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Preparation and characterization of Pd^{II}-ylide complexes of type $\{Pd(CNR)(\eta^3\text{-}2\text{-}XC_3H_4)[Ph_3PC(H)COMe]\}BF_4$ ($X = H, Me; R = p\text{-}C_6H_4OMe, C(Me)_3, Me, C_6H_{11}, p\text{-}C_6H_4NO_2$). Crystal structure of $\{Pd[CNC(Me)_3](\eta^3\text{-}2\text{-}MeC_3H_4)[Ph_3PC(H)COMe]\}BF_4$

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Abstract

Seven compounds of general formula $\{Pd(CNR)(\eta^3\text{-}2\text{-}XC_3H_4)[Ph_3PC(H)COMe]\}BF_4$ ($X = H$, $R = p\text{-}C_6H_4OMe$ (**1**), $R = C(Me)_3$ (**2**); $X = Me$, $R = p\text{-}C_6H_4OMe$ (**3**), $C(Me)_3$ (**4**), Me (**5**), C_6H_{11} (**6**), $p\text{-}C_6H_4NO_2$ (**7**)) have been prepared by chloride abstraction from $PdCl(\eta^3\text{-}2\text{-}XC_3H_4)[Ph_3PC(H)COMe]$ ($X = H$, Me) with $AgBF_4$ and subsequent reaction of the cationic intermediate with the appropriate isocyanide ligand. All the complexes have been characterized by analytical and spectroscopic (IR, ^1H and $^{31}P\{^1H\}$ NMR) data. They have been shown to be a mixture of two diastereoisomeric forms arising from the simultaneous presence on the palladium atom of the asymmetric ylidic carbon atom and the η^3-allyl ligand. The determination of the crystal structure of complex **4** showed that in the solid state only one diastereoisomer is present. The crystals are monoclinic, space group *Pc* with a 9.833(3), b 14.383(4), c 11.762(4) Å, β 114.68(3)°, and $Z = 2$. Final full-matrix least-squares refinement, based on 2413 reflections, converged to $R = 0.050$. The keto-stabilized ylide ligand is C bonded to the metal with a Pd–C distance of 2.175 (9) Å.

Introduction

An important general characteristic of transition metal complexes of ylides is the stability of the metal–C(ylide) σ-bond [1]. This stability, which is greater than that of normal metal–alkyl σ-bonds and in several cases is comparable with that of metal–fluoroalkyl bonds [1b], is mainly due to the inductive effect and π-acceptor character of the adjacent onium group. However, the nature of the substituents on the ylidic carbon atom and that of the organometallic coordinated fragment can also play an important role in the stabilization of the M–C(ylide) bond.

We have previously reported the synthesis and characterization of palladium-ylide derivatives of type **A** (eq. 1) [2]. These complexes, which are stable in the solid state,

$$\tfrac{1}{2}\left[PdCl(\eta^3\text{-}2\text{-}XC_3H_4)\right]_2 + Ph_3\overset{+}{P}\text{-}\bar{C}(H)COR \rightleftarrows$$

(X = H, Me; R = Me, Ph)

$$\left\{\overset{-}{Pd}Cl(\eta^3\text{-}2\text{-}XC_3H_4)\left[Ph_3\overset{+}{P}\text{-}C(H)COR\right]\right\} \qquad (1)$$

(**A**)

show an extremely labile Pd–C(ylide) bond in solution. Thus, it has been observed that the C-coordinated ylide spontaneously dissociates in CH_2Cl_2 or $CHCl_3$ solution at room temperature, giving rise to an equilibrium mixture between the compound **A** and its comparants.

Rupture of the M–C(ylide) bond is not a frequently observed process. Nevertheless, it may be involved in some reactions, such as in the *cis–trans* isomerization of $\{PdCl_2L[ER_nC(H)COPh]\}$ (L = PMe_3, PMe_2Ph; ER_n = $PMePh_2$, $AsPh_3$, SMe_2) [3] or in the reversible dissociation of $PdCl_2[C(H)(SMe_2)COPh]_2$ [4] in solution.

We describe here the preparation and characterization of a series of Pd^{II}–P–ylide complexes containing an isocyanide ligand (see Scheme 1). Replacement in compounds of type **A** of an anionic (Cl^-) by a neutral π-acceptor (CNR) ligand would be expected to stabilize the M–C(ylide) bond to a greater extent towards dissociation, thus allowing a more datailed study of this type of bond in allyl-Pd(II) derivatives.

