Synthesis and Characterization of Palladium(II)–η^3-Allyl–Ylide Complexes. *X*-Ray Crystal Structure of $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\{Ph_3PC(H)COMe\}]$ †

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The complexes $[PdCl(\eta^3\text{-}2\text{-}XC_3H_4)\{Ph_3PC(H)COR\}]$ [R = Me, X = H (**1**) or Me (**2**); R = Ph, X = H (**3**) or Me (**4**)] have been obtained in high yields by treatment of the dimers $[\{PdCl(\eta^3\text{-}2\text{-}XC_3H_4)\}_2]$ with the keto-stabilized ylides $Ph_3PC(H)COMe$ [ampp, (acetylmethylene)triphenylphosphorane] and $Ph_3PC(H)COPh$ [bmpp, (benzoylmethylene)triphenylphosphorane] in CH_2Cl_2 solution. They have been characterized by analytical data, i.r., low-temperature ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r., and for complex (**2**) also by ^{13}C n.m.r. spectroscopy. Spectroscopic evidence indicates that complexes (**1**)—(**4**) in solution at low temperature are present as two diastereoisomeric forms arising from co-ordination on the metal centre of the asymmetric ylidic carbon atom and of the η^3-allyl ligand. In CH_2Cl_2 solution at room temperature the complexes are in equilibrium with their reagents. Reaction with PPh_3 and $[AsPh_4]Cl$ gives $[PdCl(\eta^3\text{-}2\text{-}XC_3H_4)(PPh_3)]$ and $[AsPh_4][PdCl_2(\eta^3\text{-}2\text{-}XC_3H_4)]$, respectively, and the free ylide. The *X*-ray crystal structure of complex (**2**) was determined showing that, in the solid state, only one diastereoisomer is present. The crystals are monoclinic, space group $P2_1/n$ with $a = 9.668(3)$, $b = 14.879(4)$, $c = 16.226(3)$ Å, $\beta = 99.85(2)°$, and $Z = 4$. Final full-matrix least-squares refinement, based on 3 063 reflections, converged to $R = 0.031$. The keto-stabilized ylide ligand is C bonded to the metal with a Pd–C distance of 2.193(3) Å.

Phosphorus ylides are carbanions stabilized by the presence of the phosphonium group directly bonded to the anionic carbon atom, so that these species are represented by the resonance $R_3\overset{+}{P}\text{–}\overset{-}{C}R_2 \longleftrightarrow R_3P{=}CR_2$. This bonding feature makes phosphorus ylides attractive reagents in organic[1,2] as well as in organometallic chemistry.[3,4] In this latter field of research, they are used as versatile ligands. In particular, a wide variety of stable transition-metal complexes with metal–C(ylide) σ bonds have been reported.[3,4] The stability of the metal–ylide σ bond is generally greater than of normal metal–alkyl σ bonds, owing to the lack of possible β-hydride abstraction and to the ability of the co-ordinated ylide ligand to remove positive charge from the metal atom.[5]

Continuing our interest in the reactivity and catalytic aspects of transition metal–allyl complexes,[6] we thought it interesting to synthesize η^3-allylic species of palladium(II) with a palladium–ylide σ bond, in the case of keto-stabilized phosphorus ylides.

Palladium(II)–η^3-allyl complexes having a Pd–C σ bond in the metal co-ordination sphere are quite unstable[7,8a] and are frequently invoked as intermediates in oligomerization, co-oligomerization, and telomerization of 1,3-dienes.[8b]

Nucleophilic attack on Pd^{II}–η^3-allyl complexes can follow different paths depending on the nucleophilic power of the entering species.[9] Therefore the broad spectrum of nucleophilicity of ylides can offer a chance to observe nucleophilic attack on the metal centre or on the co-ordinated η^3-allyl group.

Experimental

General.—All reactions were carried out under a nitrogen atmosphere using an all glass vacuum line. Before use, solvents were freshly distilled under argon from appropriate drying agents.[10,11] I.r. spectra were recorded on a Perkin-Elmer 983 spectrophotometer as Nujol mulls, or in CH_2Cl_2 and $CHCl_3$ solutions. Hydrogen-1, $^{31}P\text{-}\{^1H\}$, and ^{13}C n.m.r. spectra were recorded on a Varian FT-80 A spectrometer. Elemental analyses were performed by the Analytical Chemistry Institute of the University of Padova. The dimers $[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2]$ and $[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$[12] and the keto-stablized ylides ampp [(acetylmethylene)triphenylphosphorane, $Ph_3PC(H)COMe$] and bmpp [(benzoylmethylene)triphenylphosphorane, $Ph_3PC(H)COPh$] were prepared according to literature methods.[13] All other chemicals were reagent grade and used without further purification.

Preparation of $[PdCl(\eta^3\text{-}2\text{-}XC_3H_4)Y]$ [Y = ampp, X = H (**1**) *or* Me (**2**); Y = bmpp, X = H (**3**) *or* Me (**4**)].—All these compounds were prepared by a standard procedure which is decribed here in detail for complex (**2**).

To a solution of the dimer $[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2]$ (0.197 g, 0.50 mmol) in CH_2Cl_2 (20 cm^3), ampp (0.318 g, 1.00 mmol) dissolved in CH_2Cl_2 (10 cm^3) was added dropwise at 0 °C. The reaction mixture was stirred for 3 h at room temperature and then concentrated to small volume (3 cm^3). A pale yellow solid was formed by slow addition of diethyl ether and was filtered off and dried under vacuum. Yield 0.492 g. Analytical and spectral data for complexes (**1**)—(**4**) are reported in Tables 1 and 2.

