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Oxygen *vs.* carbon co-ordination of α-keto-stabilized phosphorus ylides $Ph_3P{=}C(H)COR$ (R = Me, Ph or OMe) to palladium(II) cationic complexes

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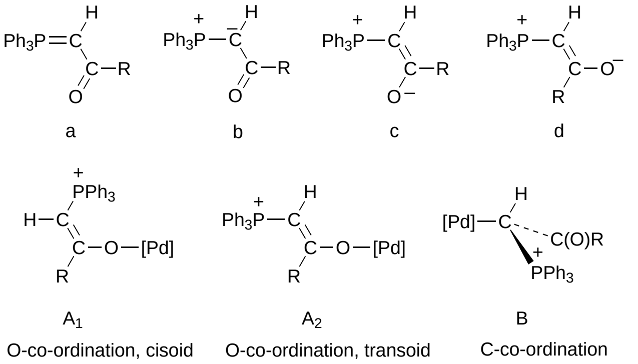
The reactivity of several C,N-cyclometallated palladium(II) complexes $[Pd(C_6H_4CH_2NMe_2\text{-}2)L(L')]ClO_4$ and $[Pd\{R\text{-}C_6H_4CH(Me)NMe_2\text{-}2\}L(L')]ClO_4$ [L = PPh_3 or pyridine (py), L′ = NCMe or thf (tetrahydrofuran); L = L′ = NCMe] towards α-keto-stabilized phosphorus ylides $Ph_3P{=}C(H)COR$ (R = Me, Ph or OMe) has been studied. When L = PPh_3, L′ = thf the ylide co-ordinates invariably through the carbonyl oxygen atom, and *trans* to the orthometallated C_6H_4 group, a rather unusual mode for the soft palladium(II) centre. When L = py, L′ = thf the co-ordination mode of the ylide and its site varies as a function of the nucleophilic character of the ylidic carbon atom. Thus, $Ph_3P{=}C(H)COMe$ (where the ylidic carbon is a poor nucleophile) co-ordinates through the carbonyl oxygen atom (*trans* to the C_6H_4 group), while the better nucleophile $Ph_3P{=}C(H)CO_2Me$ co-ordinates through the ylidic carbon and *trans* to the NMe_2 group. When L = L′ = NCMe the less nucleophilic ylides $Ph_3{=}C(H)COR$ (R = Me or Ph), give products in which a mixture of both O- and C-co-ordination modes are found, while $Ph_3P{=}C(H)CO_2Me$ gives exclusively C-co-ordination *trans* to the NMe_2 group. Infrared and NMR spectroscopies allow the unambiguous characterization of these products, and the crystal structure of $[Pd(C_6H_4CH_2NMe_2\text{-}2)(py)\{C(H)(CO_2Me)PPh_3\}]ClO_4$ has also been determined.

Among the phosphorus ylides of general stoichiometry $R_3P{=}CR'(R'')$ (R, R′, R″ = alkyl, aryl, alkoxy, *etc.*) the α-keto-stabilized ylides $Ph_3P{=}C(H)COR$ have shown useful applications in organometallic chemistry (due to their ambidentate character as ligands[1]) and as reactants or valuable key intermediates in metal-mediated organic synthesis.[1,2] This ambidentate character facilitates the preparation of stable metal complexes in which the ylide could be O- (forms **A$_1$**, **A$_2$**, Scheme 1)[3] or C-co-ordinated (**B**),[4] with both modes rationalized in terms of the resonance forms **a**–**c** together with the isomeric form **d**. However, while a large number of compounds containing C-co-ordinated ylides are known,[1–4] very few examples of O-bonded ones have been reported.[3]

We have recently described[5] the synthesis and structural characterization of the cationic complex $[Pd(C_6H_4CH_2NMe_2\text{-}2)(py)\{OC(Me){=}C(H)PPh_3\}]ClO_4$ (py = pyridine), in which the $Ph_3P{=}C(H)COMe$ ylide is O-co-ordinated to the soft Pd^{II}. This mode is unusual for the classical soft metals, in the sense that a classical 'hard' oxygen atom is bonded to a 'soft' palladium centre. However, and as was discussed there, some questions remained. Why, for example, does the ylide selectively adopt one co-ordination mode; what is the role of the electronic and steric influences of the different substituents on the ylide and on the starting complex, *etc.* Aiming to shed some light on these questions, we have conducted a systematic study of the reactivity of the solvated species $[Pd(C{-}N)L(L')]ClO_4$ [C−N = $C_6H_4CH_2NMe_2$-2 or R-$C_6H_4CH(Me)NMe_2$-2; L = PPh_3 or py, L′ = tetrahydrofuran (thf); L = L′ = NCMe] towards the α-keto-stabilized ylides $Ph_3P{=}C(H)COR$ (R = Me, Ph or OMe). Our choice of these solvated complexes rests on several factors: (*i*) their facile use in large-scale preparations; (*ii*) the presence in the C−N cyclometallated ligand of two donor atoms with very different electronic and steric properties; (*iii*) the possibility of modulation of the electronic and steric requirements of the ligand L, *trans* to the NMe_2 group, and (*iv*) the presence of one or two weakly co-ordinated ligands, susceptible to displacement by the ylide.



Scheme 1

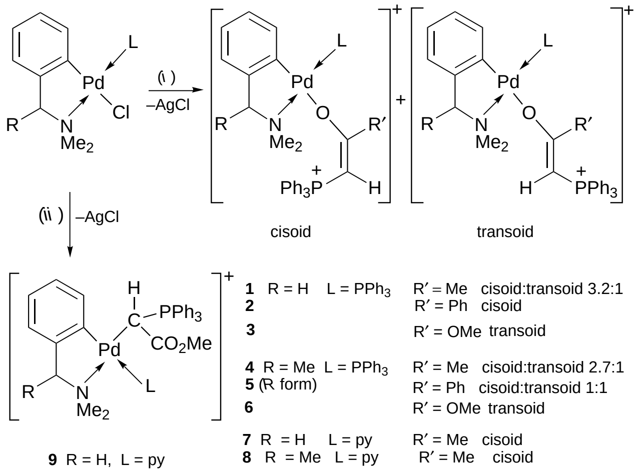
Results and Discussion

Reactions of $[Pd(C{-}N)(PPh_3)(thf)]ClO_4$ with ylides

All the reactions were carried out following the same experimental work-up: to a solution of the starting reagent $[PdCl(C{-}N)(PPh_3)]$ [C−N = $C_6H_4CH_2NMe_2$-2 or R-$C_6H_4CH(Me)NMe_2$-2] in thf at room temperature was added a stoichiometric amount of $AgClO_4$ (1:1 molar ratio). After filtration of the insoluble AgCl, the freshly prepared solution of $[Pd(C{-}N)(PPh_3)(thf)]ClO_4$ was cooled at 0 °C and allowed to react with a stoichiometric amount of the corresponding ylide $Ph_3P{=}C(H)COR$ (R = Me, Ph or OMe) (1:1 molar ratio). Either by direct precipitation or by evaporation of the solvent and treatment of the residue with Et_2O, it is possible to obtain white solids of stoichiometry $[Pd(C{-}N)(PPh_3)(Ph_3PCHCOR)]ClO_4$ **1**–**6** (see Scheme 2), as characterized by their elemental analyses and mass spectra. (After crystallization from CH_2Cl_2–hexane most of the products showed the presence of CH_2Cl_2 of crystallization in varying proportions, as determined by integration of their corresponding ^1H NMR spectra).

The elucidation of the co-ordination mode of the ylides in compounds **1**–**6** is based on the analysis of the following spectroscopic data: (*i*) position of the absorption due to the ν(CO) stretch in the IR spectra; (*ii*) the chemical shift of the methine proton (P=CH) and the value of the coupling constant $^2J_{\mathrm{PH}}$; (*iii*) the chemical shift of the phosphorus atom (ylide); (*iv*) the chemical shift of the ylidic carbon (P=CH) and the value of $^1J_{\mathrm{PC}}$.

Complexes **1**–**6** show, in the IR spectra, strong absorptions in the range 1490–1547 $\mathrm{cm^{-1}}$ (see Table 1), which are shifted to lower energies with respect to the corresponding free ylide [$\Delta\nu = \nu(\mathrm{CO})_{\mathrm{complex}} - \nu(\mathrm{CO})_{\mathrm{free\ ylide}}$]. Bonding through the carbonyl oxygen implies a major contribution of the form **c** or **d** (Scheme 1) and a decrease in the carbonyl stretching frequency,[3] as can be observed for **1**–**6**, suggesting an O-bonding mode for the ylides. The ^{1}H NMR spectra (see Table 2) show doublet resonances attributed to the methine proton (δ 3.55–4.75) with coupling constants $^2J_{\mathrm{PH}}$ ranging from 18 to 28 Hz. In all cases this resonance is shifted downfield with respect to those for the corresponding free ylides, and has a value of $^2J_{\mathrm{PH}}$ close to those observed for the free ylides and other O-bonded complexes[3c–e,5] (a C-co-ordinated ylide shows a lower $^2J_{\mathrm{PH}}$ value, as will be seen later). The ^{31}P-{^{1}H} NMR spectra of **1**–**6** show two singlet resonances: that at low field (at about δ 42) is attributed to the $\mathrm{PPh_3}$ ligand, while the resonance at high field (at about δ 15) is attributed to the phosphorus of the ylide. This resonance has undergone a small upfield shift with respect to the free ylide, indicative of O-co-ordination.[3e,5] Finally, the ^{13}C-{^{1}H} NMR spectra show the resonance attributed to the ylidic carbon as a doublet shifted downfield with respect to the corresponding free ylide and with a coupling constant $^1J_{\mathrm{PC}}$ very similar to that observed for the free ylide; all of these results are in keeping with O-co-ordination.[3e,5]