Experimental

General. All operations were carried out under nitrogen. Solvents were distilled under argon from appropriate drying agents [5] immediately before use. IR spectra were recorded on a Perkin–Elmer 983 spectrophotometer as Nujol Mulls or CH_2Cl_2 solutions. ^1H NMR spectra were recorded on a Bruker AM-400 and $^{31}P\{^1H\}$ NMR spectra on a Varian FT-80A spectrometer. Microanalyses were performed by the Department of Analytical Chemistry of the University of Padua. The dimers $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ and $[PdCl(\eta^3\text{-}C_3H_5]_2$ [6] and the keto-stabilized ylide ampp [(acetylmethylene)triphenylphosphorane, $Ph_3\overset{+}{P}\text{-}\bar{C}(H)COMe$] [7] were prepared by published methods, as were *p*-methoxyphenyl isocyanide [8], methyl isocyanide [8], and *p*-nitrophenyl isocyanide [9]. t-Butyl isocyanide and cyclohexyl isocyanide were purchased, and used as received. All other chemicals were reagent grade and used without further purification.

Table 1

Analytical data and characteristic IR bands for the complexes $[Pd(CNR)(\eta^3\text{-}2\text{-}XC_3H_4)\text{-}\{Ph_3PC(H)COCH_3\}]BF_4$

Compound	X	R	M.p. (°C) [a]	Yield (%)	Analysis (Found(calcd.)(%)) C	H	N	IR (cm^{-1}) [b] ν(C≡N)	ν(C=O)
1	H	p-C_6H_4OMe	94–96	81.2	56.26	4.65	2.12	2188s [d]	1628s [d]
					(56.04)	(4.56)	(2.04)	2190s [c]	1632s [c]
2	H	$C(Me)_3$	109–110	78.8	54.54	5.02	2.35	2196s [d]	1631s [d]
					(54.79)	(5.23)	(2.20)	2200s [c]	1632s [c]
3	Me	p-C_6H_4OMe	147–149	73.8	56.28	4.43	2.08	2188s [d]	1629s [d]
					(56.64)	(4.75)	(2.00)	2190s [c]	1631s [c]
4	Me	$C(Me)_3$	154–156	75.0	55.81	5.68	2.14	2201s [d]	1640s [d]
					(55.45)	(5.43)	(2.16)	2203s [c]	1634s [c]
5	Me	Me	107–108	80.5	52.95	4.65	2.47	2227s [d]	1629s [d]
					(53.36)	(4.81)	(2.31)	2232s [c]	1633s [c]
6	Me	C_6H_{11}	127–129	82.7	56.59	5.40	2.20	2205s [d]	1631s [d]
					(56.87)	(5.52)	(2.07)	2208s [c]	1635s [c]
7	Me	p-$C_6H_4NO_2$	115–118	71.3	54.02	4.28	4.08	2177s [d]	1629s [d]
					(53.77)	(4.23)	(3.92)	2179s [c]	1630s [c]

[a] All complexes decompose on melting. [b] s = strong. [c] Dichloromethane solution. [d] Nujol mull.

Preparation of $\{Pd(CNR)(\eta^3\text{-}2\text{-}XC_3H_4)[Ph_3PC(H)COMe]\}BF_4$ (X = H, R = p-C_6H_4OMe (**1**), $C(Me)_3$ (**2**); X = Me, R = p-C_6H_4OMe (**3**), C(Me) (**4**), Me (**5**), C_6H_{11} (**6**), p-$C_6H_4NO_2$ (**7**)). Compounds **1**–**7** were obtained by the procedure reported below for complex **3** (see Scheme 1, path a).

A solution of 0.548 *M* $AgBF_4$ (1.83 cm^3, 1.00 mmol) in acetone was added dropwise to a suspension of $\overset{-}{Pd}Cl(\eta^3\text{-}2\text{-}MeC_3H_4)[Ph_3\overset{+}{P}C(H)COMe]$ (0.498 g, 1.00 mmol) in acetone (20 cm^3) at −20 °C. The mixture was stirred for 1 h then allowed to warm to room temperature. The AgCl was filtered off and the filtrate treated dropwise at −20 °C with a solution of CNC_6H_4-p-OMe (0.133 g, 1.00 mmol) in acetone (10 cm^3) during 20 min. The pale yellow solution was stirred for 30 min at 0 °C, then its volume was reduced (to 2 cm^3) and Et_2O (40 cm^3) was added, to give an ivory solid, which was filtered off, washed with Et_2O (3 × 20 cm^3), and dried under vacuum. Yield 0.516 g. Analytical and spectral data for complexes **1**–**7** are reported in Table 1 and 2.

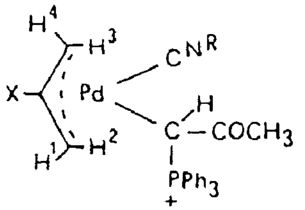
Preparation of $PdCl(CNC_6H_4\text{-}p\text{-}OMe)(\eta^3\text{-}2\text{-}MeC_3H_4)$ *(**B**).* This complex was synthesized by the procedure previously described [10] for the preparation of analogous isocyanide systems. A suspension of $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4]_2$ (0.394 g, 1.00 mmol) in anhydrous Et_2O (30 cm^3) at 0 °C was treated dropwise with CNC_6H_4-p-OMe (0.266 g, 2.00 mmol) in Et_2O (10 cm^3). The mixture was stirred for 30 min and the white suspension formed was used for the subsequent reaction without isolation of the solid, which is particularly unstable.

