Synthesis of Mono- and Di-nuclear Palladium(II) Complexes containing Ylide Ligands $[PPh_2(CHCO_2R)_2]^-$ (R = Me or Et). Crystal Structures of $[Pd\{(CHCO_2Et)_2PPh_2\}_2]$, $[Pd\{(CHCO_2Et)_2PPh_2\}Cl(PPh_3)]$, and $[Pd\{(CHCO_2Et)_2PPh_2\}(NC_5H_5)_2]ClO_4$†

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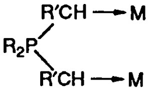
Complexes $[Ag_2\{\mu-(CHCO_2R)_2PPh_2\}_2]$ (R = Me or Et) react (1 : 1) with *trans*-$[PdCl_2(NCPh)_2]$ to give spirane complexes $[Pd\{(CHCO_2R)_2PPh_2\}_2]$ [R = Me, (**1a**); or Et, (**1b**)] which, in turn, react with $PdCl_2$ (1 : 1) to give $[Pd_2\{(CHCO_2R)_2PPh_2\}_2(\mu-Cl)_2]$ [R = Me, (**2a**); or Et, (**2b**)]. Complex (**1a**) can also be obtained by treating (**2a**) with $[Ag_2\{\mu-(CHCO_2Me)_2PPh_2\}_2]$ (1 : 1). Complexes (**2a**) and (**2b**) react with neutral ligands to yield $[Pd\{(CHCO_2R)_2PPh_2\}ClL]$ [R = Me, L = pyridine (py), (**3a**), or PPh_3, (**4a**); R = Et, L = py, (**3b**), or PPh_3, (**4b**)] or with neutral ligands in the presence of $NaClO_4$ to give $[Pd\{(CHCO_2R)_2PPh_2\}L_2]ClO_4$ [R = Me, L_2 = 2,2′-bipyridyl, (**5a**), or 1,2-bis(diphenylphosphino)ethane, (**6a**); R = Et, L = py, (**7b**)]. When (**2a**) is treated with Tl(acac) (Hacac = acetylactone) or Tl(cp) (cp = cyclopentadienyl) (1 : 2), $[Pd\{(CHCO_2Me)_2PPh_2\}(acac)]$ (**8a**) or $[Pd\{(CHCO_2Me)_2PPh_2\}(\eta-cp)]$ (**9a**) are obtained, respectively. The *X*-ray structures of complexes (**1b**) (which displays crystallographic inversion symmetry), (**4b**), and (**7b**) have been determined, showing a chelating co-ordination of all ylide ligands, the methine carbon donor atoms of which adopt *RR* or *SS* configurations. The chelate rings are non-planar. The Pd–C bond lengths reflect the various *trans* influences.

We have recently developed new syntheses of silver(I)[1] and gold-(I), -(II), and -(III)[2] complexes containing ylides $Ph_2P(CHCO_2R)_2^-$ (R = Me or Et). This type of anionic ylide $R_2P(CHR')_2^-$ can adopt two different co-ordination modes, as bridging (**A**) or chelating (**B**) ligands;[3] they are good illustrations of the variety of ylide–metal interactions. Thus there are complexes containing two or more of these ylides all bridging, or all chelating, or including both kinds of co-ordination in the same molecule.[4,5] Whereas complexes of the copper group fall in the first class, the nickel group shows examples of all three types. However, only a few complexes have been structurally characterized. The structures are of interest, in particular for complexes containing chelating ligands, because the bonding could be described simply as a normal bidentate chelating σ bonding as in (**B**) or as a pseudo-phospha-allyl type (**C**). This difference has been established by comparing the structures $[Ni_2\{(CH_2)_2PPh_2\}_2\{\mu-[(CH_2)_2PPh_2]_2\}]$ and $[CoMe_2\{(CH_2)_2PPh_2\}(PMe_3)_2]$.[5] In addition, the presence of two chiral carbon centres on each ylide ligand makes these complexes interesting from a structural and synthetic standpoint.