Scheme 2 Reactions performed in the synthesis of complexes **1**–**9**. The counter ion is always $\mathrm{ClO_4^-}$. (*i*) $\mathrm{AgClO_4}$, $\mathrm{Ph_3PC(H)COR'}$, thf, 0 °C; (*ii*) $\mathrm{AgClO_4}$, $\mathrm{Ph_3PC(H)CO_2Me}$, thf, 0 °C

Table 1 Relevant IR absorptions ($\mathrm{cm^{-1}}$) for complexes **1**–**13**

Complex	ν(CO)	ν(CO) (free ylide)	Δν
1	1505	1539	−34
2	1490	1529	−39
3	1546	1621	−75
4	1511	1539	−28
5	1495	1529	−34
6	1547	1621	−83
8	1514	1539	−25
9	1692	1621	+71
10	1582, 1509	1539	+43, −30
11	1582, 1498	1529	+53, −31
12	1688	1621	+67
13	1684	1621	+63

Further evidence for the O-bonding mode comes from the fact that the observation of isomers is independent of the presence of a chiral or non-chiral C,N-cyclometallated ligand. Assuming a retention in the configuration around the Pd atom (which is our case, since the phosphine ligand is very reluctant to co-ordinate *trans* to the σ-bonded $\mathrm{C_6H_4}$ group, see below), the C-co-ordination will transform the prochiral ylidic carbon (in the free ylide) into a chiral centre. Thus, complexes **1**–**3** with the non-chiral $\mathrm{C_6H_4CH_2NMe_2}$ ligand would be obtained as indistinguishable enantiomers (in a non-chiral medium such as $\mathrm{CDCl_3}$ or $\mathrm{CD_2Cl_2}$) and **4**–**6**, with the chiral *R*-$\mathrm{C_6H_4CH(Me)NMe_2}$, would be obtained as separable diastereoisomers. However, as is evident from Table 2, **1** is obtained as two separate isomers and **6** as a single isomer, all data thus indicating that the isomerism results from the ylide acting as an O-donor ligand.

Once the O-co-ordination mode for the ylides has been established, we would expect two isomers (cisoid/transoid, see Scheme 1) for this bonding mode. In fact, complexes **1**, **4** and **5** are obtained as a mixture of two isomers, while **2**, **3** and **6** show the presence of a single isomer. The nature of the carbonyl resonance in the ^{13}C-{^{1}H} NMR spectra enable us to distinguish between them. For **1** two resonances are present in the carbonyl region; that corresponding to the major isomer (δ 191.0) appears as a singlet, indicating a cisoid conformation,[5] while that corresponding to the minor isomer (δ 189.3) appears as a doublet, indicating a transoid conformation, and with a coupling constant of $^2J_{\mathrm{PC}} = 15.1$ Hz. In addition, for the same complex, the methyl carbon of the ylide ligand $\mathrm{Ph_3P{=}C(H)CO}Me$ appears as a doublet for the major isomer (δ 30.2, $^3J_{\mathrm{PC}} = 14$ Hz),

Table 2 Relevant NMR data (δ, ^nJ/Hz) for complexes **1**–**13**

Complex	δ(C*H*)	$^2J_{\mathrm{PH}}$	δ(P)	δ(*C*H)	$^1J_{\mathrm{PC}}$	δ(*C*O)	Comments
1	3.99/4.75	23/18	13.95/14.75	60.67/62.55	106/106	191.0 (s)/189 (d)	cisoid : transoid 3.2 : 1
2	4.63	20	15.08	62.08	120	185.6 (s)	cisoid
3	3.60	21	16.19	35.15	113	173.7 (d)	transoid
4	3.92/4.70	22/18	13.93/14.71	62.49/60.15	106/107	190.3 (s)/188.6 (d)	cisoid : transoid 2.7 : 1
5	4.63/4.61[a]	19/20[a]	14.83/14.62[a]	61.27 (both)	108	185.2 (s) (both)	cisoid : transoid 1 : 1[a]
6	3.55	28	16.23	38.11	116	173.0 (d)	transoid
8	4.02	24	13.56	59.27	99	190.1 (s)	cisoid
9	4.07	13	27.61	21.70	45	174.7 (s)	
10o[b]	3.98/4.51	23/22	14.19/14.07	62.12 (both)	108	191.0 (both)	cisoid : transoid ≈ 1 : 1
10c[b]	4.15[c]	—	25.62	28.53	28	204.3 (s)	**o** : **c** ≈ 2 : 1
11o[b]	4.83	22	16.12	58.80	110	191.8 (s)	cisoid
11c[b]	4.60	—	28.29	32.58[c]	—	199.3 (s)	**o** : **c** ≈ 1.8 : 1
12	3.58	4	25.96	20.79	51	174.1 (s)	
13	3.61/3.60[c]	4/—	25.77/24.97	20.75/20.50	52/51	174.9/174.8	major : minor 1.75 : 1
$\mathrm{Ph_3P{=}C(H)COMe}$	3.67	27	14.85	51.61	108	190.8	Room temperature
$\mathrm{Ph_3P{=}C(H)COPh}$	4.41	25	17.20	50.68	112	184.9	Room temperature
$\mathrm{Ph_3P{=}C(H)CO_2Me}$	2.87	n.o.	18.24	29.77	126	171.7	Room temperature

[a] At 248 K. [b] At 188 K. [c] Broad; both = both isomers; n.o. = not observed; **o** = O-co-ordinated ylide; **c** = C-co-ordinated ylide.

in keeping with the cisoid conformation.[5] This resonance appears as a singlet for the minor isomer, also in agreement with the transoid form. Thus, the character of these resonances allows us to discriminate not only between the different conformations (cisoid/transoid) of the co-ordinated ylide, but also indicates that the sole source of isomerism arises from the two forms of the ylide ligand and not from rearrangements of ligands around the metal or diastereoisomerism at the ylidic carbon.

Unfortunately, it seems that there is not a clear correlation between the nature and/or the size of the R substituent on the carbonyl group (Me, Ph, OMe) and the final conformation mode adopted by the co-ordinated ylide. It has been suggested that a cisoid structure would be preferred for the free ylides on electrostatic grounds,[6–8] and this is supported by the accurate determination of the structure of Ph_3P=C(H)COPh by X-ray diffraction methods[9] which shows the O atom oriented *cis* to the P atom. In spite of this clear tendency of the free ylides, we have found an almost random distribution of the co-ordinated ylides for which there is no sensible explanation; Ph_3P=C(H)-COMe was found to have both conformations in **1** and **4**, while it adopts only the cisoid form in **7**[5] and **8** (see below), Ph_3P=C(H)COPh adopts only the cisoid conformation in **2**, and both in **5**, and $Ph_3P=CO_2Me$ selectively adopts the transoid form in **3** and **6**.

Reactions of [Pd(C–N)(py)(thf)]ClO_4 with ylides

The solvated complexes [Pd(C–N)(py)(thf)]ClO_4 [C–N = $C_6H_4CH_2NMe_2$-2 or $C_6H_4CH(Me)NMe_2$-2] {prepared in thf, as described previously, from the corresponding [PdCl(C–N)(py)] starting material and $AgClO_4$ in 1:1 molar ratio} react with Ph_3P=C(H)COMe (1:1 molar ratio) to give [Pd(C–N)(py)[OC-(Me)=C(H)PPh_3]]ClO_4 **7**[5] or **8**, in which the ylide is O-bonded. The O-bonding mode and the cisoid conformation for the ylide are inferred from their IR and NMR data (see Tables 1 and 2, and ref. 5) and from the determination of the crystal structure of **7**.[5] On the other hand, the reactions of [Pd(C–N)(py)(thf)]-ClO_4 with Ph_3P=C(H)COPh under the same conditions gave intensely coloured solutions from which a very complex mixture of products was obtained.

A different behaviour has been observed in the reaction of [Pd($C_6H_4CH_2NMe_2$-2)(py)(thf)]ClO_4 with the more nucleophilic ylide $Ph_3P=C(H)CO_2Me$ (1:1 molar ratio, same experimental conditions). A white solid of stoichiometry [Pd($C_6H_4CH_2NMe_2$-2)(py)(Ph_3PCHCO_2Me)]ClO_4 **9** can be isolated from the reaction mixture in good yield. However, its spectroscopic data (see Tables 1 and 2) are quite different from those observed for this ylide in **3** and **6**, for which we postulated O-co-ordination. Thus, the IR spectrum shows the ν(CO) absorption at 1692 cm^{-1}, shifted to higher energies with respect to the free ylide ($\Delta\nu = +71\ cm^{-1}$) and suggesting a C-bonding mode for the ylide (bonding through the ylidic carbon atom implies a major contribution of form **b**, Scheme 1, and an increase in the carbonyl stretching frequency). The NMR data for **9** point to the same conclusion: the resonance of the methine proton appears as a doublet at δ 4.07 with a coupling constant of $^2J_{PH} = 13$ Hz, notably smaller than those found for **3** or **6**, and the resonance of the ylidic carbon atom [$^{13}C-\{^1H\}$] appears at δ 21.70 (shifted upfield with respect to the free ylide) and also with a small coupling constant ($^1J_{PC} = 45$ Hz). Finally, the phosphorus resonance [$^{31}P-\{^1H\}$] appears at δ 27.61, shifted downfield with respect to the free ylide. All of these data can be explained by assuming a change in the hybridization of the ylidic carbon ($sp^2 \longrightarrow sp^3$) as a result of the C-co-ordination of the ylide.[4] The determination of the molecular structure of **9** provides further characterization.

Crystal structure of [Pd($C_6H_4CH_2NMe_2$-2)(py){CH(CO_2Me)-(PPh_3)}]ClO_4 9

Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of compound **9** at room temperature. A drawing of the cationic organometallic fragment is shown in Fig. 1, and selected bond distances and angles are collected in Table 3.