*Synthesis of complex 3 starting from **B**.* The suspension of **B** was treated with a solution of 0.548 *M* $AgBF_4$ (1.83 cm^3, 1.00 mmol) in acetone at −20 °C. The mixture was stirred for 1 h then allowed to warm to room temperature. The AgCl was filtered off and the filtrate was treated with an equimolar amount of ampp and stirred for 30 min. The solution was concentrated to small volume (3 cm^3) and by

Table 2

Proton and $^{31}P\{^1H\}$ NMR data for the complexes $[Pd(CNR)(\eta^3\text{-}2\text{-}XC_3H_4)\{Ph_3PC(H)COCH_3\}]BF_4$

Compound



Allyl resonances

Compound	$\delta(H^1)$	$^3J(H^1X)$	$\delta(H^2)$	$^3J(H^2X)$	$\delta(H^3)$	$^3J(H^3X)$	$\delta(H^4)$	$^3J(H^4X)$	$\delta(X)$
1	3.40(d), 3.44(d)	7.02, 7.42	2.56(d), 2.54(d)	12.81, 13.30	2.93(d), 2.80(d)	12.83, 13.09	4.38(d), 4.44(d)	6.88, 7.13	5.07(m), 5.30(m)
2	3.40(dd), 3.13(dd)	6.68, 6.79	2.57(d), ^{b}	13.26	2.79(d), 2.82(d)	12.89	4.25(dd), 4.30(dd)	6.58, 6.81	5.11(m), 5.16(m)
3	3.46(d), 3.91(d)		2.50(s), 2.53(s)		2.76(s), 2.86(s)		4.20(d) ^{c}		1.63(s), 1.73(s)
4	3.20(d), 3.67(d)		1.94(s), 2.16(s)		2.63(s), 2.73(s)		4.04(d) ^{c}		1.59(s), 1.72(s)
5	3.11(d), 3.35(d)		1.96(s), 2.53(s)		2.58(s), 2.78(s)		4.09(d), 4.15(d)		1.49(s), 1.72(s)
6	3.23(d), 3.63(d)		2.32(s), 2.41(s)		2.66(s), 2.75(s)		4.07(d), 4.09(d)		1.58(s), 1.64(s)
7	3.46(d), 3.87(d)		2.51(s), 2.57(s)		2.87(s), 3.00(s)		4.39(d) ^{c}		1.66(s), 1.71(s)

	Ylide resonances					Isocyanide resonances
	$\delta(CH)$	$^2J(HP)$	$\delta(CH_3)$	$^4J(HP)$	$\delta(P)$	$\delta(R)$
1	5.19(d), 5.31(d)	3.82, 4.32	2.29(d) ^{d}	2.34	23.25(s), 24.09(s)	3.77(s) ^{e,d}
2	5.06(d), 5.15(d)	3.59, 4.16	2.20(d), 2.24(d)	1.98, 2.40	23.17(s), 23.75(s)	1.33(s), 1.58(s)
3	5.32(d) ^{d}	4.30	2.30(d), 2.36(d)	2.36, 2.38	23.26(s), 23.90(s)	3.81(s) ^{e}, 3.83(s) ^{e}
4	5.13(d), 5.16(d)	4.23, 4.39	2.21(d), 2.29(d)	2.45, 2.60	23.51(s), 23.90(s)	1.28(s), 1.30(s)
5	5.01(d) ^{d}	3.55	2.27(d), 2.28(d)	2.33, 2.36	23.80(s), 25.14(s)	1.72(s)
6	5.15(d) ^{d}	4.13	2.26(d), 2.30(d)	2.25, 2.26	23.81(s), 24.41(s)	
7	5.34(d) ^{d}	4.31	2.32(d), 2.37(d)	2.39, 2.50	23.24(s), 24.10(s)	

[a] Spectra recorded in $CDCl_3$ at 303 K; δ in ppm, J in Hz; ^1H and $^{31}P\text{-}\{^1H\}$ NMR chemical shifts are relative to internal $SiMe_4$ and H_3PO_4 (85%), respectively; s = singlet, d = doublet, m = multiplet. [b] Obscured by CH_3 signals of the ylide ligand. [c] The resonances of the H^4 protons of species (Ia) and (Ib) appear as single doublet. [d] Only one doublet for the two diastereoisomeric forms Ia and Ib. [e] δ(OMe).

adding of Et_2O (30 cm^3) a white solid precipited which was identified as compound **3**. Yield 0.453 g, 74%.

