces a decrease in nucleophilicity and the compound is stable in the atmosphere.

The reaction of a keto-stabilized phophorus ylide (Y) with $PdCl_2$, $PdCl_2L_2$ (L = labile ligand) or $[Pd(\mu\text{-}Cl)ClL]_2$ leads to formation of neutral ylide complexes [3–7]. Alternatively, onium ylide halopalladate salts can be converted into neutral ylide complexes by HX abstraction with base [8]. Although numerous neutral complexes of Pd^{II} containing a keto-stabilized phosphorus ylide have been reported, there is to our knowledge only one report [9] of cationic complexes of Pd^{II}, namely $[Pd(C_5H_5)PPh_3(Y)]ClO_4$ ($Y = PPh_3CHCOCH_3$, $PPh_3CHCOPh$), which contain this type of unidentate ylide as a ligand. All the previously reported CO-stabilized Pd compounds are σ-C(ylidic)–Pd-bonded.

We describe below some neutral or cationic pentafluorophenyl complexes of Pd containing APPY. IR, ^1H and ^{31}P NMR studies of the complexes show that there is *O*-coordination of the APPY ligand in the cationic complexes. This mode of coordination of keto-stabilized ylides is unprecedented in palladium chemistry.

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TABLE 1

ANALYSES, CONDUCTIVITIES (IN ACETONE), AND MELTING POINTS OF THE COMPLEXES

Complex	Found (calcd.)(%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	M.p. (°C)
	C	H	N		
$[Pd(C_6F_5)(PPh_3)_2(APPY)]ClO_4$ (I)	62.00 (62.23)	4.57 (4.06)		140	198 (decomp.)
$[Pd(C_6F_5)(PBu^n_3)_2(APPY)]ClO_4$ (II)	55.85 (55.89)	6.94 (6.70)		131	128
$[Pd(C_6F_5)(bipy)(APPY)]ClO_4$ (III)	52.71 (52.45)	3.30 (3.21)	3.37 (3.30)	138	179
$[Pd(Cl)(C_6F_5)(tht)(APPY)]$ (IV)	52.05 (52.05)	3.99 (3.80)		0.8	160

Results and discussion

The reaction between benzene solutions of $[Pd(OClO_3)(C_6F_5)L_2]$ ($L = PPh_3$ or PBu^n_3, $L_2 =$ bipy) and acetylmethylenetriphenylphosphorane (APPY) leads to the formation of cationic complexes $[Pd(C_6F_5)L_2(APPY)]ClO_4$, according to eq. 1:

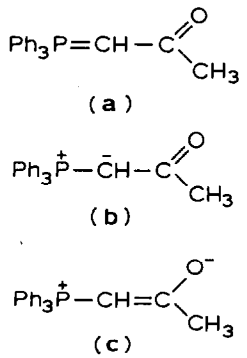
$$[Pd(OClO_3)(C_6F_5)L_2] + APPY \rightarrow [Pd(C_6F_5)L_2(APPY)]ClO_4 \qquad (1)$$

($L = PPh_3$ (I); $L = PBu^n_3$ (II); $L_2 =$ bipy (III))

On the other hand, APPY cleaves the chloro bridges in $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ (tht = tetrahydrothiophene) to give the neutral complex $[Pd(Cl)(C_6F_5)(tht)(APPY)]$, according to eq. 2:

$$[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2 + 2\ APPY \rightarrow \underset{(IV)}{2[Pd(Cl)(C_6F_5)(tht)(APPY)]} \qquad (2)$$

The analyses, conductivities, and melting points of the new complexes are listed in Table 1. The infrared spectral data are summarized in Table 2. The ^1H NMR and ^{31}P NMR data are listed in Table 3.



Acetylmethylenetriphenylphosphorane
(APPY)

TABLE 2

RELEVANT IR FREQUENCIES (cm^{-1})

	ν(C=O)	$\Delta\nu$(C=O) [a]
APPY	1540	
$[Ph_3PCH_2COCH_3]Cl$	1700	+160
I	1515	−25
II	1518	−22
III	1520	−20
IV	1655	+115

[a] $\Delta\nu = \nu$(compound)$-\nu$(free ylide).