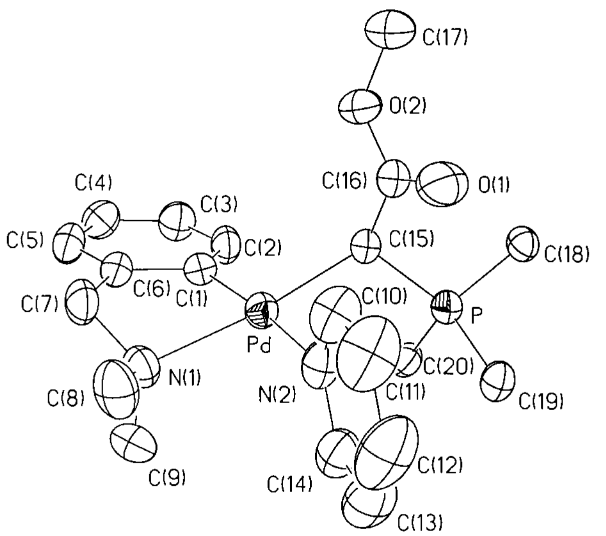


Fig. 1 Thermal ellipsoid plot of the [Pd($C_6H_4CH_2NMe_2$-2)(py)-{CH(CO_2Me)PPh_3}]$^+$ cation. The Ph groups of the PPh_3 fragment (except C_{ipso}) and H atoms are omitted for clarity. Atoms are drawn at the 50% probability level

Table 3 Selected bond distances (Å) and angles (°) for compound **9**

Pd–C(1)	2.001(3)	C(16)–O(1)	1.198(4)
Pd–C(15)	2.098(3)	C(16)–O(2)	1.331(4)
Pd–N(1)	2.137(3)	C(15)–C(16)	1.487(5)
Pd–N(2)	2.139(3)	C(17)–O(2)	1.445(4)
P–C(15)	1.782(3)		
C(1)–Pd–N(1)	81.40(13)	N(1)–Pd–N(2)	92.22(11)
N(2)–Pd–C(15)	95.01(13)	C(15)–Pd–C(1)	91.29(14)
Pd–C(15)–C(16)	111.8(2)	Pd–C(15)–P	116.1(2)
O(1)–C(16)–C(15)	126.4(3)	O(2)–C(16)–C(15)	111.1(3)
O(1)–C(16)–O(2)	122.5(3)	C(16)–O(2)–C(17)	116.0(3)

The palladium atom is located in a slightly distorted square-planar environment, surrounded by the C and N atoms of the cyclometallated ligand, the N atom of the pyridine and the ylidic carbon of the $Ph_3P=C(H)CO_2Me$ ligand, thus confirming the C-co-ordination of the latter. The Pd–C(1) and Pd–N(1) (of $C_6H_4CH_2NMe_2$) bond distances are similar to those found in other complexes,[5,10] and the Pd–N(2) (py) distance also falls in the usual range of distances found for this type of bond.[5,11] However, both the Pd–N(1) and Pd–N(2) distances are larger than their homologues found in **7**,[5] due to the fact that both N atoms are *trans* to σ(Pd–C) bonds which display a large *trans* influence. The Pd–C(15) distance [2.098(3) Å] is at the low end of the range found for this kind of bond, as can be seen from Table 4, and falls in the usual range of σ(Pd–C) distances.[12] Once co-ordinated the ylidic carbon becomes a chiral centre, which in the enantiomer shown in Fig. 1 displays the *S* configuration (following the system of priorities of Cahn, *et al.*[13]). However, the crystal structure as a whole is racemic, since the space group ($P2_1/c$) is centrosymmetric. The P–C(15) bond distance [1.782(3) Å] is slightly shorter than the average of the other P–C single-bond distances present in the molecule (1.804 Å). A brief comparison of relevant bond distances between **9** and other C-co-ordinated ylides is presented in Table 4. Both the C(15) and P atoms have slightly distorted tetrahedral environments (average of bond angles: 113.5 and 109.4°, respectively).

It is also evident from Fig. 1 that an isomerization process has taken place during the reaction; the pyridine ligand is found to be *cis* to the orthometallated C_6H_4 group in the starting

Table 4 Comparison of relevant bond distances (Å) in compound **9** and other ylide complexes

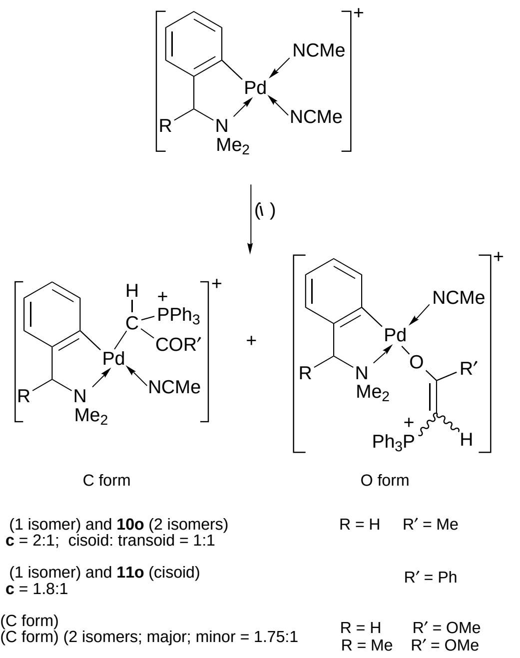
Complex	P–C (ylide)	C(ylide)–C(O)	C=O	Pd–C(ylide)	Ref.
9 $[Pd(C_6H_4CH_2NMe_2\text{-}2)(py)\{C(H)(CO_2Me)PPh_3\}]^+$	1.782(3)	1.487(5)	1.198(4)	2.098(3)	This work
7 $[Pd(C_6H_4CH_2NMe_2\text{-}2)(py)\{OC(Me)=C(H)PPh_3\}]^+$	1.732(3)	1.366(4)	1.275(4)		5
$[\{PdCl_2[C(H)(COPh)(PBu^n_3)]\}_2]$	1.786(5)	1.478(6)	1.225(7)	2.149(5)	4(*h*)
$[Pd(\eta^3\text{-}C_3H_4Me\text{-}2)(CNCMe_3)\{C(H)(COMe)(PPh_3)\}]^+$	1.744(9)	1.46(1)	1.21(1)	2.175(9)	4(*j*)
$[Pd(\eta^3\text{-}C_3H_4Me\text{-}2)Cl\{C(H)(COMe)(PPh_3)\}]$	1.769(3)	1.452(5)	1.228(4)	2.193(3)	4(*g*)
$[\{HgCl_2[C(H)(COPh)(PPh_3)]\}_2]$	1.798(8)	1.504(9)	1.229(8)		4(*l*)
$[\{HgI_2[C(H)(COPh)(PPh_3)]\}_2]$	1.806(10)	1.453(14)	1.224(13)		4(*l*)

compound $[PdCl(C_6H_4CH_2NMe_2\text{-}2)(py)]$[14] (pyridine usually bonds *cis* to palladated carbon atoms[15]) while in **9** it is *cis* to the NMe_2 unit (and, therefore, *trans* to the C_6H_4 group). We must note here that the spectroscopic data for crude **9** and those of the crystals are identical and that we have not detected the presence of two or more isomers in a freshly precipitated sample of **9**. Thus, the isomerization process does not take place during the crystallization; the crude **9** already contains the isomerized product.

The resulting arrangement of ligands around the Pd^{II} could be consistent with the known antisymbiotic behaviour of this metal:[16] the C-co-ordinated ylide behaves as a soft base, even softer than the pyridine ligand (which is considered to be a 'borderline' base[17]), and will be stabilized when it is co-ordinated *trans* to the hardest donor group of the $C_6H_4CH_2NMe_2$ ligand (the N atom of the NMe_2 unit), while the 'hard' pyridine (compared with the ylide) can be accommodated *trans* to the 'soft' C-donor atom of the C_6H_4 cyclometallated group.[11]

A consideration of the antisymbiotic effect shown by the Pd^{II}[18] and the relative hardness and softness of the different ligands ($C_6H_4CH_2NMe_2$, PPh_3, py, ylides) is helpful in understanding the puzzling behaviour of the ylides. For instance, the invariable O-co-ordination found in complexes **1**–**6**, which is independent of the nucleophilic character of the ylidic carbon, can be explained by noting that the soft PPh_3 ligand (which forms stable Pd–P bonds and is reluctant to be co-ordinated *trans* to the σ-bonded carbon[18]) will be stabilized *trans* to the hard N atom of the $C_6H_4CH_2NMe_2$ ligand. Thus, an O-co-ordination of the ylide (the oxygen atom is a hard base) will be stabilized *trans* to a soft donor atom, *i.e.* the carbon of the C_6H_4 group, while a C-co-ordination of the ylide *trans* to the σ-bonded carbon will be rather destabilized.* In fact, in each of the examples of C-bonded ylides described in this work the ylide is co-ordinated *trans* to the N atom of the cyclometallated ligand (see below). Steric factors also need to be considered since O-co-ordination of the ylide results in a lower steric requirement than does C-co-ordination, and would be more favourable when the *cis* position is occupied by a large ligand such as PPh_3. Other factors, such as the nucleophilic character of the ylidic carbon, do not seem to be relevant here (in light of the results obtained) but the former seems to be a discriminating factor when other ligands, such as pyridine, are present (complexes **7**–**9**).