Reaction of complex 3 with CNC_6H_4-p-OMe. A solution of complex **3** (0.175 g, 0.25 mmol) in 1,2-dichloroethane (20 cm^3) was treated with CNC_6H_4-*p*-OMe (0.033 g, 0.25 mmol). The solution was stirred for 30 min at room temperature and then taken to dryness under reduced pressure. The residue was extracted with C_6H_6 (40 cm^3) and the insoluble portion filtered off, washed with Et_2O (2 × 10 cm^3), and identified as $[Pd(CNC_6H_4\text{-}p\text{-}OMe)_2(\eta^3\text{-}2\text{-}MeC_3H_4)]BF_4$. Yield 0.110 g, 83%; m.p. 133–135 °C. IR (CH_2Cl_2; cm^{-1}): $\nu(C{\equiv}N)$ 2192s; ^1H NMR ($CDCl_3$, ppm): $\delta(OCH_3)$ 3.85s, $\delta(Me)_{allyl}$ 2.04s, $\delta(H_{syn})$ 4.17br, $\delta(H_{anti})$ 3.34br; elemental analysis: Found: C, 47.09; H, 4.08; N, 5.10. $C_{20}H_{21}N_2O_2BF_4Pd$ calc.: C, 46.68; H, 4.11; N, 5.45%. The free ylide (0.071 g, 89%) was recovered from the benzene extract by concentration and addition of n-pentane.

Structure determination of $\{Pd(CNCMe_3)(\eta^3\text{-}2\text{-}MeC_3H_4)[Ph_3PC(H)COMe]\}BF_4$ (4). Crystals were obtained as a racemic mixture from a solution of **4** in dichloromethane/ethyl ether (1/2) at −20 °C.

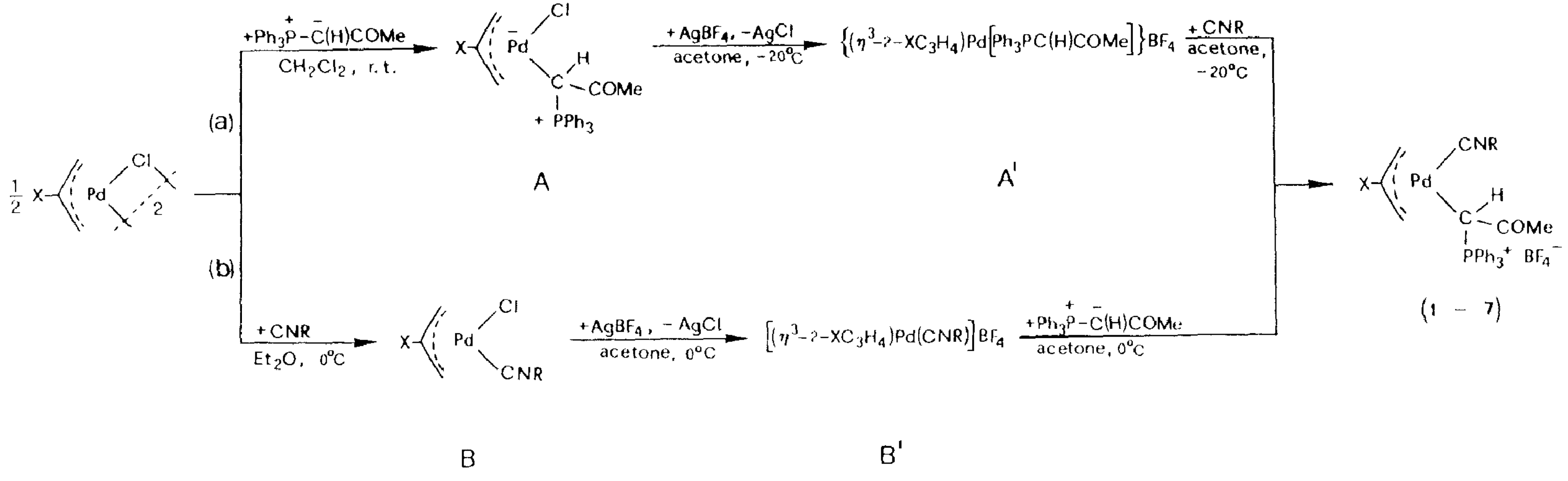
Crystal data. $C_{30}H_{35}BF_4NOPPd$, $M = 515.4$, monoclinic, a 9.833(3), b 14.383(4), c 11.762(4) Å, β 114.68(3)°, U 1512(1) $Å^3$, space group Pc, $Z = 2$, D_c 1.428 g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 7.0$, $\lambda(Mo\text{-}K_\alpha) = 0.71069$ Å.

Data collection and processing. Intensity data were recorded on an Enraf–Nonius CAD4 diffractometer, ω–2θ mode, Mo-K_α radiation, graphite monochromator. Four standard reflections measured periodically during data collection revealed no significant decay. 2413 Unique reflections with $I > 3\sigma(I)$ ($3 < \theta < 27°$ at room temperature) were corrected for Lorentz-polarization effects. An empirical absorption correction was applied by using the Ψ-scan data from close to axial (i.e. $\chi > 80°$) reflections. Anomalous dispersion corrections were applied to all non-hydrogen atoms [11a].