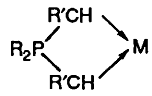
In this paper we report the syntheses and structural characterization of several palladium(II) complexes containing carbonyl-stabilized ylides $Ph_2P(CHCO_2R)_2^-$.

Results and Discussion

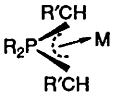
Complexes $[Ag_2\{\mu-(CHCO_2R)_2PPh_2\}_2]$ (R = Me or Et) react (1:1) with *trans*-$[PdCl_2(NCPh)_2]$ to give AgCl and spirane complexes $[Pd\{(CHCO_2R)_2PPh_2\}_2]$ [R = Me, (**1a**); or Et, (**1b**)] (see Scheme). Such reactions are new examples of the recently reported[2,6] 'ylide transfer reactions', which involve the transfer of an ylide from one metal centre to another; the present case is the first involving a transfer from Ag^I to Pd^{II}. A Pd^{II} to Pd^{II} transfer can also be effected in the reaction of (**1a**) or (**1b**) with $PdCl_2$ (1:1), leading to dinuclear complexes $[Pd_2\{(CHCO_2R)_2PPh_2\}_2(\mu-Cl)_2]$ [R = Me, (**2a**); or Et, (**2b**)]. The syntheses of complex (**1a**) or (**2a**), by treating $[Ag_2(\mu-(CHCO_2Me)_2PPh_2\}_2]$ with (**2a**) (1:1) or with $[PdCl_2(NCMe)_2]$ (1:2), respectively, are new examples of 'ylide transfer reactions' from Ag^I to Pd^{II}. The complex (**2a**) is obtained by this route in a better yield.



(**A**)



(**B**)



(**C**)

Complexes (**2a**) and (**2b**) react with neutral ligands to yield $[Pd\{(CHCO_2R)_2PPh_2\}ClL]$ [R = Me, L = pyridine (py), (**3a**)

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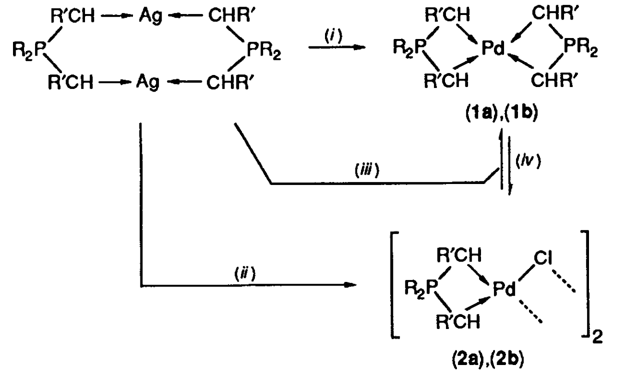
† Bis(1,3-diethoxycarbonyl-2,2-diphenyl-2-phosphoniapropanedi-ido-κ^2C^1,C^3)palladium, chloro-1,3-diethoxycarbonyl-2,2-diphenyl-2-phosphoniapropanedi-ido-κ^2C^1,C^3)(triphenylphosphine)palladium, and (1,3-diethoxycarbonyl-2,2-diphenyl-2-phosphoniapropanedi-ido-κ^2C^1,C^3)bis(pyridine)palladium perchlorate.

Supplementary data available: further details of the structure determinations (H-atom co-ordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 54761.

Table 1. Analytical and other data for complexes (**1**)—(**9**)