In the case of complexes **7** and **8** [$Ph_3P=C(H)COMe$ as ylide] the weak nucleophilic character of the ylidic carbon[6–8] and the nature of the 'vacant' co-ordination site (the weakly co-ordinated thf ligand, which is *trans* to the C_6H_4 group) favour O-co-ordination in this position, with the position of the pyridine ligand unchanged. However, the strong nucleophilic character of the carbon atom in $Ph_3P=C(H)CO_2Me$ enforces its C-co-ordination in **9**, which would be destabilized *trans* to the carbon atom and is thus accommodated by a shift to a position *trans* to the harder nitrogen atom, giving rise to the observed isomerism. This migration cannot take place when a phosphine is bound to palladium, and for this reason complexes **3** and **6** show an O-co-ordination. Similar conclusions about the antisymbiotic effect and the relative hardness and softness of the ligands have been reported for the reactivity of C,N-cyclometallated derivatives with carbonyl metalates.[16b]



Scheme 3 Reactions performed in the synthesis of complexes **10**–**13**. The counter ion is always ClO_4^-. **o**, O-co-ordinated ylide, **c**, C-co-ordinated ylide; (*i*) $Ph_3PC(H)COR'$, CH_2Cl_2, 25 °C

Reactions of [PdC–N)(NCMe)$_2$]ClO$_4$ with ylides

The reaction of $[Pd(C\text{–}N)(NCMe)_2]ClO_4$ [C–N = $C_6H_4CH_2NMe_2$-2 or *R*-$C_6H_4CH(Me)NMe_2$-2] with a stoichiometric amount of the ylides $Ph_3P=C(H)COR$ (R = Me, Ph or OMe) (1 : 1 molar ratio) in CH_2Cl_2 at room temperature gave, after solvent evaporation and Et_2O addition, white or pale yellow solids of stoichiometry $[Pd(C\text{–}N)(Ph_3PCHCOR)(NCMe)]ClO_4$ **10**–**13** (see Scheme 3). All complexes give satisfactory elemental analyses for the proposed stoichiometry. The mass spectra (positive-ion FAB, see Experimental section) do not show the molecular peak, but it is possible to observe weak peaks corresponding to loss of the NCMe ligand. However, several attempts to displace the NCMe ligand by addition of a second equivalent of ylide were not successful. No reaction was observed at room temperature and, on heating (refluxing $CHCl_3$ or toluene) for **10** and **11** decomposition takes place, while for **12** or **13** the mixture of the ylide and the starting complex was recovered unchanged.

Analysis of the IR and NMR data for compounds **10**–**13**

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* However, this fact does not imply their non-existence. The reaction of $[Pd\{R\text{-}C_6H_4CH(Me)NMe_2\text{-}2\}(thf)_2]ClO_4$ with the phosphine ylides $Ph_2PCH_2PPh_2=C(H)COR$ gives $[Pd\{R\text{-}C_6H_4CH(Me)NMe_2\text{-}2\}(Ph_2PCH_2PPh_2CHCOR)]ClO_4$ as two diastereoisomers in which the phosphine PPh_2 moiety is *trans* to the N and both C atoms are mutually *trans*.[19]

reveals some interesting differences among the corresponding reactions (see Tables 1 and 2). Thus, the IR spectra of **10** and **11** show two intense absorptions in the range 1600–1500 cm^{-1}, one of them shifted to higher energies with respect to the free ylide (indicating C-co-ordination) and the other shifted to lower energies (pointing to O-co-ordination). The IR spectra of **12** and **13** show only one absorption each, shifted to higher energies, in keeping with C-co-ordination. The ^1H NMR spectra of **10** and **11** show broad resonances at room temperature, which are resolved into well defined peaks at low temperature (CD_2Cl_2, 188 K). At this temperature it is possible to observe the presence of three different complexes for **10** and two for **11**, corresponding to the mixture of the O- and the C-bonded ylides (**10o**/**10c** and **11o**/**11c**). Moreover, the O-co-ordinated ylide in **10o** is present as mixture of the cisoid and transoid isomers, while **11o** shows only the cisoid conformation. The ^{31}P-{^1H} and ^{13}C-{^1H} NMR data reflect the same situation and are consistent with the ^1H NMR analysis.

A less complicated situation has been found in complexes **12** and **13**; the ^1H NMR spectrum (as well as the ^{31}P-{^1H} and ^{13}C-{^1H}) of **12** shows a single set of signals, corresponding to the existence of a single product, in which the ylide is C-bonded (see Table 2 for the more relevant resonances), as was expected from IR data. Presumably, **12** is obtained as the racemic mixture of the *R* and *S* enantiomers. Moreover, complex **13** shows in the ^1H NMR spectrum two sets of signals, corresponding to the two possible diastereoisomers (*RR*/*RS*), and the same is observed in its ^{31}P-{^1H} and ^{13}C-{^1H} NMR spectra. A small diastereoselective induction has been detected (major : minor ratio = 1.75 : 1; diastereometric excess = 27.3%) but we have not been able to determine which is the dominant isomer (see below).

Once the co-ordination mode of the ylide in each complex was established, the site for the C-co-ordinated ylides was determined by $^1H-^1H$ (nuclear Overhauser effect spectroscopy) (NOESY) measurements performed on **12** using $(CD_3)_2CO$ as solvent (this gave a better separation of the signals than with $CDCl_3$). The methine P=C*H* resonance shows a strong NOE interaction with the H^6 proton of the $C_6H_4CH_2NMe_2$ ligand, indicating the proximity of the interacting nuclei. In addition, the NCMe resonance also shows NOE interactions with both Me groups of the NMe_2 unit. Thus, the C-bonded ylide is *cis* to the C_6H_4 group and *trans* to the NMe_2 unit, an arrangement of ligands similar to that found for **9**.

As has been seen in complexes **9** and **12**, the C-bonded ylides are co-ordinated *trans* to the N atom of the C,N-orthometallated ligand, in good agreement with the antisymbiotic behaviour of the soft palladium(II) centre. By extension of these results we suggest for complexes **10c**, **11c** and **13** the same structure (as depicted in Scheme 3), with the NCMe ligand *trans* to the C atom of the C−N ligand. We do not have a direct evidence for complexes **10o** and **11o** ($^1H-^1H$ NOESY or crystal structure), but taking into account the observed structures for complexes **1**–**8** (mainly **7** and **8**, which contain an N-donor ligand) we propose the O-bonded ylides to be *trans* to the orthometallated carbon atom (as shown in Scheme 3).

On the other hand the presence of both O- and C-co-ordination modes in complexes **10** and **11** clearly reflects the ambidentate character of these ylides and the low nucleophilic character of the ylidic carbon in the ylides $Ph_3P=C(H)COMe$ and $Ph_3P=C(H)COPh$, almost comparable to that of the oxygen atom.

Finally, the small diastereoselective induction observed in complex **13** seems to be a consequence of the co-ordination site of the ylide. In fact the role of the NMe_2 unit [in the *R*-$C_6H_4CH(Me)NMe_2$ ligand] as a 'reflecting' group of the chirality of the adjacent stereogenic carbon has been demonstrated.[20] It is suggested that the steric interactions between the Me groups of the NMe_2 unit and the substituents of a prochiral (or chiral) group *cis* co-ordinated are at the origin of a diastereoselective induction.* In keeping with that, a C-co-ordination *trans* to the NMe_2 unit leaves the ylide too far from any source of chirality, thus giving a sensible explanation of the observed low diastereoselectivity.

Experimental

CAUTION: perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great caution.[21]

General procedures

Solvents were dried and distilled under nitrogen before use: diethyl ether and tetrahydrofuran over diphenyl ketyl, dichloromethane over P_2O_5 and hexane over sodium. Elemental analyses were carried out on a Perkin-Elmer 240-B microanalyser. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 883 spectrophotometer from Nujol mulls between polyethylene sheets, ^1H (300.13), ^{13}C-{^1H} (75.47) and ^{31}P-{^1H} (121.49 MHz) NMR spectra in $CDCl_3$ or CD_2Cl_2 solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer. The ^1H and ^{13}C-{^1H} spectra were referenced using the solvent signal as internal standard and ^{31}P-{^1H} was externally referenced to H_3PO_4 (85%). The two-dimensional $^1H-^1H$ NOESY experiment for complex **12** was performed at a measuring frequency of 300.13 MHz. The data were acquired into a 636 × 2048 matrix, and then transformed into 2048 × 2048 points using a sine window in each dimension. The mixing time was 400 ms. Mass spectra (positive-ion FAB) were recorded on a V. G. Autospec spectrometer. The starting compounds [PdCl(C−N)L][14] and $[Pd(C-N)(NCMe)_2]ClO_4$,[22] [C−N = $C_6H_4CH_2NMe_2$-2 or *R*-$C_6H_4CH(Me)NMe_2$-2; L = NC_5H_5 or PPh_3], $Ph_3P=C(H)COR$ (R = Me or Ph)[23] and $Ph_3P=C(H)CO_2Me$[24] were prepared according to published methods.