Structure analysis and refinement. The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms except the B and F atoms. Hydrogen atoms were included at calculated positions and held fixed during refinement (B 5 $Å^2$). The final values of the discrepancy indices were $R = \Sigma || F_o | - | F_c || / \Sigma | F_o | = 0.050$ and $R' = [\Sigma w(| F_o | - | F_c |)^2 / - \Sigma w F_o^2] = = 0.055$. Unit weights were used. No significant difference in the R factors was observed upon change of the enantiomorph. Neutral atom scattering factors were taken from the literature [11b]. Data processing was performed on a PDP 11/44 computer by use of the Enraf–Nonius SDP program library [12]. Tables of thermal parameters, hydrogen atom coordinates, and observed and calculated structure factors are available from the authors.

Results and discussion

The route to complexes **1**–**7** from Pd dimers is illustrated in Scheme 1. Two synthetic routes can be used. The first (a) involves initial formation of the Pd^{II}-η^3-allyl-ylide derivatives (**A**) [2], subsequent halide abstraction by $AgBF_4$, and final reaction of the cationic intermediate (**A′**) with the isocyanide ligand. The second (b) involves the preparation of Pd^{II}-η^3-allyl-isocyanide compounds (**B**), followed by halide abstraction and then reaction of the cationic intermediate (**B′**) with ampp. Complexes **1**–**7** were obtained by route (a), while compound **3** was also obtained by

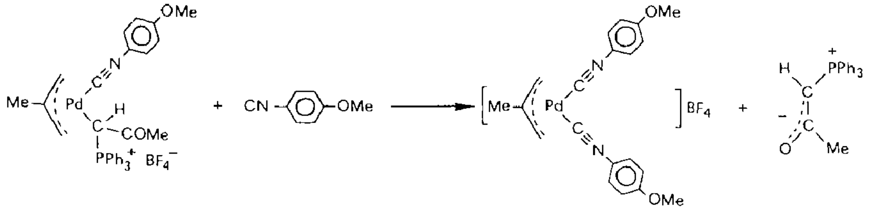


X = H; R = p-C_6H_4OMe (**1**), $C(Me)_3$ (**2**)

X = Me; R = p-C_6H_4OMe (**3**), $C(Me)_3$ (**4**), Me (**5**), C_6H_{11} (**6**), p-$C_6H_4NO_2$ (**7**)

Scheme 1

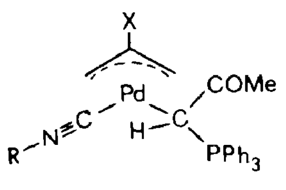
path (b). The products **1–7** are indefinitely stable as solids at 0 °C. In solution in chlorinated or alcoholic solvents they do not spontaneously dissociate, as their parent compound (**A**) does [2], but gradually decompose during a few days. When compounds **1–7** are treated with a stoichiometric amount of $[AsPh_4]Cl$ in CH_2Cl_2 solution, the IR spectra show an immediate appearance of the strong band corresponding to the free ylide at 1529 cm^{-1}. The ylide ligand is also replaced by reaction with isocyanides. Thus compound **3** reacts immediately with one equivalent of CNC_6H_4-*p*-OMe in 1,2-dichloroethane to give the bis-isocyanide derivative $[Pd(CNC_6H_4\text{-}p\text{-}OMe)_2(\eta^3\text{-}2\text{-}MeC_3H_4)]BF_4$ and the free ylide, as depicted in eq. 2.



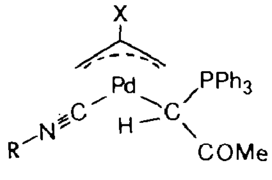
(2)

These experimental evidences suggest that the Pd–ylide bonds in compounds **1–7**, is slightly stronger than those in the complexes of type **A**, but still weak enough to be readily replaced by a Cl^- ion or CNR ligand. This lability is also consistent with the structural data, which show a high value (2.175(9) Å) for the Pd–C(ylide) bond distance in the X-ray crystal structure of complex **4** (see below). All the derivatives **1–7** were characterized by analytical and spectroscopic (IR, ^1H and $^{31}P\{^1H\}$ NMR) data, and in the case of complex **4** also by an X-ray diffraction study.

The IR spectra of the final products **1–7** show a strong absorption in the range 2177–2232 cm^{-1} (CH_2Cl_2 solution) characteristic of isocyanide ligands coordinated to Pd^{II} complexes [13]. The ylide ligand in all complexes **1–7** is coordinated to the metal through the ylidic carbon atom. This is indicated by IR spectra, which display a strong absorption in the range 1630–1634 cm^{-1} (ν(C=O) in CH_2Cl_2 solution) with $\Delta\nu = \nu(C{=}O)_{coord.} - \nu(C{=}O)_{free}$ of 101–105 cm^{-1} characteristic for Pd^{II}–C(ylide) systems of keto-stabilized ylides [2,3]. The C(ylide)-coordination to the metal centre involves a $sp^2 \rightarrow sp^3$ rehybridization of the ylidic carbon to produce an asymmetric carbon atom. The simultaneous presence of an η^3-allylic group and an asymmetric carbon bonded to palladium atom may amount for the existence for all complexes **1–7** of the two diastereoisomeric forms (Ia) and (Ib), as found also for derivatives of type **A** [2].