Reaction of Complex (**2**) *with* PPh_3.—A solution of complex (**2**) (0.052 g, 0.10 mmol) dissolved in CH_2Cl_2 (10 cm^3) was

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† [Acetyl(triphenylphosphonio)methanide-*C*]chloro(η^3-2-methylallyl)palladium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Analytical data and characteristic i.r. bands for the ylide ligands and the complexes $[PdCl(\eta^3\text{-}2\text{-}XC_3H_4)\{Ph_3PC(H)COR\}]$

Compound	X	R	M.p.[a]/°C	Yield (%)	Analysis[b]/% C	Analysis[b]/% H	I.r.[c]/cm^{-1} ν(C=O)	I.r.[c]/cm^{-1} ν(Pd–Cl)
ampp			205—206		79.0	5.90	1 533s[d]	
					(79.25)	(6.00)	1 529s[e]	
(1)	H	Me	122—123	92.5	57.3	4.80	1 624s[d]	272m
					(57.5)	(4.85)	1 616s[e]	
(2)	Me	Me	166—167	95.5	57.95	4.85	1 621s[d]	272m
					(58.25)	(5.10)	1 614s[e]	
bmpp			183—184		82.35	5.40	1 513s[d]	
					(82.1)	(5.55)	1 513s[e]	
(3)	H	Ph	121—122	97.2	61.6	4.45	1 601s[d]	261m
					(61.95)	(4.65)	1 601s[e]	
(4)	Me	Ph	156—157	87.5	62.0	4.50	1 598s[d]	273m
					(62.4)	(4.90)	1 600s[e]	

[a] All complexes decompose on melting. [b] Calculated values in parentheses. [c] s = Strong, m = medium. [d] Nujol mull. [e] Dichloromethane solution.

treated with solid PPh_3 (0.026 g, 0.10 mmol). The i.r. spectrum of the solution showed the disappearance of the ν(C=O) band of the starting complex and the formation of a band at 1 529 cm^{-1} due to the free ylide. The reaction mixture was stirred for 30 min at room temperature and then concentrated to small volume. Addition of Et_2O (30 cm^3) afforded a solid which was filtered off and identified as $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ (**A**) by comparison with an authentic sample.[14a] Yield 0.036 g (78.3%). Concentration of the mother-liquors and addition of n-pentane yielded 0.026 g (81.3%) of free ylide.

Reaction of Complex (**2**) *with* $[AsPh_4]Cl$.—To a solution of complex (**2**) (0.078 g, 0.15 mmol) in CH_2Cl_2 (10 cm^3) solid $[AsPh_4]Cl$ (0.063 g, 0.15 mmol) was added in one portion. An i.r. spectrum in CH_2Cl_2 solution showed a strong ν(C=O) absorption at 1 529 cm^{-1} corresponding to the free ylide. The mixture was stirred for 30 min and Et_2O (30 cm^3) added. The precipitate was filtered off and identified as $[AsPh_4][PdCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]$ (**B**) by comparison with an authentic sample independently prepared.[14c] Yield 0.081 g (74.8%). The free ylide 0.038 g (79.2%) was obtained from the mother-liquors by concentration and addition of n-pentane.

Structure Determination of $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\{Ph_3PC(H)COMe\}]$ (**2**).—Crystals were grown from a solution of (**2**) in dichloromethane–diethyl ether (1:3) at −20 °C and a single crystal of dimensions 0.22 × 0.31 × 0.35 mm selected for the crystallographic study.

Crystal data. $C_{25}H_{26}ClOPPd$, $M = 515.4$, monoclinic, $a = 9.668(3)$, $b = 14.879(4)$, $c = 16.226(3)$ Å, $\beta = 99.85(2)°$, $U = 2\,300(1)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.448$ g cm^{-3}, $F(000) = 1\,048$, $\mu(\text{Mo-}K_\alpha) = 9.9$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å.

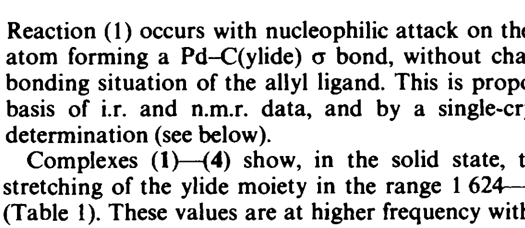
Data collection and processing. Intensity data were recorded on an Enraf–Nonius CAD4 diffractometer; ω—2θ mode, Mo-K_α radiation, graphite monochromator. Four standard reflections measured periodically during data collection revealed no significant decay. 3 063 Unique reflections with $I > 3\sigma(I)$ $(3 < \theta < 30°$ 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.[15a]

Structure analysis and refinement. The structure was solved by the heavy-atom method and refinement was by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen 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 $R = \Sigma\,||F_o| - |F_c||/\Sigma|F_o| = 0.031$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}} = 0.031$. Unit weights were used. Neutral atom scattering factors were taken from the literature.[15b]

Data processing was performed on a PDP 11/44 computer using the Enraf–Nonius SDP program library.[16]

Results and Discussion

Preparation and Identification of Compounds.—The complexes $[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$ and $[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2]$ react in CH_2Cl_2 solution at room temperature with equivalent amounts of $Ph_3PC(H)COR$ (R = Me or Ph) affording pale yellow palladium–ylide complexes [equation (1)] in high yields.



(1)

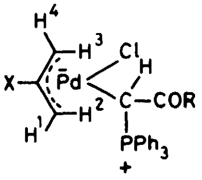
R = Me, X = H (**1**) or Me (**2**); R = Ph, X = H (**3**) or Me (**4**)

Reaction (1) occurs with nucleophilic attack on the palladium atom forming a Pd–C(ylide) σ bond, without changes in the bonding situation of the allyl ligand. This is proposed on the basis of i.r. and n.m.r. data, and by a single-crystal *X*-ray determination (see below).