Complex	Λ_M/Ω^{-1} cm^2 mol^{-1}	Analysis (%)[a] C	H	N	M.p. (°C)	Yield (%)
(**1a**) $[Pd\{(CHCO_2Me)_2PPh_2\}_2]$	0[b]	57.0 (56.5)	5.2 (4.7)		252	89
(**1b**) $[Pd\{(CHCO_2Et)_2PPh_2\}_2]$	0[c]	57.6 (58.1)	5.4 (5.4)		240[d]	85
(**2a**) $[Pd_2\{(CHCO_2Me)_2PPh_2\}_2(\mu-Cl)_2]$	7[c]	45.6 (45.9)	4.1 (3.8)		175	83
(**2b**) $[Pd_2\{(CHCO_2Et)_2PPh_2\}_2(\mu-Cl)_2]$	3[c]	47.9 (48.1)	4.6 (4.4)		210	78
(**3a**) $[Pd\{(CHCO_2Me)_2PPh_2\}Cl(py)]$	2[c]	49.6 (50.2)	4.5 (4.2)	2.8 (2.5)	163	87
(**3b**) $[Pd\{(CHCO_2Et)_2PPh_2\}Cl(py)]$	2[c]	52.3 (51.9)	4.9 (4.7)	2.4 (2.4)	167	68
(**4a**) $[Pd\{(CHCO_2Me)_2PPh_2\}Cl(PPh_3)]$	4[c]	58.5 (58.9)	4.4 (4.5)		123	94
(**4b**) $[Pd\{(CHCO_2Et)_2PPh_2\}Cl(PPh_3)]$	2[c]	60.6 (59.9)	5.5 (4.9)		192	82
(**5a**) $[Pd\{(CHCO_2Me)_2PPh_2\}(bipy)]ClO_4$	134[c]	47.8 (48.6)	3.7 (3.9)	3.9 (4.0)	130	77
(**6a**) $[Pd\{(CHCO_2Me)_2PPh_2\}(dppe)]ClO_4$	112[c]	56.3 (56.6)	5.0 (4.5)		136	86
(**7b**) $[Pd\{(CHCO_2Et)_2PPh_2\}(py)_2]ClO_4$	107	49.6 (49.9)	4.8 (4.5)	3.9 (3.9)	186	83
(**8a**) $[Pd\{(CHCO_2Me)_2PPh_2\}(acac)]$	1	51.2 (51.6)	5.3 (4.7)		173	81
(**9a**) $[Pd\{(CHCO_2Me)_2PPh_2\}(\eta-cp)]$	1	55.3 (55.2)	4.6 (4.6)		139[d]	43

[a] Calculated values in parentheses. [b] 3 × 10^{-4} mol dm^{-3} CH_2Cl_2 solutions. [c] 5 × 10^{-4} mol dm^{-3} acetone solutions. [d] With decomposition.



Scheme. (*i*) $+[PdCl_2(NCPh)_2]$, $-2AgCl$; (*ii*) $+2[PdCl_2(NCMe)_2]$, $-2AgCl$; (*iii*) $-2AgCl$; (*iv*) $+PdCl_2$

or PPh_3, (**4a**); R = Et, L = py, (**3b**), or PPh_3, (**4b**)] or with neutral ligands in the presence of $NaClO_4$ to give $[Pd\{(CHCO_2R)_2PPh_2\}L_2]ClO_4$ [R = Me, L_2 = 2,2′-bipyridyl (bipy), (**5a**), or 1,2-bis(diphenylphosphino)ethane (dppe), (**6a**); R = Et, L_2 = py, (**7b**)]. When (**2a**) is treated with Tl(acac) (Hacac = acetylacetone) or Tl(cp) (cp = cyclopentadienyl) (1:2), $[Pd\{(CHCO_2Me)_2PPh_2\}(acac)]$ (**8a**) or $[Pd\{(CHCO_2Me)_2PPh_2\}(\eta-cp)]$ (**9a**) are obtained, respectively. Table 1 gives elemental analyses, m.p., and molar conductivities of complexes (**1**)—(**9**) and yields of the corresponding processes. Table 2 presents spectroscopic data.