(Ia)



(Ib)

The $^{31}P\{^1H\}$ NMR spectra confirm this showing for all the complexes **1–7** two signals, in ca. 1/1 ratio, in the range δ 23.17–25.14 ppm characteristic of a phosphonium moiety [3]. The resonances are shifted by ca. 9–11 ppm downfield with respect to the signal of free ampp. These shifts well agree with those found for others palladium complexes of keto-stabilized ylides [2,14], and favour C-coordination rather than O-coordination [15].

Also the ^{1}H NMR spectra of the compounds **1**–**7** suggest the existence of two species (Ia) and (Ib). The complexes **1**–**7** show the signals of the methine proton of the ylidic ligand in the range δ 4.99–5.34 ppm as doublets arising from ^{1}H-^{31}P coupling. Compounds **1**, **2** and **4** display two distinct doublets attributable to the diastereoisomeric forms (Ia) and (Ib), while compounds **3**, **5**–**7** show a single doublet. The values of the ^2J(HP) coupling constant between methine proton and phosphorus atom of the ylidic ligand of derivatives **1**–**7** are in the range 3.55–4.39 Hz, these values are lower by 22–23 Hz than those for free ampp as a consequence of the $sp^2 \rightarrow sp^3$ rehybridization of the ylidic carbon upon coordination to the metal centre [14,16]. The methyl group of the coordinated ylide gives rise to a doublet in the ^{1}H NMR spectrum for each diastereoisomer (Ia) and (Ib) owing to the coupling with the ylidic phosphorus atom. The ^4J(HP) coupling constants are in the range 1.98–2.60 Hz, in agreement with those found for analogous derivatives **A** contaiing ampp [2].

The allyl protons in the ^{1}H NMR spectra of complexes **1**–**7** give rise to two sets of signals attributable to the two diastereoisomeric forms (Ia) and (Ib). The assignment of the allylic *syn* and *anti* protons is based on the values of the ^3J(HH) couplings with the central proton ($^3J(\text{H}_{syn}\text{H}) > {}^3J(\text{H}_{anti}\text{H})$ [17] for complexes **1** and **2**. Furthermore, for all the complexes **1**–**7** it was assumed that *syn* and *anti* protons *trans* to the coordinated isocyanide ligand undergo a greater shift than *syn* and *anti* protons *trans* to coordinated ylide with respect to those observed for the allylic protons in similar derivatives of type **A** [2]. However, it is not possible to assign the corresponding signals to the separate diastereoisomers since integration ratios in the ^{31}P{^{1}H} NMR spectra indicate that the two forms are present in similar amounts. Finally, the signals of the *syn* allyl protons, in complexes **2**, **4**–**7**, show a distinct *syn*–*syn* coupling, with values of ^4J(HH) in the range 2.14–2.80 Hz, in agreement with those reported in the literature [18].

Figure 1 shows the ^{1}H NMR spectrum of compound **1** as a typical example. It exhibits the characteristic AMYZ-X pattern of allylic protons [19] for both diastereoisomeric species (Ia) and (Ib). The two multiplets centered at δ 5.07 and 5.30 ppm are attributed to central proton. On the basis of the above assumptions, the two doublets centred at δ 4.44 and 4.38 ppm are assigned to the *syn* proton *trans* to ylide, and the doublets at δ 3.40 and 3.44 ppm to the *syn* proton *trans* to isocyanide. The two pairs of doublets, at δ 2.93 and 2.80 ppm and at δ 2.54 and 2.56 ppm, are attributed respectively to the *anti* protons *trans* and *cis* to the ylide group.

X-Ray Structure of {$Pd(CNCMe_3)(\eta^3\text{-}2\text{-}MeC_3H_4)[Ph_3PC(H)COMe]$}$BF_4$ *(**4**)*. The structure of the cation is depicted in Fig. 2, along with the atom numbering scheme. For clarity only two C atoms of the phenyl groups are labeled. Final fractional coordinates are given in Table 3, and selected bond lengths and angles in Table 4.