Complexes (**1**)—(**4**) show, in the solid state, the ν(C=O) stretching of the ylide moiety in the range 1 624—1 598 cm^{-1} (Table 1). These values are at higher frequency with respect to free ylides [ampp, ν(C=O) 1 533 and bmpp ν(C=O) 1 513 cm^{-1} in Nujol mull] and *ca.* 80—110 cm^{-1} higher than those reported for palladium O-bonded ylides.[17] Instead, they are comparable to those reported for other transition-metal complexes of keto-stabilized ylides, such as *trans*-$[PdCl_2(PMe_2Ph)\{Ph_2MePC(H)COPh\}]$ [ν(C=O) 1 607][18] and *trans*-$[PdCl_2(PMe_3)\{Ph_2MePC(H)COPh\}]$ [ν(C=O) 1 621 cm^{-1}],[18] in which the ylide has been shown to be C-bonded to the metal. Complexes (**1**)—(**4**) display ν(Pd–Cl) vibrations in the range 273—261 cm^{-1}, in agreement with values reported for $[PdCl(\eta^3\text{-}2\text{-}XC_3H_4)L]$ ($L = PPh_3$, $AsPh_3$, or $SbPh_3$) systems.[14]

In all cases, the simultaneous presence on the metal centre of the asymmetric ylide carbon atom and of the η^3-allyl group may

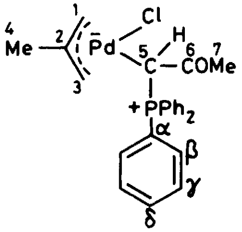
Table 2. Proton and $^{31}P-\{^{1}H\}$ n.m.r. data for the ylide ligands and the complexes $[PdCl(\eta^{3}-2-XC_3H_4)\{Ph_3PC(H)COR\}]^a$



Compound	X	R		Allyl resonances									Ylide resonances				
				δ(H¹)	$^3J(H^1X)$	δ(H²)	$^3J(H^2X)$	δ(H³)	$^3J(H^3X)$	δ(H⁴)	$^3J(H^4X)$	δ(X)	δ(CH)	$^2J(HP)$	δ(R)	$^4J(HP)$	δ(P)
ampp													3.64(d)	26.5	2.05(d)	1.8	14.31(s)
(1)	H	Me	(Ia)	1.62(d)	6.5	2.13(d)	12.2	3.00(d)	12.2	4.05(d)	7.5	4.62(m)	4.86(d)	8.5	2.54(d)	2.3	23.06(s)
			(Ib)	*b*		1.28(d)	12.5	2.94(d)	13.0	4.19(d)	7.4	5.28(m)	4.81(d)	8.5	2.36(d)	2.0	25.91(s)
(2)	Me	Me	(Ia)		1.94—2.09(m)^c			2.59(s)		3.75(s)		1.79(s)	4.65(d)	8.6	2.24(d)	2.2	25.54(s)
			(Ib)					2.84(s)				1.24(s)	4.73(d)	7.8	2.40(d)	2.2	25.68(s)
bmpp													4.41(d)	23.2			16.64(s)
(3)	H	Ph	(Ia)	1.72(d)	6.4	2.02(d)	12.3	2.81(d)	12.9	3.97(d)	6.5	4.59(m)	5.36(d)	6.8			25.45(s)
			(Ib)	2.36(d)	6.4	1.19(d)	12.6			4.06(d)	6.5	5.05(m)	5.30(d)	9.9			27.94(s)
(4)	Me	Ph	(Ia)		2.05—2.24(m)^c			2.58(s)		3.78(s)		1.24(s)	5.28(d)	7.1			27.15(s)
			(Ib)					2.77(s)		3.85(s)		1.16(s)	5.32(d)	6.6			28.31(s)

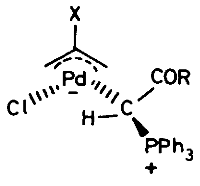
[a] Spectra recorded in $CDCl_3$ at 223 K; δ in p.p.m., *J* in Hz; ^1H and $^{31}P-\{^1H\}$ n.m.r. chemical shifts were referenced to internal $SiMe_4$ and H_3PO_4 (85%), respectively; s = singlet, d = doublet, m = multiplet. [b] Obscured by CH_3 signals of the ylide ligand. [c] Multiplet attributed to H¹ and H² protons of the diastereoisomers (**Ia**) and (**Ib**).

Table 3. $^{13}C-\{^1H\}$ N.m.r. data for ampp and complex (**2**)^a

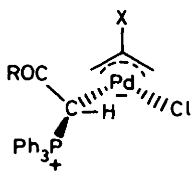


Compound	Allyl resonances					Ylide resonances						Phenyl resonances							
	δ(C¹)	$^3J(C^1P)$	δ(C²)	δ(C³)	δ(C⁴)	δ(C⁵)	$^1J(C^5P)$	δ(C⁶)	$^2J(C^6P)$	δ(C⁷)	$^3J(C^7P)$	δ(C_α)	$^1J(C_\alpha P)$	δ(C_β)	$^2J(C_\beta P)$	δ(C_γ)	$^3J(C_\gamma P)$	δ(C_δ)	$^4J(C_\delta P)$
ampp						51.29	107.9	190.53	2.2	28.22	16.2	127.06	90.5	132.78	10.3	128.51	11.9	131.66	2.7
(2)	62.16	2.5	128.04	63.99	21.84	36.42	59.5	200.05	4.1	30.93	11.9	124.20	88.2	133.56	10.0	128.79	12.6	132.59	2.5
	65.82	1.8	*b*	65.45	22.90	36.96	57.6	201.39	4.0	31.17	12.3								

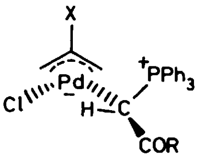
[a] Spectra recorded in $CDCl_3$ at 223 K; δ in p.p.m., *J* in Hz; chemical shifts reported from $SiMe_4$ by taking the chemical shift of $CDCl_3$ as +77.0 p.p.m. [b] Obscured by signals of the phenylic carbon atoms.



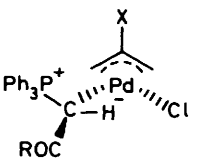
(Ia)



(Ia′)



(Ib)



(Ib′)

lead, for each complex (**1**)—(**4**), to two diastereoisomeric forms (**Ia**) and (**Ib**) with their corresponding enantiomers (**Ia**′) and (**Ib**′).