Preparations

$[Pd(C_6H_4CH_2NMe_2\text{-}2)(PPh_3)\{OC(Me)=C(H)PPh_3\}]ClO_4$ 1. To a solution of $[PdCl(C_6H_4CH_2NMe_2\text{-}2)(PPh_3)]$ (0.176 g, 0.327 mmol) in thf (20 cm^3) at room temperature, was added $AgClO_4$ (0.069 g, 0.33 mmol). The resulting suspension was stirred for 20 min at room temperature and filtered. The freshly obtained solution was cooled at 0 °C in an ice-bath, then $Ph_3P=C(H)COMe$ (0.106 g, 0.333 mmol) was added. After 20 min of stirring at 0 °C complex **1** precipitated as a white solid, which was filtered off and air-dried (0.256 g, 71% yield). Complex **1**·1.5CH_2Cl_2 recrystallized from CH_2Cl_2–hexane was used for elemental analysis and NMR measurements. (Found: C, 56.8; H, 4.5; N, 1.35. $C_{48}H_{46}ClNO_5P_2Pd\cdot 1.5CH_2Cl_2$ requires C, 56.7; H, 4.7; N, 1.35%). Positive-ion FAB mass spectrum: *m*/*z* 820 (M^+, 15%). IR (ν_{CO}): 1505 cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 7.64–7.29 (m, Ph), 6.95 (d, C_6H_4, $^3J_{HH} = 7$), 6.83 (false t, C_6H_4, $^3J_{HH} = 7$), 6.29 (m, C_6H_4), 4.75 (d, CH ylide, transoid, minor isomer, $^2J_{PH} = 18$), 4.16 (s, CH_2N, transoid), 3.99 (d, CH ylide, cisoid, major isomer, $^2J_{PH} = 23$), 3.99 (s, CH_2N, cisoid), 2.85 (s, NMe_2, transoid), 2.26 (s, NMe_2, cisoid), 1.59 (d, COMe, cisoid, $^4J_{PH} = 1$), and 1.25 (s, COMe, transoid); ^{31}P-{^1H}, δ 42.61 (Pd−PPh_3, cisoid), 42.15 (Pd−PPh_3, transoid), 14.75 (P^+Ph_3, transoid), and 13.95 (P^+Ph_3, cisoid); ^{13}C-{^1H}, δ 191.0 (s, CO, cisoid), 189.3 (d, CO, transoid, $^2J_{PC} = 15$), 149.2 (2C), 145.2, 144.0, 139.8, 139.0, 137.6 ($J_{PC} = 15$), 133.9 ($J_{PC} = 15$), 133.6, 133.2 ($J_{PC} = 8$), 131.6, 130.4 ($J_{PC} = 8$), 130.2, 129.8, 129.6 ($J_{PC} = 15$), 129.1 ($J_{PC} = 8$), 128.7, 125.0 ($J_{PC} = 30$) (C_6H_4 +

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* We can explain the diastereoselectivity observed in the different diastereoisomers of $[Pd\{R\text{-}C_6H_4CH(Me)NMe_2\text{-}2\}(Ph_2PCH_2PPh_2CHCOR)]ClO_4$ (up to 80%, see ref. 19) by taking into account the *cis* disposition of the ylidic chiral carbon and the NMe_2 group.

PPh$_3$), 72.0 (CH$_2$N, both isomers), 62.5 (d, CH ylide, transoid, $^1J_{PC}$ = 106), 60.7 (d, CH ylide, cisoid, $^1J_{PC}$ = 106), 50.8 (NMe$_2$, transoid), 49.8 (NMe$_2$, cisoid), 30.2 (d, CO*Me*, cisoid, $^3J_{PC}$ = 14 Hz) and 27.2 (s, CO*Me*, transoid).

[Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(PPh$_3$){OC(Ph)=C(H)PPh$_3$}]ClO$_4$ 2. Complex **2** was synthesized similarly to **1**: [PdCl(C$_6$H$_4$CH$_2$-NMe$_2$-2)(PPh$_3$)] (0.200 g, 0.372 mmol) was treated with AgClO$_4$ (0.078 g, 0.38 mmol) and Ph$_3$P=C(H)COPh (0.144 g, 0.378 mmol) in thf at 0 °C to give **2** as a white solid (0.160 g, 44% yield). This complex did not need recrystallization (Found: C, 64.5; H, 4.7; N, 1.4. C$_{53}$H$_{48}$ClNO$_5$P$_2$Pd requires C, 64.75; H, 4.9; N, 1.4%). Positive-ion FAB mass spectrum: *m/z* 882 (M^+, 11%). IR (ν_{CO}): 1490 cm^{-1}. NMR (CD$_2$Cl$_2$): ^{1}H, δ 8.05–7.10 (m, Ph), 6.99 (d, 1 H, C$_6$H$_4$, $^3J_{HH}$ = 9), 6.83 (m, 1 H, C$_6$H$_4$), 6.30 (m, 2 H, C$_6$H$_4$), 4.63 (d, 1 H, CH ylide, $^2J_{PH}$ = 20), 4.42 (d, 1 H, CH$_2$N, $^2J_{HH}$ = 14), 3.63 (dd, 1 H, CH$_2$N, $^4J_{HH}$ = 4), 2.26 (s, 3 H, NMe$_2$), and 2.21 (d, 3 H, NMe$_2$, $^4J_{PH}$ = 3); ^{31}P-{^{1}H}, δ 42.63 (Pd–PPh$_3$) and 15.08 (P$^+$Ph$_3$); ^{13}C-{^{1}H}, δ 185.6 (CO), 148.8, 142.7, 140.4, 139.8, 124.9, 123.3 (C$_6$H$_4$), 135.4 (J_{PC} = 12), 134.1 (J_{PC} = 10), 133.8, 131.4, 130.8, 130.3, 129.8 (J_{PC} = 12), 128.8 (J_{PC} = 11), 127.0, 125.5, 125.1 (J_{PC} = 37) (C$_6$H$_5$ + PPh$_3$), 72.0 (CH$_2$N), 62.1 (d, CH ylide, $^1J_{PC}$ = 120 Hz), 50.6 and 49.6 (NMe$_2$).

[Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(PPh$_3$){OC(OMe)=C(H)PPh$_3$}]ClO$_4$ 3. Complex **3** was synthesized similarly to **1**: [PdCl(C$_6$H$_4$CH$_2$-NMe$_2$-2)(PPh$_3$)] (0.200 g, 0.372 mmol) was treated with AgClO$_4$ (0.077 g, 0.37 mmol) and Ph$_3$P=C(H)CO$_2$Me (0.125 g, 0.372 mmol) in thf at 0 °C to give **3** as a white solid (0.320 g, 92% yield). Complex **3**·CH$_2$Cl$_2$ recrystallized from CH$_2$Cl$_2$–hexane was used for elemental analysis and NMR measurements (Found: C, 57.85; H, 4.9; N, 1.4. C$_{48}$H$_{46}$ClNO$_6$P$_2$Pd·CH$_2$Cl$_2$ requires C, 57.6; H, 4.75; N, 1.35%). Positive-ion FAB mass spectrum: *m/z* 836 (M^+, 12%). IR (ν_{CO}): 1546 cm^{-1}. NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.67–7.25 (m, Ph), 7.06 (d, 1 H, C$_6$H$_4$, $^3J_{HH}$ = 8), 6.91 (false t, 1 H, C$_6$H$_4$, $^3J_{HH}$ = 7), 6.37 (m, 2 H, C$_6$H$_4$), 4.16 (s, br, 2 H, CH$_2$N), 3.60 (d, br, 1 H, CH ylide, $^2J_{PH}$ = 21) and 2.85 (s, br, 9 H, NMe$_2$ + OMe); at −90 °C some signals split; 4.66, 3.67 (AX system, 2 H, CH$_2$N, $^2J_{HH}$ = 13), 3.05, 2.83 and 2.60 (3s, 9 H, NMe$_2$ + OMe); ^{31}P-{^{1}H}, δ 42.49 (Pd–PPh$_3$) and 16.19 (P$^+$Ph$_3$); ^{13}C-{^{1}H}, δ 173.8 (d, CO, $^2J_{PC}$ = 17), 149.0, 143.8, 139.0, 130.2, 125.2, 123.6 (C$_6$H$_4$), 135.4 (J_{PC} = 15), 133.3 (br, 131.7, 129.7 (J_{PC} = 15), 128.9 (J_{PC} = 8), 126.1 (J_{PC} = 32) (PPh$_3$), 71.9 (CH$_2$N), 51.4 (2C), 50.6 (NMe$_2$ + OMe) and 35.2 (d, CH ylide, $^1J_{PC}$ = 113 Hz).

[Pd{*R*-C$_6$H$_4$CH(Me)NMe$_2$-2}(PPh$_3$){OC(Me)=C(H)PPh$_3$}]-ClO$_4$ 4. Complex **4** was synthesized similarly to **1**, except that the reaction was performed at 25 °C: [PdCl{*R*-C$_6$H$_4$CH(Me)-NMe$_2$-2}(PPh$_3$)] (0.205 g, 0.370 mmol) was treated with AgClO$_4$ (0.076 g, 0.37 mmol) and Ph$_3$P=C(H)COMe (0.117 g, 0.370 mmol) in thf to give **4** as a white solid after solvent evaporation and Et$_2$O (25 cm^3) addition (0.284 g, 94% yield) (Found: C, 62.8; H, 5.5; N, 1.3. C$_{49}$H$_{48}$ClNO$_5$P$_2$Pd requires C, 62.95; H, 5.2; N, 1.50%). Positive-ion FAB mass spectrum: *m/z* 834 (M^+, 10%). IR (ν_{CO}): 1511 cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 7.57–7.23 (m, Ph), 6.85 (d, C$_6$H$_4$, $^3J_{HH}$ = 7), 6.75 (false t, C$_6$H$_4$, $^3J_{HH}$ = 7), 6.23 (m, C$_6$H$_4$), 4.70 (d, CH ylide, transoid, minor isomer, $^2J_{PH}$ = 18), 3.92 (d, CH ylide, cisoid, major isomer, $^2J_{PH}$ = 22), 3.85 [m, C$_6$H$_4$C*H*(Me)NMe$_2$, transoid], 3.69 [m, C$_6$H$_4$C*H*(Me)NMe$_2$, cisoid], 2.90, 2.66 (2s, NMe$_2$, transoid), 2.35, 2.01 (2s, NMe$_2$, cisoid), 1.74 [s, br, C$_6$H$_4$CH(*Me*)N-Me$_2$ + COMe, transoid], 1.65 [d, C$_6$H$_4$CH(*Me*)NMe$_2$, cisoid, $^3J_{HH}$ = 6] and 1.56 (s, COMe, cisoid); ^{31}P-{^{1}H}, δ 41.99 (Pd–PPh$_3$, transoid), 41.87 (Pd–PPh$_3$, cisoid), 14.71 (P$^+$Ph$_3$, transoid), and 13.93 (P$^+$Ph$_3$, cisoid); ^{13}C-{^{1}H}, δ 190.3 (CO, cisoid), 188.7 (d, CO, transoid, $^2J_{PC}$ = 13), 154.3, 143.3, 139.1, 138.4, 134.9 (J_{PC} = 12), 133.7, 133.4 (J_{PC} = 10), 133.2, 132.7 (J_{PC} = 10), 131.2, 130.0, 129.9, 129.4, 129.3 (J_{PC} = 13), 128.6 (J_{PC} = 11), 124.7 (J_{PC} = 41), 123.5 (J_{PC} = 9), 122.7 (C$_6$H$_4$ + PPh$_3$), 74.2 [C$_6$H$_4$*C*H(Me)NMe$_2$, transoid], 73.8 [C$_6$H$_4$*C*H-(Me)NMe$_2$, cisoid], 62.5 (d, CH ylide, cisoid, $^1J_{PC}$ = 106), 60.1 (d, CH ylide, transoid, $^1J_{PC}$ = 107), 51.2 (NMe$_2$, transoid), 49.9 (NMe$_2$, cisoid), 45.6 (NMe$_2$, transoid), 45.0 (NMe$_2$, cisoid), 30.1 (CO*Me*, transoid), 29.9 (d, CO*Me*, cisoid, $^3J_{PC}$ = 13 Hz), 26.7 [C$_6$H$_4$CH(*Me*)NMe$_2$, cisoid] and 22.7 [C$_6$H$_4$CH(*Me*)-NMe$_2$, transoid].