The results of the structure analysis show that the crystal contains only one enantiomeric form of the diastereoisomer (Ia), showing that upon crystallization, the two enantiomers separate as a racemic mixture of the sterically less hindered

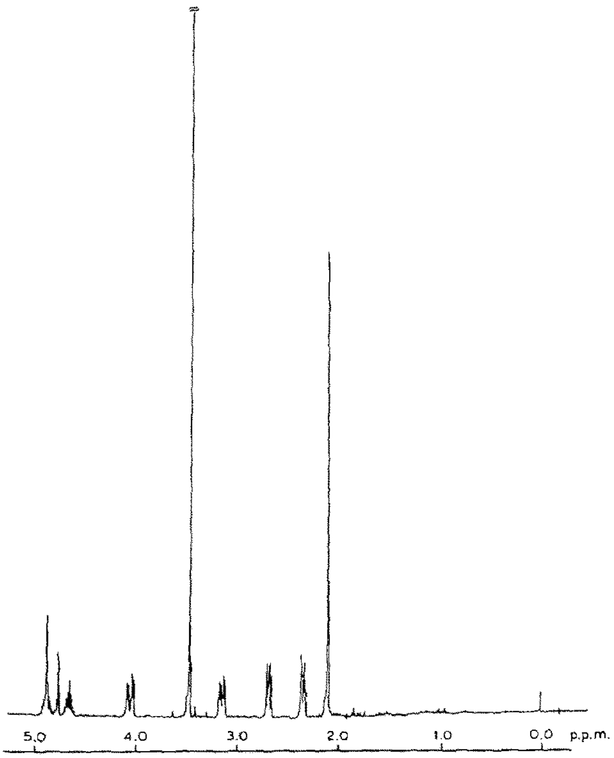


Fig. 1. Proton NMR spectrum in the 0.0–5.0 ppm range of $\{Pd(CNC_6H_4\text{-}p\text{-}OMe)(\eta^3\text{-}C_3H_5)[Ph_3PC(H)COMe]\}BF_4$ (**1**) in $CDCl_3$ at 299 K.

species. A similar shift of the equilibrium between (Ia) and (Ib) was previously observed for the derivatives of type **A** [2].

The arrangement of the ligands around the palladium atom in the cation of **4**, $\{Pd(CNCMe_3)(\eta^3\text{-}2\text{-}MeC_3H_4)[Ph_3PC(H)COMe]\}^+$, is quite similar to that in the

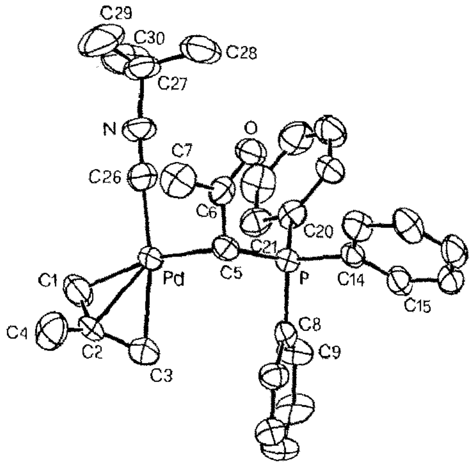


Fig. 2. ORTEP drawing of the cation **4**, $\{Pd(CNCMe_3)(\eta^3\text{-}2\text{-}MeC_3H_4)[Ph_3PC(H)COMe]\}^+$, showing the atom numbering scheme.

Table 3

Final fractional coordinates with e.s.d.s. in parentheses for $\{Pd(CNCMe_3)(\eta^3\text{-}2\text{-}MeC_3H_4)[Ph_3PC(H)CO\text{-}Me]\}BF_4$ (**4**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	0.500	0.15949(5)	0.500	C(17)	−0.190(1)	0.2760(8)	−0.097(1)
P	0.1746(3)	0.2291(2)	0.2966(2)	C(18)	−0.046(1)	0.2702(8)	−0.0811(9)
O	0.3950(8)	0.3261(5)	0.2345(6)	C(19)	0.068(1)	0.2581(8)	0.0366(9)
N	0.665(1)	0.3498(6)	0.5303(8)	C(20)	0.200(1)	0.3356(8)	0.3843(8)
C(1)	0.625(1)	0.1035(8)	0.688(1)	C(21)	0.267(1)	0.3341(8)	0.513(1)
C(2)	0.565(1)	0.0290(7)	0.601(1)	C(22)	0.293(1)	0.418(1)	0.581(1)
C(3)	0.413(1)	0.0274(8)	0.533(1)	C(23)	0.254(1)	0.5018(9)	0.512(1)
C(4)	0.669(1)	−0.030(1)	0.570(1)	C(24)	0.190(1)	0.5023(8)	0.387(1)
C(5)	0.347(1)	0.1834(7)	0.3059(9)	C(25)	0.159(1)	0.4196(8)	0.322(1)
C(6)	0.425(1)	0.2442(8)	0.2543(8)	C(26)	0.607(1)	0.2801(8)	0.5235(9)
C(7)	0.552(1)	0.203(1)	0.229(1)	C(27)	0.724(1)	0.4429(8)	0.527(1)
C(8)	0.092(1)	0.1415(7)	0.3585(8)	C(28)	0.608(2)	0.4940(9)	0.422(1)
C(9)	0.036(1)	0.1597(8)	0.446(1)	C(29)	0.863(2)	0.432(1)	0.509(2)
C(10)	−0.027(1)	0.0906(9)	0.492(1)	C(30)	0.758(2)	0.485(1)	0.651(2)
C(11)	−0.029(1)	0.0007(9)	0.447(1)	B	0.299(2)	0.220(1)	0.817(2)
C(12)	0.026(1)	−0.0179(9)	0.361(1)	F(1)	0.165(1)	0.2613(8)	0.7451(9)
C(13)	0.084(1)	0.0511(8)	0.3161(9)	F(2)	0.295(2)	0.130(1)	0.765(1)
C(14)	0.034(1)	0.2495(6)	0.1392(9)	F(3)	0.414(1)	0.258(1)	0.802(1)
C(15)	−0.113(1)	0.2550(8)	0.122(1)	F(4)	0.315(1)	0.2005(9)	0.930(1)
C(16)	−0.226(1)	0.2679(8)	0.004(1)				