Low-temperature ^{31}P-{^{1}H} n.m.r. spectra of complexes (**1**)—(**4**) display the ylidic phosphorus as two non-equivalent sharp singlets in the range δ 23.06—28.31 p.p.m., which are shifted by about 10—14 p.p.m. downfield with respect to the resonance of the corresponding unco-ordinated ylide (Table 2). These data agree with those found for [PdCl$_2$(adep)] [δ(PR$_3$) = 24.7] and [PdCl$_2$(bdep)] [δ(PR$_3$) = 29.3 p.p.m.], where adep and bdep are the chelate ylides (acetylmethylene)(2-diphenylphosphinoethyl)diphenylphosphorane, Ph$_2$P(CH$_2$)$_2$PPh$_2$C(H)COMe, and (benzoylmethylene)(2-diphenylphosphinoethyl)diphenylphosphorane, Ph$_2$P(CH$_2$)$_2$PPh$_2$C(H)COPh, respectively.[19]

Consistently, the ^{1}H n.m.r. spectra at low temperature show the ylide methine proton resonances as two distinct doublets, relating to the presence of (**Ia**) and (**Ib**) diastereoisomers, in the range δ = 4.65—4.86 p.p.m. for complexes (**1**) and (**2**) and δ = 5.28—5.36 p.p.m. for complexes (**3**) and (**4**), owing to ^{1}H–^{31}P coupling. These resonances are shifted *ca.* 0.9—1.2 p.p.m. downfield relative to the methine proton of the free ylides, as a consequence of the inductive effect of the metal atom bonded to the ylide methine group.[18,20] Furthermore, the values of the ^2J(HP) coupling constants between the methine proton and the phosphorus atom of the ylide ligands in complexes (**1**)—(**4**) are in the range 6.6—9.9 Hz. These values are lower than those of free ylides by about 16—20 Hz (Table 2), suggesting that $sp^2 \longrightarrow sp^3$ rehybridization of the ylide carbon occurs upon co-ordination to the palladium atom.[18,21]

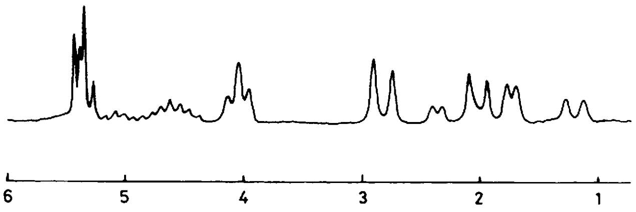


Figure 1. Proton n.m.r. spectrum of [PdCl(η^3-C$_3$H$_5$){Ph$_3$PC(H)-COPh}] (**3**) in CDCl$_3$ at 223 K

Finally, the presence in the ^{1}H n.m.r. spectra of complexes (**1**) and (**2**), at low temperature, of two doublets in the range 2.24—2.54 p.p.m., assigned to the methyl protons of the acetyl substituent of the ylide ligand, confirms the existence under these experimental conditions of both diastereoisomeric forms (**Ia**) and (**Ib**).

For the allyl group, in the temperature range 223—263 K, two sets of signals are observed in the ^{1}H n.m.r. specta (Table 2), again supporting the presence of two distinct species. At 223 K the ^{1}H n.m.r. spectra of all compounds display the typical AMYZ-X pattern of allyl protons[6a,b] for both diastereoisomers (**Ia**) and (**Ib**). An example is shown in Figure 1 for complex (**3**). The multiples centred at 4.59 and 5.05 p.p.m. are attributed to the central proton of forms (**Ia**) and (**Ib**), respectively. Signals for each diastereoisomer are tentatively assigned on the basis of the relative abundances obtained from the integration ratio in the ^{31}P-{^{1}H} n.m.r. spectra, considering the less sterically hindered isomer (**Ia**) as more abundant. The assignment of the allylic proton signals is based on the coupling constants of the *syn* and *anti* protons with the central proton [^3J(H$_{syn}$H) > ^3J(H$_{anti}$H)],[14a] and on the assumption that the protons on the allylic carbon atom, *trans* to the co-ordinated ylide (which has greater *trans* influence than the chloro ligand[22]), are shifted downfield with respect to *cis* protons.[14a] The doublets centred at 1.72 and 2.36 p.p.m. are attributed to the *syn* allylic protons on the carbon atom *cis* to the ylide ligand; the *anti* proton appears as two doublets at 2.02 and 1.19 p.p.m. *anti* Protons on the allylic carbon atom, *trans* to the ylide group, are observed in CD$_2$Cl$_2$ as one doublet for each diastereoisomer [(**Ia**), δ 2.60, ^3J(HH) = 12.5; (**Ib**), δ 2.69 p.p.m., ^3J(HH) = 12.6 Hz], whereas in CDCl$_3$ they are not distinct for (**Ia**) and (**Ib**). *syn* Protons are present as two doublets at 3.97 and 4.06 p.p.m. for (**Ia**) and (**Ib**), respectively.

The presence of the diastereoisomers (**Ia**) and (**Ib**) also leads to splitting of the signals in the ^{13}C n.m.r. spectrum. The ^{13}C n.m.r. spectrum of compound (**2**) is shown in Figure 2. Doublets at 36.42 [^1J(CP) = 59.5] and 36.96 p.p.m. [^1J(CP) = 57.6 Hz]

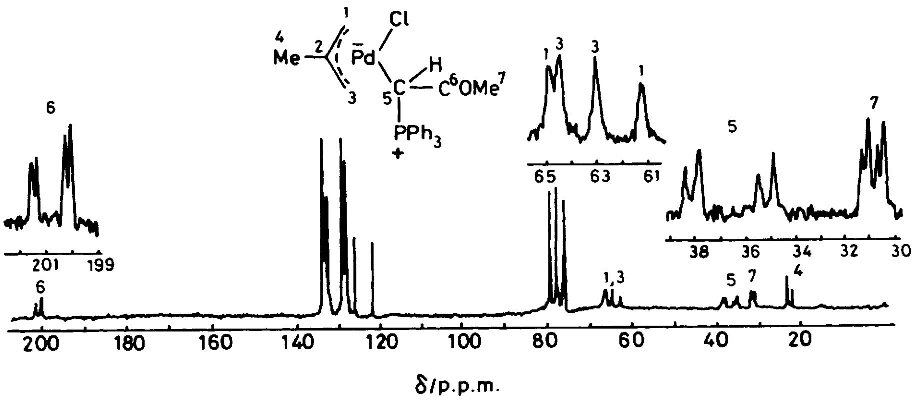


Figure 2. ^{13}C N.m.r. spectrum of [PdCl(η^3-2-MeC$_3$H$_4$){Ph$_3$PC(H)COMe}] (**2**) in CDCl$_3$ at 243 K