TABLE 3

^{1}H NMR [a] AND ^{31}P {^{1}H} NMR [b] DATA

	δ(CH)	^2J(PH)	$\delta(CH_3)$	^4J(PH)	PPh_3 (ylide)	PR_3
APPY [21,22]	3.69(d)	27.0	2.07(d)	1.8	15.86(s)	
I A	3.72(d)	19.2	1.91(d)	1.7	11.94(s)	18.40(m)
B	3.86(d)	17.6	0.73(s)		14.52(s)	20.50(m)
II A	4.56(d)	20.7	2.58(d)	1.2	9.64(s)	6.44(m)
B	5.05(d)	16.8	1.75(s)		10.33(s)	6.88(m)
III A	4.45(d)	22.8	2.45(d)	1.2	13.73(s)	
IV	5.71(s)		2.69(s)		30.43(s)	

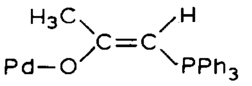
[a] In $CDCl_3$, values in ppm relative to internal TMS, J values in Hz. [b] In $CDCl_3$, values relative to external 85% H_3PO_4.

Keto-stabilized ylides can coordinate to a metal centre through either the ylidic carbon atom or the oxygen atom. From the resonance forms for the free ylide APPY (**a**–**c**) it can be expected that oxygen-bonding (where form **c** is a major contribution) should cause a decrease in the ν(C=O) frequency relative to that of the free ylide, whilst coordination through the nucleophilic methine carbon should lead to a high-frequency shift as a consequence of the increased contribution of form **b**. Hence, the carbonyl stretching frequency may be a convenient indicator of the type of coordination of the ylide to the metal.

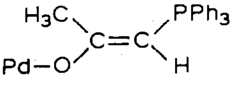
All the keto-stabilized ylide complexes of Pd^{II} described in the literature show an IR band ν(C=O) in the range 1700–1600 cm^{-1} corresponding to a *C*-coordination of the ylide ligand ($\Delta\nu$ positive; $\Delta\nu = \nu$(CO) (complex) $- \nu$(CO)(ylide)), and in the case of $PdCl_2(Me_2SCHCOPh)_2$ [10] and $PdCl_2(PPh_2CH_2CH_2PPh_2CHCOPh)$ [11] this has been confirmed by X-ray crystallography.

Surprisingly, our cationic complexes I–III have the ν(C=O) bands at values at frequencies as low as 1520–1515 cm^{-1} with $\Delta\nu < 0$. The observed range is close to the values of ν(C=O) reported for complexes of the type $R_3M(Cl)(Y)$ [12] (M = Sn, Pb; Y = keto-stabilized ylide), which are in the range 1510–1465 cm^{-1} ($\Delta\nu < 0$); in those complexes the ylide ligand was considered to be attached through the oxygen atom, and this was confirmed by the X-ray crystal structure of $[SnMe_3Cl(APPY)]$ [13]. The IR data of our complexes I–III point clearly to *O*-coordination of the ylide ligand, and this is confirmed by the NMR data (see below). Such coordination is unprecedented in palladium chemistry. In contrast, the neutral complex IV has ν(C=O) at 1655 cm^{-1}, within the range of the usual *C*-coordinated keto-stabilized ylide complexes.

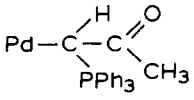
In our complexes $[Pd(C_6F_5)L_2(APPY)]^+$ there are several possibilities for isomerism: Firstly, there can be a *cis* or *trans* arrangement of the L ligands around the Pd center; the ^{31}P NMR spectra (discussed later) prove that for $L = PPh_3$, PBu^n_3, only the *trans*-isomer is formed, whereas for $L_2 =$ bipy the complex is necessarily the *cis*-isomer. Secondly there can be *O*- or *C*-coordination of the ylide ligand, as discussed above. Finally, if the APPY ligand is *O*-coordinated, the important contribution of the canonical form **c** hinders the internal rotation around the C=C bond so that two conformational isomers, the cisoid (**A**) and the transoid (**B**), can exist; if the APPY ligand is attached to the Pd atom through the C-ylidic atom (**C**) then two enantiomers, *R* and *S*, can be formed but these are indistinguishable in non-chiral solvents.



cisoid (A)



transoid (B)



(C)