[Pd{*R*-C$_6$H$_4$CH(Me)NMe$_2$-2}(PPh$_3$){OC(Ph)=C(H)PPh$_3$}]-ClO$_4$ 5. Complex **5** was synthesized similarly to **1**, except that the reaction was performed at 25 °C: [PdCl{*R*-C$_6$H$_4$CH(Me)-NMe$_2$-2}(PPh$_3$)] (0.200 g, 0.362 mmol) was treated with AgClO$_4$ (0.075 g, 0.36 mmol) and Ph$_3$P=C(H)COPh (0.138 g, 0.362 mmol) in thf to give **5** as a white solid after solvent evaporation and Et$_2$O (25 cm^3) addition (0.261 g, 81% yield) (Found: C, 64.55; H, 5.0; N, 1.4. C$_{54}$H$_{50}$ClNO$_5$P$_2$Pd requires C, 65.05; H, 5.05; N, 1.4%). Positive-ion FAB mass spectrum: *m/z* 896 (M^+, 5.0%). IR (ν_{CO}): 1495 cm^{-1}. NMR (CDCl$_3$, 248 K): ^{1}H, δ 8.02 (m), 7.75–6.80 (m), 6.27 (m) (C$_6$H$_4$ + Ph), 4.63 (d, CH ylide, $^2J_{PH}$ = 19), 4.61 (d, CH ylide, $^2J_{PH}$ = 20), 3.79 [m, C$_6$H$_4$C*H*(Me)NMe$_2$], 3.59 [m, C$_6$H$_4$C*H*(Me)NMe$_2$], 2.51, 2.10, 2.00, 1.87 (4s, 2NMe$_2$), 1.74 [d, C$_6$H$_4$CH(*Me*)NMe$_2$, $^3J_{HH}$ = 6] and 1.47 [d, C$_6$H$_4$CH(*Me*)NMe$_2$, $^3J_{HH}$ = 6]; ^{31}P-{^{1}H}, δ 42.18, 41.38 (Pd–PPh$_3$), 14.83 and 14.62 (P$^+$Ph$_3$); ^{13}C-{^{1}H}, δ 185.2 (CO, both isomers), 153.8, 141.1, 139.4, 138.7, 134.8 (J_{PC} = 11), 133.5, 131.0, 130.4, 129.9, 129.3 (J_{PC} = 12), 128.4 (J_{PC} = 10), 126.6, 125.0, 124.6, 123.2 (J_{PC} = 40) (C$_6$H$_4$ + Ph), 74.1 [C$_6$H$_4$*C*H(Me)NMe$_2$, both isomers], 61.3 (d, CH ylide, both isomers, $^1J_{PC}$ = 108 Hz), 50.6, 49.9, 45.5, 44.9 (NMe$_2$, both isomers), 23.1, 21.2 [C$_6$H$_4$CH(*Me*)NMe$_2$, both isomers].

[Pd{*R*-C$_6$H$_4$CH(Me)NMe$_2$-2}(PPh$_3$){OC(OMe)=C(H)-PPh$_3$}]ClO$_4$ 6. Complex **6** was synthesized similarly to **1**, except that the reaction was performed at 25 °C: [PdCl{*R*-C$_6$H$_4$-CH(Me)NMe$_2$-2}(PPh$_3$)] (0.210 g, 0.380 mmol) was treated with AgClO$_4$ (0.078 g, 0.38 mmol) and Ph$_3$P=C(H)CO$_2$Me (0.127 g, 0.380 mmol) in thf to give **6** as a white solid after solvent evaporation and Et$_2$O (25 cm^3) addition (0.321 g, 89%) (Found: C, 61.9; H, 4.55; N, 1.3. C$_{49}$H$_{48}$ClNO$_6$P$_2$Pd requires C, 61.9; H, 5.1; N, 1.45%). Positive-ion FAB mass spectrum: *m/z* 850 (M^+, 10%), IR (ν_{CO}): 1538 cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 7.65–7.23 (m, Ph), 6.95 (br, 1 H, C$_6$H$_4$), 6.86 (br, 1 H, C$_6$H$_4$), 6.34 (br, 1 H, C$_6$H$_4$), 6.26 (br, 1 H, C$_6$H$_4$), 3.88 [m, 1 H, C$_6$H$_4$C*H*-(Me)NMe$_2$], 3.55 (d, 1 H, CH ylide, $^2J_{PH}$ = 28), 2,89, 2.85, 2.63 (3s, 9 H, NMe$_2$ + OMe), and 1.77 [d, 3 H, C$_6$H$_4$CH(*Me*)NMe$_2$, $^3J_{HH}$ = 6]; ^{31}P-{^{1}H}, δ 41.87. (Pd–PPh$_3$) and 16.23 (P$^+$Ph$_3$); ^{13}C-{^{1}H}, δ 173.05 (d, CO, $^2J_{PC}$ = 4), 154.42, 138.20, 131.91, 131.76, 124.58, 122.97 (C$_6$H$_4$), 134.73 (J_{PC} = 12), 132.88, 132.42 (J_{PC} = 8), 131.04, 129.18 (J_{PC} = 11), 128.29 (J_{PC} = 11), 125.45 (J_{PC} = 87) (PPh$_3$), 73.83 [C$_6$H$_4$*C*H(Me)NMe$_2$], 51.01, 50.62, 45.30 (NMe$_2$ + OMe), 38.11 (d, CH ylide, $^1J_{PC}$ = 116 Hz) and 21.98 [C$_6$H$_4$CH(*Me*)NMe$_2$].

[Pd{*R*-C$_6$H$_4$CH(Me)NMe$_2$-2}(py){OC(Me)=C(H)PPh$_3$}]-ClO$_4$ 8. Complex **8** was synthesized similarly to **1**: [PdCl{*R*-C$_6$H$_4$CH(Me)NMe$_2$-2}(py)] (0.200 g, 0.541 mmol) was treated with AgClO$_4$ (0.112 g, 0.541 mmol) and Ph$_3$P=C(H)COMe (0.172 g, 0.541 mmol) in thf at 0 °C to give **8** as a white solid after solvent evaporation and Et$_2$O (25 cm^3) addition (0.305 g, 75% yield) (Found: C, 57.1; H, 4.95; N, 3.5. C$_{36}$H$_{38}$ClN$_2$O$_5$PPd requires C, 57.55; H, 5.1; N, 3.7%). Positive-ion FAB mass spectrum: *m/z* 651 (M^+, 10%) and 572 ([M − py]$^+$; 30%). IR (ν_{CO}): 1514 cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 8.20 (s, br, 2 H, py), 8.00 (t, 1 H, py, $^3J_{HH}$ = 7), 7.66–7.48 (m, 15 H, Ph), 7.39 (dd, 2 H, py, $^3J_{HH}$ = 6.5), 6.90 (false t, 1 H, C$_6$H$_4$, $^3J_{HH}$ = 7), 6.78 (d, 1 H, C$_6$H$_4$ $^3J_{HH}$ = 7), 6.67 (false t, 1 H, C$_6$H$_4$), 5.83 (d, 1 H, C$_6$H$_4$), 4.02 (d, 1 H, CH ylide, $^2J_{PH}$ = 24), 3.81 [q, 1 H, C$_6$H$_4$C*H*-(Me)NMe$_2$, $^3J_{HH}$ = 6], 2.38 (s, 3 H, NMe$_2$), 2.06 (s, 3 H, COMe), 1.99 (s, 3 H, NMe$_2$) and 1.49 [d, 3 H, C$_6$H$_4$CH(*Me*)NMe$_2$]; ^{31}P-{^{1}H}, δ 13.56 (P$^+$Ph$_3$); ^{13}C-{^{1}H}, δ 190.09 (CO), 152.82, 139.29, 125.97 (py), 152.50, 144.95, 132.72, 125.58, 124.79, 122.24 (C$_6$H$_4$), 133.04 (d, J_{PC} = 10), 129.27 (d, J_{PC} = 12), 124.94 (d, $^1J_{PC}$ = 96) (PPh$_3$), 74.76 [C$_6$H$_4$*C*H(Me)NMe$_2$], 59.27 (d, CH ylide, $^1J_{PC}$ = 99), 50.98, 45.35 (NMe$_2$), 28.96 (d, CO*Me*, $^3J_{PC}$ = 14 Hz) and 18.69 [C$_6$H$_4$CH(*Me*)NMe$_2$].

[Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(py){C(H)(CO$_2$Me)PPh$_3$}]ClO$_4$ 9. Complex **9** was synthesized similarly to **1**: [PdCl(C$_6$H$_4$CH$_2$NMe$_2$-2)(py)] (0.200 g, 0.563 mmol) reacted with AgClO$_4$ (0.117 g, 0.563 mmol) and Ph$_3$P=C(H)CO$_2$Me (0.188 g, 0.563 mmol) in thf at 0 °C to give **9** as a white solid (0.288 g, 68% yield). Complex **9**·0.5CH$_2$Cl$_2$ recrystallized from CH$_2$Cl$_2$–hexane was used for elemental analysis and NMR measurements (Found: C, 53.6; H, 4.3; N, 3.9. C$_{35}$H$_{36}$ClN$_2$O$_6$PPd·0.5CH$_2$Cl$_2$ requires C, 53.55; H, 4.7; N, 3.5%). Positive-ion FAB mass spectrum: *m*/*z* 574 ([*M* − py]$^+$, 21%). IR (ν_{CO}): 1692 cm^{-1}. NMR (CD$_2$Cl$_2$): ^{1}H, δ 8.85 (d, br, 2 H, py), 8.00–7.50 (m, Ph), 6.98 (d, br, 2 H, py), 6.88 (t, 1 H, py, $^3J_{HH}$ = 7), 6.77 (m, br, 1 H, C$_6$H$_4$), 6.64 (d, 2 H, C$_6$H$_4$, $^3J_{HH}$ = 7), 5.98 (d, 1 H, C$_6$H$_4$, $^3J_{HH}$ = 8), 4.07 (d, 1 H, CH ylide, $^2J_{PH}$ = 13), 3.88, 3.19 (AX system, 2 H, CH$_2$N, $^2J_{HH}$ = 11), 3.51 (s, 3 H, OMe), 2.65 (s, 3 H, NMe$_2$) and 2.36 (s, 3 H, NMe$_2$); ^{31}P-{^{1}H}, δ 27.61 (P$^+$Ph$_3$); ^{13}C-{^{1}H}, δ 174.7 (CO), 150.6, 139.4, 125.8 (py), 153.0, 148.0, 133.2, 129.4, 124.7, 123.5 (C$_6$H$_4$), 134.6 (J_{PC} = 10), 134.3, 129.7 (J_{PC} = 13), 122.8 (J_{PC} = 48) (PPh$_3$), 73.0 (CH$_2$N), 52.2, 51.0, 50.2 (NMe$_2$ + OMe) and 21.7 (d, CH ylide, $^1J_{PC}$ = 45 Hz).

Reactions of [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(NCMe)$_2$]ClO$_4$. *With* Ph$_3$P=C(H)COMe. To a solution of [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(NCMe)$_2$]ClO$_4$ (0.210 g, 0.497 mmol) in CH$_2$Cl$_2$ (25 cm^3), was added Ph$_3$P=C(H)COMe (0.158 g, 0.497 mmol). The pale yellow solution was stirred at room temperature for 1 h, then the solvent was evaporated to dryness and the oil residue treated with Et$_2$O (25 cm^3), giving 0.287 g (83% yield) of a pale yellow solid, which was identified by spectroscopic methods as a mixture of complexes **10c** and **10o** in 1:2.15 molar ratio. This mixture was recrystallized from CH$_2$Cl$_2$–hexane, giving pale yellow crystals of **10**·0.75CH$_2$Cl$_2$, which were used for elemental analysis and NMR measurements (Found: C, 51.2; H, 4.65; N, 3.4. C$_{32}$H$_{34}$ClN$_2$O$_5$PPd·0.75CH$_2$Cl$_2$ requires C, 51.55; H, 4.7; N, 3.65%). Positive-ion FAB mass spectrum: *m*/*z* 558 ([*M* − NCMe]$^+$, 12%). IR: 2327, 2281 (NCMe), 1582 (ν_{CO}, **10c**), 1509 cm^{-1} (ν_{CO}, **10o**). NMR (CD$_2$Cl$_2$): ^{1}H (188 K), δ 7.80–7.50 (m, Ph), 7.05 (m, C$_6$H$_4$), 6.88 (m, C$_6$H$_4$), 4.51 (d, CH ylide, **10o**, $^2J_{PH}$ = 22), 4.29 (d, CH$_2$N, **10o** both isomers, $^2J_{HH}$ = 14), 4.15 (s, br, CH ylide, **10c**), 3.98 (d, CH ylide, **10o**, $^2J_{PH}$ = 23), 3.74 (s, br, CH$_2$N, **10c**), 3.56 (d, CH$_2$N, **10o**), 3.37 (d, CH$_2$N, **10o**), 2.79 (s, NMe$_2$, **10o**), 2.69 (s, NMe$_2$, **10o**), 2.58 (s, 2NMe$_2$, **10o** + **10c**), 2.49 (s, NMe$_2$,**10o**), 2.44 (s, NMe$_2$, **10c**), 2.33 (s, COMe), 2.02 (s, COMe), 1.85 (s, NCMe) and 1.75 (s, NCMe); ^{31}P-{^{1}H}. (188 K), δ 25.62 (**10c**), 14.19 (**10o**) and 14.07 (**10o**); ^{13}C-{^{1}H} (218 K), δ 204.28 (CO, **10c**), 191.01 (CO, **10o**, both isomers), 148.17, 147.10, 146.92, 141.27, 134.94, 131.68, 130.26, 125.76, 125.29, 124.34, 124.07, 122.21 (C$_6$H$_4$, non-quaternary C), 134.06 (d, J_{PC} = 10), 133.48, 133.28, 133.06 (d, J_{PC} = 10), 129.28 (d, J_{PC} = 11), 129.12 (d, J_{PC} = 12) (PPh$_3$), 121.01 (N*C*Me), 120.21 (N*C*Me), 119.06 (N*C*Me) 72.99, 72.82, 72.28 (CH$_2$N), 62.12 (d, CH ylide, **10o**, $^1J_{PC}$ = 108, both isomers), 52.60, 52.49, 52.28, 52.01, 51.74, 50.52 (NMe$_2$), 32.64, 31.63, 31.49 (CO*Me*), 28.53 (d, CH ylide, **10c**, $^1J_{PC}$ = 28 Hz), 3.28 (NC*Me*) and 2.78 (2NC*Me*).

With Ph$_3$P=C(H)COPh. To a solution of [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(NCMe)$_2$]ClO$_4$ (0.210 g, 0.497 mmol) was added Ph$_3$P=C(H)COPh (0.189 g, 0.497 mmol) in CH$_2$Cl$_2$ (25 cm^3). The pale yellow solution was stirred at room temperature for 1 h, then the solvent was evaporated to dryness and the oil residue treated with Et$_2$O (25 cm^3), giving 0.364 g (96% yield) of a pale yellow solid which was identified by spectroscopic methods as a mixture of complexes **11c** and **11o** in 1:2.3 molar ratio. This mixture was recrystallized from CH$_2$Cl$_2$–hexane, giving pale yellow crystals of **11**·0.25CH$_2$Cl$_2$, which were used for elemental analysis and NMR measurements (Found: C, 57.3; H, 4.85; N, 3.2. C$_{37}$H$_{36}$ClN$_2$O$_5$PPd·0.25CH$_2$Cl$_2$ requires C, 57.15; H, 4.7; N, 3.55%). Positive-ion FAB mass spectrum: *m*/*z* 620 ([*M* − NCMe]$^+$, 10%). IR: 2326, 2281 (NCMe), 1581 (ν_{CO}, **11c**), 1498 cm^{-1} (ν_{CO}, **11o**). NMR (CD$_2$Cl$_2$): ^{1}H (188 K), δ 8.32–7.34 (m, Ph), 6.96 (d, C$_6$H$_4$, $^3J_{HH}$ = 7), 6.86 (m, C$_6$H$_4$), 6.71 (m, C$_6$H$_4$), 4.83 (d, CH ylide, **11o**, $^2J_{PH}$ = 22), 4.60 (s, br, CH ylide, **11c**), 4.24 (d, CH$_2$N, **11c**, $^2J_{HH}$ = 12), 3.74 (s, br, CH$_2$N, **11o**), 3.47 (d, CH$_2$N, **11c**), 2.59 (s, NMe$_2$,**11c**), 2.46 (s, NMe$_2$, **11c**), 2.04 (s, NMe$_2$, **11o**), 1.94 (s, NCMe, **11o**) and 1.82 (s, NCMe, **11c**); ^{31}P-{^{1}H} (188 K), δ 28.29 (**11c**) and 16.12 (**11o**); ^{13}C-{^{1}H} (218 K), δ 199.34 (CO, **11c**), 191.82 (CO, **11o**), 150.57, 148.08, 146.66, 138.61, 132.10, 131.33, 130.72, 130.24, 126.95, 125.61, 124.70, 121.49 (C$_6$H$_4$), 134.19 (d, J_{PC} = 9), 133.50, 133.26, 132.91 (d, J_{PC} = 11), 129.39 (d, J_{PC} = 14), 129.12 (d, J_{PC} = 12) (Ph + PPh$_3$), 120.47 (N*C*Me), 119.08 (N*C*Me), 72.99, 72.27 (CH$_2$N), 58.80 (d, CH ylide, **11o**, $^1J_{PC}$ = 110 Hz), 51.47, 50.58, 47.90, 43.00 (NMe$_2$), 32.58 (s, br, CH ylide, **11c**), 3.53 (NC*Me*) and 2.90 (NC*Me*).

[Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(NCMe){C(H)(CO$_2$Me)PPh$_3$}]ClO$_4$ 12. Complex **12** was synthesized similarly to **10**: [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(NCMe)$_2$]ClO$_4$ (0.210 g, 0.497 mmol) was treated with Ph$_3$P=C(H)CO$_2$Me (0.166 g, 0.497 mmol) in CH$_2$Cl$_2$ at room temperature to give **12** as a white solid after solvent evaporation and Et$_2$O (25 cm^3) addition (0.310 g, 87% yield) (Found: C, 53.4; H, 4.45; N, 3.6. C$_{32}$H$_{34}$ClN$_2$O$_6$PPd requires C, 53.7; H, 4.8; N, 3.9%). Positive-ion FAB mass spectrum: *m*/*z* 574 ([*M* − NCMe]$^+$, 15%). IR: 2313, 2282 (NCMe), 1692 cm^{-1} (ν_{CO}), NMR (CDCl$_3$) ^{1}H, δ 7.79–7.73 (m, 6 H, Ph), 7.61–7.56 (m, 3 H, Ph), 7.46–7.40 (m, 6 H, Ph), 7.07 (d, 1 H, C$_6$H$_4$, $^3J_{HH}$ = 7), 6.91 (m, 2 H, C$_6$H$_4$), 6.84 (m, 1 H, C$_6$H$_4$), 4.20, 3.40 (AX system, 2 H, CH$_2$N, $^2J_{HH}$ = 13.5), 3.63 (s, 3 H, OMe), 3.58 (d, 1 H, CH ylide, $^2J_{PH}$ = 4.15), 2.64 (s, 3 H, NMe$_2$), 2.44 (s, 3 H, NMe$_2$) and 1.92 (s, 3 H, NCMe); ^{31}P-{^{1}H}, δ 25.96 (P$^+$Ph$_3$); ^{13}C-{^{1}H}, δ 174.10 (CO), 147.89, 147.57, 133.50, 123.37, 122.80, 122.21 (C$_6$H$_4$), 133.82 (d, J_{PC} = 10), 133.60 (d, J_{PC} = 2), 129.07 (d, J_{PC} = 13), 125.18 (d, $^1J_{PC}$ = 87) (PPh$_3$), 118.05 (N*C*Me), 72.36 (CH$_2$N), 52.19, 51.83, 49.77 (NMe$_2$ + OMe), 20.79 (d, CH ylide, $^1J_{PC}$ = 51 Hz) and 2.23 (NC*Me*).

[Pd{*R*-C$_6$H$_4$CH(Me)NMe$_2$-2}(NCMe){C(H)(CO$_2$Me)PPh$_3$}]ClO$_4$ 13. Complex **13** was synthesized similarly to **10**: [Pd{*R*-C$_6$H$_4$CH(Me)NMe$_2$-2}(NCMe)$_2$]ClO$_4$ (0.162 g, 0.370 mmol) was treated with Ph$_3$P=C(H)CO$_2$Me (0.124 g, 0.370 mmol) in CH$_2$Cl$_2$ at room temperature to give **13** as a white solid after solvent evaporation and Et$_2$O (25 cm^3) addition (0.310 g, 87% yield). Diastereomeric ratio (major : minor) = 1.75 : 1 (Found: C, 53.8; H, 4.75; N, 3.55. C$_{33}$H$_{36}$ClN$_2$O$_6$PPd requires C, 54.35; H, 4.95; N, 3.85%). Positive-ion FAB mass spectrum: *m*/*z* 588 ([*M* − NCMe]$^+$, 18%). IR: 2314, 2285 (NCMe), 1684 cm^{-1} (ν_{CO}). NMR (CDCl$_3$): ^{1}H, δ 7.94–7.41 (m, Ph), 7.27 (d, C$_6$H$_4$, $^3J_{HH}$ = 7), 6.94 (m, C$_6$H$_4$), 6.79 (m, C$_6$H$_4$) (both diastereoisomers), 4.03 [q, C$_6$H$_4$C*H*(Me)NMe$_2$, minor, $^3J_{HH}$ = 7], 3.69 (s, OMe, major), 3.67 (s, OMe, minor), 3.61 (d, CH ylide, minor, $^2J_{PH}$ = 4), 3.60 (s, br, CH ylide, major), 3.33 [q, C$_6$H$_4$C*H*(Me)NMe$_2$, major, $^3J_{HH}$ = 6], 2.71 (s, NMe$_2$, minor), 2.54 (s, NMe$_2$, major), 2.46 (s, NMe$_2$, major), 2.34 (s, NMe$_2$, minor), 1.91 (s, 2 NCMe, both isomers), 1.42 [d, C$_6$H$_4$CH(*Me*)NMe$_2$, major] and 1.39 [d, C$_6$H$_4$CH(*Me*)NMe$_2$, minor]; ^{31}P-{^{1}H}, δ 25.77 (P$^+$Ph$_3$, minor) and 24.97 (P$^+$Ph$_3$, major); ^{13}C-{^{1}H}, δ 174.88 (CO, minor), 174.80 (CO, major), 154.37, 135.45, 125.85, 124.82, 123.60, 122.57 (C$_6$H$_4$, major), 152.13, 135.45, 126.02, 124.50, 123.13, 122.45 (C$_6$H$_4$, minor), 133.90 (d, J_{PC} = 13, PPh$_3$ both isomers), 133.69 (s, PPh$_3$, major), 133.62 (s, PPh$_3$, minor), 130.46 (d, PPh$_3$, minor, J_{PC} = 13), 129.33 (d, PPh$_3$, major, J_{PC} = 13), 122.79 (d, PPh$_3$, both, $^1J_{PC}$ = 87), 119.58 (N*C*Me, major), 117.99 (N*C*Me, minor), 75.17 [C_6H_4*C*H(Me)NMe$_2$, minor], 72.93 [C_6H_4*C*H(Me)NMe$_2$, major], 52.34, 51.60, 47.34 (NMe$_2$ + OMe, major), 53.62, 49.51, 43.84 (NMe$_2$ + OMe, minor), 22.88 [C_6H_4CH(*Me*)NMe$_2$, major], 20.75 (d, CH ylide, minor, $^1J_{PC} = 52$), 20.50 (d, CH ylide, major, $^1J_{PC} = 51$ Hz), 14.42 [C_6H_4CH(*Me*)NMe$_2$, minor] and 2.84 (NC*Me*, both isomers).

Crystallography

X-Ray data collection. A colourless, block-shaped crystal of compound **9** of dimensions 0.50 × 0.44 × 0.12 mm was mounted at the end of a glass fibre and covered with epoxy. Geometric and intensity data were taken at 23 °C using normal procedures on an automated four-circle Enraf-Nonius CAD4 diffractometer with Mo-Kα radiation (λ 0.710 73 Å). After initial indexing of the cell axial photos were taken for the axes *a*, *b* and *c* in order to check the lattice dimensions. The scan parameters for intensity-data collection were chosen on the basis of two-dimensional (ω–θ) plots of 25 reflections. Data were collected using a variable scan-speed technique in which the weakest data were measured at the slowest scan speed. That is to say, no measurement was skipped or measured rapidly because of weak diffraction. Azimuthal scans of nine scattering vectors were used as the basis of an absorption correction. No intensity decay was observed in three monitor reflections remeasured every 3 h during data collection. Small shifts in the crystal orientation were checked by measuring three standard reflections every 500 during data collection. The cell parameters were refined to the accurately determined positions of 25 reflections ($24.1 \leqslant 2\theta \leqslant 31.8°$) each measured at four equivalent positions.

Structure solution and refinement. After data reduction, all non-hydrogen atoms of one asymmetric unit were located by an automated procedure which incorporates Patterson analysis, difference direct methods, and Fourier peak list optimization.[25] The structure was refined to F_o^2, and all positive data were used in the refinement.[26] The hydrogen atoms of the cation were placed in idealized positions and treated as riding atoms, except for those of the methyl groups, which were first located in a local slant-Fourier calculation and then refined as riding atoms with the torsion angles about the O–C (methyl) or N–C (methyl) bonds treated as variables. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent parameter of its parent atom. The perchlorate anion was disordered and modelled as two equally populated congeners occupying the same interstice. The chlorine atom and one oxygen were common to the two components. No constraints or restraints were needed for the perchlorate anion. The refinement converged with the residuals shown in Table 5. Crystallographic calculations were done on a Local Area VAXCluster (VAX/VMS V5.5-2). Data reduction was done by the program XCAD4B.[27] Absorption corrections and molecular graphics were performed using the commercial package SHELXTL PLUS.[28]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/345.

Table 5 Crystal data for compound **9**

Formula	$C_{35}H_{36}ClN_2O_6PPd$
M	753.48
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	9.3687(5)
b/Å	20.2032(13)
c/Å	17.851(2)
β/°	91.920(6)
Z	4
F(000)	1544
U/Å^3	3376.8(4)
D_c/g cm^{-3}	1.482
μ/mm^{-1}	0.723
No. unique reflections	5918
No. reflections with $I > 2\sigma(I)$	5179
No. variables	445
$R1$*	0.0359
$wR2$*	0.0776
Goodness of fit*	1.020
Maximum shift/σ	0.000
Residual electron density/e Å^{-3}	0.444

* $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, goodness of fit $= [\Sigma w(F_o^2 - F_c^2)^2/(n_o - n_p)]^{\frac{1}{2}}$, n_o = number of observations, n_p = number of parameters. Weighting scheme $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ where $P = [\max.(F_o^2; 0) + 2F_c^2]/3$.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (Spain) for financial support (Projects PB92-0360 and PB92-0364) and Professor J. Forniés for invaluable logistical support.

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Received 4*th October* 1996; *Paper* 6/06823E