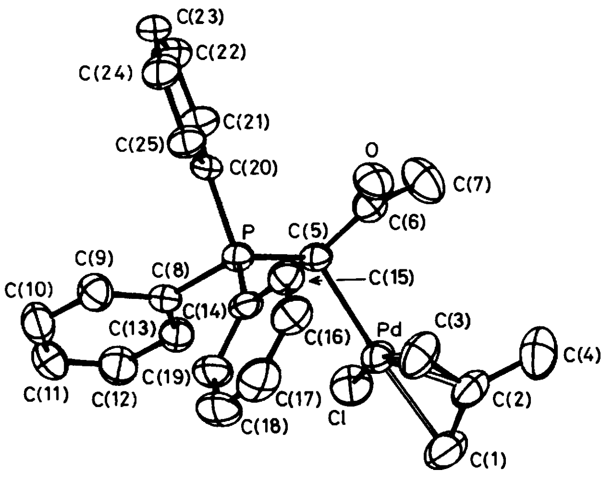


Figure 3. The molecular structure of [PdCl(η^3-2-MeC$_3$H$_4$){Ph$_3$PC(H)-COMe}] (**2**), showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity

are assigned to the palladium-bonded carbon atom for diastereoisomers (**Ia**) and (**Ib**), respectively. The signals at 200.05 [^2J(CP) = 4.1] and 201.39 p.p.m. [^2J(CP) = 4.0 Hz] are attributed to the carbonylic C atom and doublets at 30.93 [^3J(CP) = 11.9] and 31.17 p.p.m. [^3J(CP) = 12.3 Hz] to the methyl group of the ylide ligand.

A unique set of signals, attributed to the phenyl carbon atoms, is shown in the ^{13}C n.m.r. spectrum (Table 3). These data agree with the values reported for the [R–PPh$_3$]$^+$ (R = alkyl or aryl) systems[23] and are similar to those found in the ^{13}C n.m.r. spectrum of the free ylide (see Table 3). The η^3-allyl group gives rise to signals at 63.99 and 65.45 for C^3 and 62.16 [^3J(CP) = 2.5] and 65.82 p.p.m. [^3J(CP) = 1.8 Hz] for C^1. The assignment of C^1 is based on the *trans* coupling to the phosphorus atom, since C^3 does not couple to phosphorus.[24] The ^{13}C n.m.r. spectrum displays only one signal for the η^3-allylic C^2 carbon atom at 128.04 p.p.m. the other signal may be obscured by the phenyl carbon atoms. The methyl allylic carbon signals are at 21.84 and 22.90 p.p.m. for diastereoisomers (**Ia**) and (**Ib**), respectively.

X-*Ray Structure of* [PdCl(η^3-2-MeC$_3$H$_4$){Ph$_3$PC(H)COMe}] (**2**).—The structure of (**2**) is illustrated in Figure 3 along with the atom numbering scheme. Final atomic parameters are given in Table 4 and selected bond lengths and angles in Table 5.

The results of the present structure analysis show that crystals consist of the racemic mixture of the diastereoisomer (**Ia**). It seems likely that equilibria (2) and (3) (see later) are shifted, upon crystallization, towards the formation of the sterically less hindered species.

The palladium centre dislays a distorted square-planar geometry, formed by the η^3-allyl ligand, the chlorine atom, and the ylidic carbon atom. The allyl plane, defined by atoms C(1), C(2), and C(3), forms a dihedral angle of 105° with the co-ordination plane defined by Cl, Pd, and C(5). This value is in the range normally found for other symmetrically and asymmetrically co-ordinated palladium(II)–η^3-allyl systems.[25] The C(1), C(2), and C(3) allylic carbon atoms are 0.038, 0.769, and 0.056 Å, respectively, out of the co-ordination plane, whereas, generally, terminal and central allylic carbon atoms lie on opposite sides of the plane. The bulkiness of the phosphonium group, which is located below the co-ordination plane that is opposite to the MeC$_3$H$_4$ group, can justify this particular structural arrangement of the allyl moiety. The allyl methyl carbon atom is displaced by 0.268 Å from the η^3-allyl plane towards the palladium atom. This distortion is usual in similar Pd(η^3-2-MeC$_3$H$_4$) complexes.[25c,g–k] Furthermore, the C–C and Pd–C allyl bond lengths are consistent with those normally reported for a palladium η^3-co-ordinated allyl ligand.[25] However, the Pd–C(1) distance [2.180(4) Å] is slightly longer than Pd–C(3) [2.126(4) Å], reflecting the greater *trans* influence of the ylide ligand with respect to chlorine, as reported also for the ylidic complex [PdCl(1,5-C$_8$H$_{12}$){CH(SiMe$_3$)PMe$_2$Ph}]PF$_6$.[26] The Pd–Cl bond distance [2.377(1) Å] is of comparable magnitude with that found in some other anionic and neutral palladium(II)–η^3-allyl complexes such as [PdCl$_2$(η^3-C$_3$H$_5$)]$^-$[25i] [2.390(5)

Table 4. Atomic co-ordinates (× 10^4), with estimated standard deviations (e.s.d.s) in parentheses, for [PdCl(η^3-2-MeC$_3$H$_4$)-{Ph$_3$PC(H)COMe}] (**2**)