Table 4

Selected bond lengths (Å) and angles (°) for $\{Pd(CNCMe_3)(\eta^3\text{-}2\text{-}MeC_3H_4)[Ph_3PC(H)COMe]\}BF_4$ (**4**), with e.s.d.s. in parentheses

Pd–C(1)	2.19(1)	P–C(20)	1.804(9)
Pd–C(2)	2.168(8)	O–C(6)	1.21(1)
Pd–C(3)	2.18(1)	N–C(26)	1.14(1)
Pd–C(5)	2.175(9)	N–C(27)	1.47(1)
Pd–C(26)	1.988(9)	C(1)–C(2)	1.43(1)
P–C(5)	1.744(9)	C(2)–C(3)	1.37(1)
P–C(8)	1.810(8)	C(2)–C(4)	1.48(1)
P–C(14)	1.814(8)	C(5)–C(6)	1.46(1)
		C(6)–C(7)	1.52(1)
C(1)–Pd–C(2)	38.3(4)	C(8)–P–C(20)	109.8(4)
C(1)–Pd–C(3)	66.2(4)	C(14)–P–C(20)	108.1(4)
C(2)–Pd–C(3)	36.7(4)	C(26)–N–C(27)	173(1)
C(1)–Pd–C(5)	166.1(3)	C(1)–C(2)–C(3)	116.9(9)
C(1)–Pd–C(26)	98.0(4)	C(1)–C(2)–C(4)	119.1(9)
C(2)–Pd–C(5)	128.9(3)	C(3)–C(2)–C(4)	123(1)
C(2)–Pd–C(26)	131.1(4)	Pd–C(5)–P	110.4(6)
C(3)–Pd–C(5)	100.0(4)	Pd–C(5)–C(6)	106.0(6)
C(3)–Pd–C(26)	163.4(4)	P–C(5)–C(6)	114.1(6)
C(5)–Pd–C(26)	95.9(3)	O–C(6)–C(5)	122.2(8)
C(5)–P–C(8)	107.1(4)	O–C(6)–C(7)	120.0(8)
C(5)–P–C(14)	115.1(4)	C(5)–C(6)–C(7)	117.7(8)
C(5)–P–C(20)	112.3(4)	Pd–C(26)–N	176.4(8)
C(8)–P–C(14)	104.1(4)		

neutral Cl analogue, $\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)[Ph(H)COMe]\}$ [2]. The geometry of the allyl group is comparable with that usually found in palladium(II)-η^3-allyl complexes [20]. Thus the allyl plane, defined by atoms C(1), C(2), and C(3) forms a dihedral angle of 110 ° with the coordination plane defined by Pd, C(5), and C(26). The displacement of C(1), C(2), and C(3) from the coordination plane are 0.002, 0.592, and −0.181 Å, respectively, with the allyl methyl carbon atom, C(4), 0.265 Å out of the allyl plane on the same side as the Pd.

The average value of the allylic Pd–C bond distance, 2.18(1) Å, is slightly longer than normal [20], in agreement with the *trans* influence of the ylidic, C(5), and isocyanide, C(26), carbon atoms. This value is comparable with those found in other compounds having the allyl group *trans* to a ylidic carbon atom [2,21].

The Pd–C(5) bond length of 2.175(9) Å is slightly shorter than that of 2.193(3) Å in the Cl analogue [2]. This feature is consistent with the observation that the Pd–C(ylide) bond is slightly stronger in the CNR compounds than in the Cl derivatives. However, the bond length is long enough to account for the observed lability of the Pd–ylide bond (see above).

The geometry around the asymmetric C(5) atom as well as the P–C(5) bond distance of 1.774(9) Å agree well with those of other metal–ylide complexes [2,21–23].

The Pd–C(26)–N–C(27) groups is essentially linear with Pd–C(26)–N and C(26)–N–C(27) bond angles of 176.4(8) and 173(1)°, respectively. The Pd–C(26), N–C(26), and N–C(27) bond lengths of 1.988(9), 1.14(1), and 1.47(1) Å, respectively, suggest that the Pd–C(26) bond is essentially a single bond, the N–C(26) bond maintaining its triple bond character.

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