O-coordination

C-coordination

The ^1H and $^{31}P\{^1H\}$ NMR spectra reveal the presence of two conformational isomers for both complex I and complex II, thus confirming the *O*-coordination of the ylide ligand. The relative intensity of the signals can be used to evaluate the cisoid to transoid ratio. Thus, the $^{31}P\{^1H\}$ NMR spectrum of complex I (Fig. 1) consists of two singlets at 11.9 and 14.5 ppm in approximately 1/4 ratio, assigned to the ylidic phosphorus, and two multiplets (arising from coupling to the fluorine atoms in C_6F_5) at 18.4 and 20.5 ppm in 2/8 ratio, assigned to the phosphine ligands. This means that the solution consists of a 1/4 mixture of the cisoid (**A**) and transoid (**B**) isomers of *trans*-$[Pd(C_6F_5)(PPh_3)_2(APPY)]^+$ and rules out the presence of the *cis*-complex, in which two inequivalent phosphines would give rise to pairs of signals of equal intensity, which are not observed. In the ^1H NMR spectrum (Fig. 2) the same 1/4 mixture is observed. The cisoid isomer displays a doublet at 3.72 ppm ($^2J(P-H)$ 19.2 Hz) for the methine proton and a doublet at 1.91 ppm ($^4J(P-H)$ 1.7 Hz) for the CH_3 protons. The transoid isomer shows a doublet at 3.86 ppm ($^2J(P-H)$ 17.6 Hz) and a singlet at 0.73 ppm. The identification of the minor component as the cisoid isomer is based on the expectation of a higher $^4J(P-H)$ coupling for this isomer than for the transoid one; this coupling was not, in fact, observed in the transoid isomer.

The detection of the cisoid and the transoid isomers is a conclusive proof of the proposed *O*-coordination of the ylide ligand. Moreover, the $^2J(P-H)$ values observed (17–20 Hz) are much larger than the small coupling constants ($<$ 6 Hz) observed for *C*-coordinated keto-stabilized ylide complexes of palladium [3,4,9], and very close to the value (24 Hz) observed for $[W(CO)_5(PPh_3CHCOPh)]$ [14], for which the presence of a band due to $\nu(C{=}O)$ at 1513 cm^{-1} again indicates *O*-coordination.

In the same way complex II is found to be an almost 1 : 1 mixture of the cisoid and the transoid isomer. For complex III signals are observed for only one isomer, but the *O*-coordination of the ylide in this complex is confirmed by the high value of $^2J(P-H)$ (22.8 Hz); the observation of $^4J(P-H)$ coupling (1.2 Hz) suggests that it is the cisoid isomer.

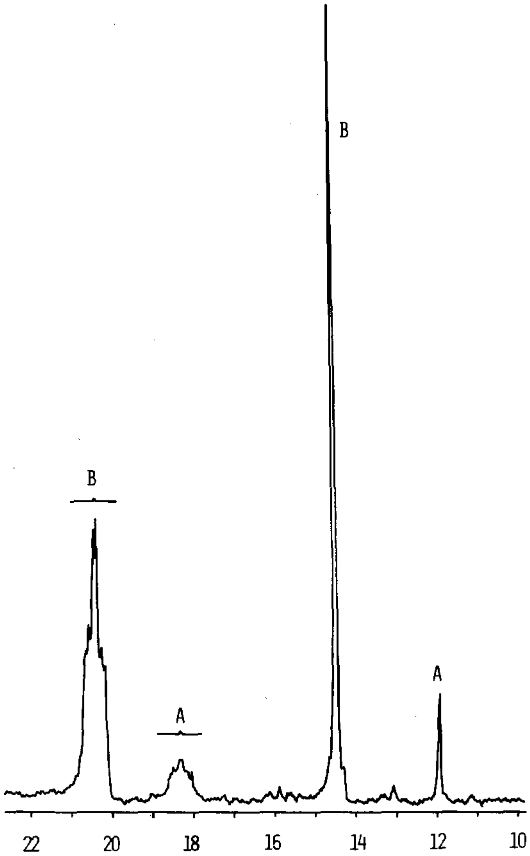


Fig. 1. $^{31}P\ \{^1H\}$ NMR spectrum of complex I (at 32.2 MHz, $CDCl_3$, ref. 85% H_3PO_4).