Atom	*x*	*y*	*z*
Pd	33 803(3)	51 606(2)	16 200(2)
Cl	4 079(1)	65 751(7)	11 474(8)
P	5 058(9)	56 373(6)	24 313(7)
O	2 551(3)	4 659(2)	3 662(2)
C(1)	4 300(5)	4 312(3)	761(3)
C(2)	4 379(4)	3 899(3)	1 532(3)
C(3)	3 071(5)	3 768(3)	1 817(3)
C(4)	5 734(5)	3 775(3)	2 102(4)
C(5)	2 353(3)	5 756(2)	2 595(3)
C(6)	3 066(4)	5 292(3)	3 334(3)
C(7)	4 505(4)	5 617(3)	3 717(3)
C(8)	−263(4)	6 524(2)	1 741(3)
C(9)	−1 709(4)	6 663(3)	1 648(3)
C(10)	−2 342(4)	7 326(3)	1 125(3)
C(11)	−1 546(5)	7 859(3)	692(3)
C(12)	−120(4)	7 741(3)	790(3)
C(13)	535(4)	7 069(3)	1 316(3)
C(14)	−162(3)	4 587(2)	1 959(3)
C(15)	−11(4)	3 792(2)	2 419(3)
C(16)	−526(4)	2 995(3)	2 045(3)
C(17)	−1 165(5)	2 990(3)	1 231(3)
C(18)	−1 309(5)	3 768(3)	758(3)
C(19)	−800(4)	4 573(3)	1 128(3)
C(20)	−190(3)	5 811(2)	3 382(2)
C(21)	250(4)	6 584(3)	3 834(3)
C(22)	−277(4)	6 802(3)	4 541(3)
C(23)	−1 210(4)	6 247(3)	4 830(3)
C(24)	−1 650(4)	5 474(3)	4 398(3)
C(25)	−1 161(4)	5 257(3)	3 669(3)

Table 5. Selected bond lengths (Å) and angles (°) for [PdCl(η^3-2-MeC$_3$H$_4$){Ph$_3$PC(H)COMe}] (**2**) with e.s.d.s in parentheses

Pd–Cl	2.377(1)	P–C(20)	1.804(4)
Pd–C(1)	2.180(4)	O–C(6)	1.228(4)
Pd–C(2)	2.126(3)	C(1)–C(2)	1.384(6)
Pd–C(3)	2.126(4)	C(2)–C(3)	1.433(5)
Pd–C(5)	2.193(3)	C(2)–C(4)	1.481(6)
P–C(5)	1.769(3)	C(5)–C(6)	1.452(5)
P–C(8)	1.807(3)	C(6)–C(7)	1.504(5)
P–C(14)	1.810(3)		
Cl–Pd–C(1)	97.9(1)	C(8)–P–C(20)	104.6(2)
Cl–Pd–C(2)	127.0(1)	C(14)–P–C(20)	109.1(2)
Cl–Pd–C(3)	165.2(1)	C(1)–C(2)–C(3)	116.0(4)
Cl–Pd–C(5)	93.7(1)	C(1)–C(2)–C(4)	121.8(4)
C(1)–Pd–C(5)	168.4(1)	C(3)–C(2)–C(4)	121.1(4)
C(2)–Pd–C(5)	132.2(2)	Pd–C(5)–P	115.0(2)
C(3)–Pd–C(5)	101.1(1)	Pd–C(5)–C(6)	113.6(2)
C(5)–P–C(8)	108.5(2)	O–C(6)–C(5)	123.5(3)
C(5)–P–C(14)	115.3(1)	O–C(6)–C(7)	118.9(3)
C(5)–P–C(20)	111.9(2)	C(5)–C(6)–C(7)	117.7(3)
C(8)–P–C(14)	106.8(2)		

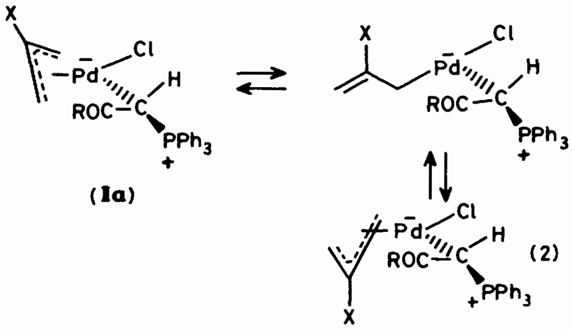
and 2.400(5) Å], $[PdCl(PPh_3)\{\eta^3\text{-}1,1\text{-}SiMe_3(Me)C_3H_3\}]$[25j] [2.372(1) Å], and $[PdCl(PPh_3)(\eta^3\text{-}2\text{-}MeC_3H_4)]$[25k] [2.381(1) Å].

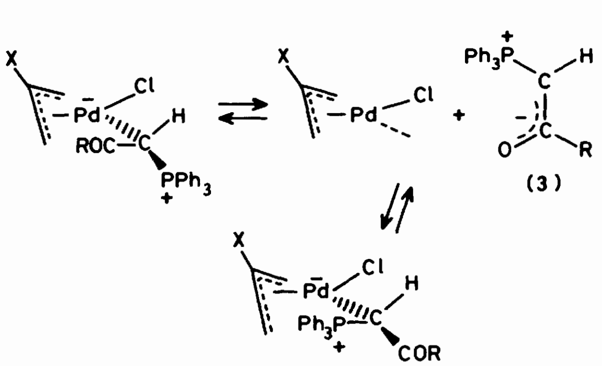
The ylide ligand is co-ordinated to palladium through the asymmetric C(5) carbon atom with a Pd–C bond length of 2.193(3) Å, which is significantly longer than usual for Pd–C σ bonds.[14b] Angles around C(5) suggest a slightly distorted sp^3 hybridization, probably generated by steric hindrance of the substituents on the carbon atom. The P–C(5) distance of 1.769(3) Å lies in the range of P–C bond lengths found in other metal co-ordinated ylide ligands[26–28] and is in agreement with accepted values for P–C(sp^3) bond lengths (1.75—1.82 Å) in phosphonium ions.[29] The geometry of the phosphorus atom is quasi tetrahedral and deviations from the idealized sp^3 situation are similar to those found in some other analogous systems.[27,30] The phosphonium and acetyl groups are arranged on opposite sides of the co-ordination plane, with the O, C(6), C(7) plane nearly perpendicular (93°) to the Pd, Cl, C(5) plane. The C(6)–O distance [1.228(4) Å] in the carbonyl moiety is characteristic for a C=O double bond in C-co-ordinated keto-stabilized ylide systems.[27a,28c]

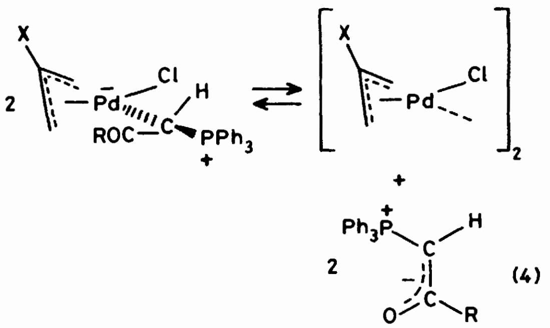
Solution Behaviour of $[PdCl(\eta^3\text{-}2\text{-}XC_3H_4)\{Ph_3PC(H)COR\}]$ *Species*.—All complexes (**1**)—(**4**) behave similarly in solution. We report the results obtained for complex (**2**).

At 223 K in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum the diastereoisomers (**Ia**) and (**Ib**) are detected as two distinct singlets. However, variable-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. experiments show, at 263 K, coalescence of peaks corresponding to (**Ia**) and (**Ib**). In the ^1H n.m.r. spectrum, the two doublets corresponding to the methine proton and the two signals of the ylidic methyl coalesce at *ca.* 273 K.

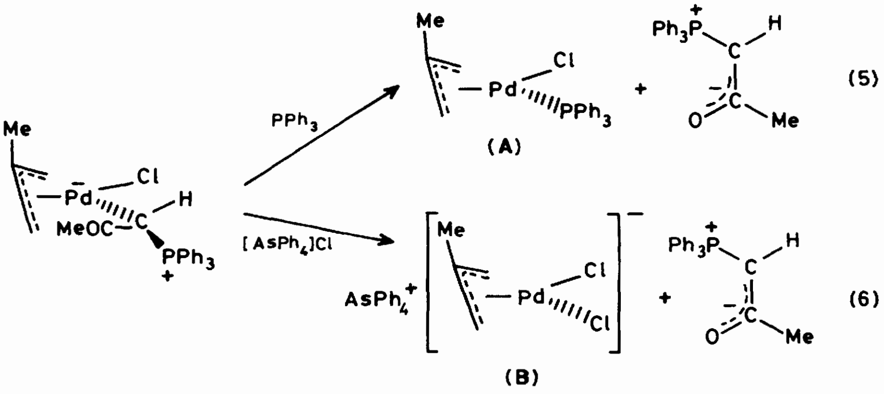
The interchange between (**Ia**) and (**Ib**) may arise either from allyl fluxional behaviour, involving the usual $\eta^3 \rightleftharpoons \sigma \rightleftharpoons \eta^3$ mechanism[31] [equation (2)], or from the inversion in the configuration of the methine ylide carbon, bonded to Pd, due to Pd–C σ-bond breaking [equation (3)]. Some significant spectroscopic evidence appears to support the dissociative mechanism [equation (3)]. Thus, above *ca.* 270 K, $^{31}P\text{-}\{^1H\}$ n.m.r. spectra show, beside (**Ia**) and (**Ib**) coalescence peak, a broad signal at *ca.* δ 14.20 p.p.m. corresponding to the free ylide (δ 14.70 p.p.m.). Infrared spectra confirm the occurrence of Pd–C(ylide) σ-bond breaking. In fact, in CH_2Cl_2 and $CHCl_3$, complex (**2**) shows, at room temperature, the characteristic band of the free ylide [ν(C=O) 1 529 cm^{-1} in CH_2Cl_2 solution] together with the absorption of the co-ordinated ligand [ν(C=O) 1 614 cm^{-1} in CH_2Cl_2 solution]. Moreover, on adding an excess of palladium dimer to the solution, the ν(C=O) signal corresponding to unco-ordinated ylide decreases, thereby suggesting the existence of equilibrium (4).


(**Ia**) (2) (**Ib**)


(3)


(4)

The cleavage of the Pd–C(ylide) σ bond is not surprising in our complexes, although ylides generally form strong metal–carbon σ bonds.[5] In the present case, however, the Pd–C(ylide) bond is longer than normal [see structure of compound (**2**)], and may therefore suggest a weaker Pd–C(ylide) interaction with consequent formation of a labile bond. This weak interaction between the palladium substrate and the ylidic ligand can be attributed to the poor nucleophilicity of keto-stabilized ylides coupled with their high steric hindrance. Furthermore, the low strength of the Pd–C(ylide) bonds in complexes (**1**)—(**4**) is confirmed by their reactivity. Thus, the ylide ligand is removed from complex (**2**) by reaction, at room temperature, with stoicheiometric amounts of PPh_3 or $[AsPh_4]Cl$ to give complexes (**A**) and (**B**), respectively, according to equations (5) and (6). It is noteworthy that these displacement reactions


(**A**) (5) (**B**) (6)

proceed under very mild conditions. Previous examples, where chelated and unidentate ylides were displaced from palladium complexes, were reported to occur under drastic conditions.[20]