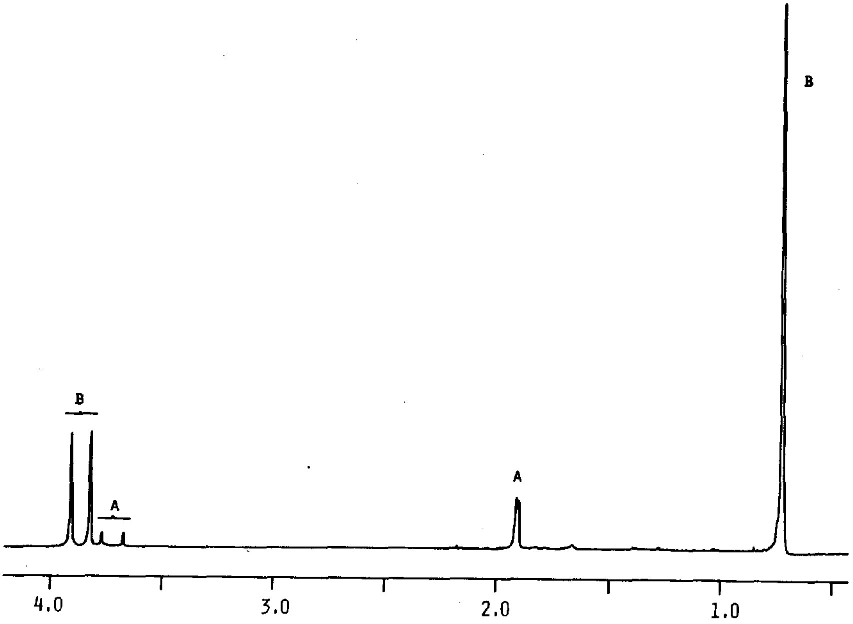


Fig. 2. ^1H NMR spectrum of complex I (at 200 MHz, $CDCl_3$, ref. TMS).

For the neutral complex [PdCl(C_6F_5)(tht)(APPY)] (IV) the IR spectrum suggests *C*-coordination of the ylide ligand. The ^{31}P {^1H} NMR spectrum shows only one singlet at significantly lower field than the preceding complexes, thus ruling out the presence of coordination of conformational isomers. More interestingly, the ^1H NMR spectrum consists of two singlets, in (1/3 ratio, related respectively to the methine and the CH_3 protons; thus $^2J(P{-}H)$ coupling is insignificant, which represents a difference from complexes I and II and a similarity to many *C*-coordinated keto-stabilized ylide complexes of palladium [8].

All the cationic complex exhibit IR absorption at ca. 1100vs,br and 620s cm^{-1}, characteristic [15] of the ClO_4^- anion (T_d), along with absorptions due to the C_6F_5 group (ca. 1500s, 950s cm^{-1}) [16] and to the neutral ligands. The complexes behave in acetone as 1 : 1 electrolytes [17], except for complex IV which is non-conducting.

Experimental

C, H and N analyses were carried out on a Perkin–Elmer 240 microanalyzer. Melting points were determined with a Buchi apparatus and are uncorrected. Conductivities were measured in approx. 5×10^{-4} *M* solutions with a Philips PW 9501/01 conductimeter. The IR spectra were recorded (in the 4000–200 cm^{-1} range) on a Perkin–Elmer 577 spectrophotometer using Nujol mulls between polyethylene sheets. NMR spectra were recorded with a Varian XL-200 spectrometer in $CDCl_3$ solution.

Standard methods were used to prepare the compounds: $CH_3COCHPPh_3$ (APPY) [18], [Pd(μ-Cl)(C_6F_5)(tht)]$_2$ [19] and [Pd($OClO_3$)(C_6F_5)L_2] [20] ($L = PPh_3$, PBu^n_3; L_2 = bipy).

[Pd(C_6F_5)L_2(APPY)]ClO_4 ($L = PPh_3$ (I), $L = PBu^n_3$ (II); L_2 = bipy (III))

A solution of APPY (0.11 g, 0.36 mmol) in 10 ml of benzene was added to a solution of [Pd($OClO_3$)(C_6F_5)L_2] ($L = PPh_3$ or PBu^n_3 L_2 = bipy) (0.33 mmol) in 20 ml of benzene. For $L = PPh_3$, a white precipitate was formed almost instantaneously. For $L = PBu^n_3$, the solution was stirred for 4 h at room temperature, then concentrated to 10 ml to give white crystals. In the case of L_2 = bipy, a yellow oil separated spontaneously, and this was recrystallised from $CHCl_3/C_6H_6$ to give a pale yellow solid.

The solids were filtered off, washed with benzene, and recrystallised from $CHCl_3/C_6H_6$. Yields: I: 99% (0.417 g), II: 78% (0.298 g), III: 75% (0.225 g).

[PdCl(C_6F_5)(tht)(APPY)] (IV)

A solution of APPY (0.400 g, 1.25 mmol) in 20 ml of acetone was added to a solution of [Pd(μ-Cl)(C_6F_5)(tht)]$_2$ (0.400 g, 0.50 mmol) in 20 ml of acetone. The solution was stirred for 48 h (at room temperature) and evaporated to dryness; the residual oil was stirred with 2 × 10 ml of hexane to give a pale yellow solid, which was filtered off, washed with 2 × 5 ml of EtOH, and dried. Yield: 70% (0.543 g).

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