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References

1 A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966 and refs. therein.
2 H. J. Bestmann, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 349.
3 H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 907.
4 W. C. Kaska, *Coord. Chem. Rev.*, 1983, **48**, 1.
5 H. H. Karsch, H. F. Klein, and H. Schmidbaur, *Chem. Ber.*, 1974, **107**, 93; H. Schmidbaur, *Acc. Chem. Res.*, 1975, **8**, 62.
6 (*a*) G. Carturan, U. Belluco, A. Del Pra', and G. Zanotti, *Inorg. Chim. Acta*, 1979, **33**, 155; (*b*) A. Scrivanti, G. Carturan, and B. Crociani, *Organometallics*, 1983, **2**, 1612; (*c*) R. Bertani, G. Carturan, and A. Scrivanti, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 246.
7 S. Numata, R. Okawara, and H. Kurosawa, *Inorg. Chem.*, 1977, **16**, 1737.
8 (*a*) B. M. Trost, *Acc. Chem. Res.*, 1980, **13**, 385; (*b*) A. Döhring, P. W. Jolly, R. Mynott, K. P. Schick, and G. Wilke, *Z. Naturforsch., Teil B*, 1981, **36**, 1198.
9 S. Numata and H. Kurosawa, *J. Organomet. Chem.*, 1977, **131**, 301; B. M. Trost and T. R. Verhoeven, *J. Am. Chem. Soc.*, 1980, **102**, 4730.
10 D. F. Schriver, 'The Manipulation of Air-Senstive Compounds,' McGraw-Hill, New York, 1969.
11 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, Oxford, 1966.
12 F. R. Hartley and S. R. Jones, *J. Organomet. Chem.*, 1974, **66**, 465.
13 F. Ramirez and S. Dershowitz, *J. Org. Chem.*, 1957, **22**, 41.
14 (*a*) J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1967, 1839; (*b*) G. Wilkinson, F. G. A. Stone, and E. W. Abel, 'Comprehensive Organometallic Chemistry,' Pergamon, Oxford, 1982, vol. 6, p. 408; (*c*) R. J. Goodfellow and L. M. Venanzi, *J. Chem. Soc. A*, 1966, 784.
15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, (*a*) Table 2.1.B; (*b*) Table 2.2.B.
16 B. A. Frenz and Associates, Inc., College Station, Texas 77840; Enraf-Nonius, Delft, Holland, 1982.
17 R. Uson, J. Fornies, R. Navarro, P. Espinet, and C. Mendivil, *J. Organomet. Chem.*, 1985, **290**, 125.
18 H. Koezuka, G. Matsubayashi, and T. Tanaka, *Inorg. Chem.*, 1976, **15**, 417.
19 Y. Oosawa, H. Urabe, T. Saito, and Y. Sasaki, *J. Organomet. Chem.*, 1976, **122**, 113.
20 E. T. Waleski, jun., J. L. Silver, M. D. Jansson, and J. L. Burmeister, *J. Organomet. Chem.*, 1975, **102**, 365.
21 P. S. Pregosin and R. W. Kunz, '^{31}P and ^{13}C N.M.R. of Transition Metal Phosphine Complexes,' Springer-Verlag, New York, 1979.
22 K. Itoh, M. Fukui, and Y. Ishii, *J. Organomet. Chem.*, 1977, **129**, 259.
23 B. E. Mann and B. F. Taylor, '^{13}C N.M.R. Data for Organometallic Compounds,' Academic Press, London, 1981.
24 B. E. Mann, R. Pietropaolo, and B. L. Shaw, *Chem. Commun.*, 1971, 790.
25 (*a*) A. E. Smith, *Acta Crystallogr.*, 1965, **18**, 331; (*b*) W. E. Oberhaushi and L. F. Dohl, *J. Organomet. Chem.*, 1965, **3**, 43; (*c*) R. Mason and D. R. Russel, *Chem. Commun.*, 1966, 26; (*d*) R. Mason and A. G. Wheeler, *J. Chem. Soc. A*, 1968, 2549; (*e*) R. Mason and P. O. Whimp, *J. Chem. Soc. A*, 1969, 2709; (*f*) S. J. Lippard and S. M. Morehouse, *J. Am. Chem. Soc.*, 1969, **91**, 2504; (*g*) S. J. Lippard and S. M. Morehouse, *ibid.*, 1972, **94**, 6956; (*h*) P. M. Bailey, E. A. Kelley, and P. M. Maitlis, *J. Organomet. Chem.*, 1978, **144**, C52; (*i*) L. S. Hegedus, B. Akermark, D. J. Olsen, O. P. Anderson, and K. Zetterberg, *J. Am. Chem. Soc.*, 1982, **104**, 697; (*j*) T. Ohta, T. Hosokawa, S-I. Murahashi, K. Miki, and N. Kasai, *Organometallics*, 1985, **4**, 2080; (*k*) J. W. Faller, C. Blankouship, B. Withmore, and S. Seno, *Inorg. Chem.*, 1985, **24**, 4483.
26 R. M. Buchanan and C. G. Pierpont, *Inorg. Chem.*, 1979, **18**, 3608.
27 (*a*) H. Takahashi, Y. Oosawa, A. Kobayashi, T. Saito, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1771; (*b*) J. Stein, J. P. Fackler, jun., C. Paparizos, and H-W. Chen, *J. Am. Chem. Soc.*, 1981, **103**, 2192; (*c*) C. Engelter, J. R. Moss, M. L. Niven, L. R. Nassimbeni, and G. Reid, *J. Organomet. Chem.*, 1982, **232**, C78.
28 (*a*) B. L. Barnett and C. Krüger, *J. Cryst. Mol. Struct.*, 1972, **2**, 271; (*b*) N. J. Kermode, M. F. Lappert, B. W. Skelton, A. H. White, and J. Holton, *J. Organomet. Chem.*, 1982, **228**, C71; (*c*) M. L. Illingsworth, J. A. Teagle, J. L. Burmeister, W. C. Fultz, and A. L. Rheingold, *Organometallics*, 1983, **2**, 1364.
29 J. J. Daly, 'Perspective in Structural Chemistry,' Wiley, New York, 1969, vol. 3.
30 N. E. Kolobova, L. L. Ivanov, O. S. Zhvanko, I. N. Chechulina, A. S. Batsanov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1982, **238**, 223.
31 L. M. Jackman and F. A. Cotton, 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1975, ch. 11.

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