X-Ray structure analyses of complexes (**1b**), (**4b**), and (**7b**) (see Figures 1, 2, and 3) reveal a chelating co-ordination of all ylide ligands, the carbon donor atoms of which adopt *RR* or *SS* configuration. Both configurations appear in the centrosymmetric complex (**1b**), corresponding to a *meso* form that can be represented by the notation *RR*(Pd)*SS*. Its ^1H and ^{31}P n.m.r. spectra, and also those of (**1a**), show the presence in solution of another isomer (see Table 2), which could be one of the two other *meso* forms [*cis*- or *trans*-*RS*(Pd)*RS*] or a mixture of the chiral *RR*(Pd)*RR* and *SS*(Pd)*SS* complexes. This situation is analogous to that observed in the silver complex used to prepare complexes (**1a**) and (**1b**); the isomer whose crystal structure was determined also possessed an *RR*(Ag,Ag)*SS* configuration, whereas in solution another isomer (or pair of enantiomers) was observed.[1] Given that in the four crystal structures we have solved each ylide retains the *RR* or *SS* configuration, we believe that the additional resonances observed in complex (**1b**) correspond to a mixture of the pair of enantiomers *RR*(Pd)*RR* and *SS*(Pd)*SS*. The molar ratio between the two observed isomers is 2.45:1 in (**1a**) and 1:1 in (**1b**), from n.m.r. data. Following this assignment, complexes

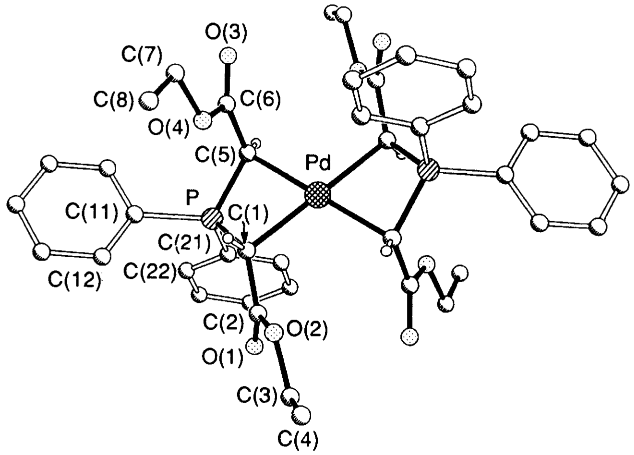


Figure 1. The structure of complex (**1b**) in the crystal, showing the atom numbering scheme of the asymmetric unit. Radii are arbitrary; H atoms (except methine H) omitted for clarity

Table 2. Spectroscopic data for complexes (**1**)—(**9**)

	I.r. data (cm^{-1})		N.m.r. data * (δ/p.p.m. J/Hz)	
Complex	$\nu_{asym.}(CO_2)$	ν(PdCl)	^1H	^{31}P-{^1H}
(**1a**)	1 675vs 1 640vs		X: 3.49 (s, Me), 2.68 (d, CH, $^2J_{PH}$ = 6) Y: 3.50 (s, Me), 2.41 (d, CH, $^2J_{PH}$ = 5) X,Y: 7—8 (m, Ph); X:Y = 2.45	20.4s 19.7s
(**1b**)	1 690vs 1 670vs		0.93 (t, 12 H, Me, $^2J_{HH}$ = 7), 0.96 (t, 12 H, Me, $^2J_{HH}$ = 7), 2.32 (d, 4 H, CH, $^2J_{PH}$ = 6), 2.61 (d, 4 H, CH, $^2J_{PH}$ = 6), 3.6—4 (m, 16 H, CH_2), 7—8 (40 H, Ph)	19.7s 19.4s
(**2a**)	1 700vs 1 685vs	275m	X: 3.51 (s, Me), 2.47 (d, CH, $^2J_{PH}$ = 5) Y: 3.48 (s, Me), 2.41 (d, CH, $^2J_{PH}$ = 5) X,Y: 7.5—8.1 (m, Ph); X:Y = 0.88	25.64s 25.22s
(**2b**)	1 680vs,br	275m	0.96 (t, 12 H, Me, $^2J_{HH}$ = 7), 0.99 (t, 12 H, Me, $^2J_{HH}$ = 7), 2.37 (d, 4 H, CH, $^2J_{PH}$ = 5), 2.40 (d, 4 H, CH, $^2J_{PH}$ = 5), 3.94 (q, 16 H, CH_2), 7.5—8 (m, 40 H, Ph)	25.85s 25.29s
(**3a**)	1 700vs 1 675vs	300m	3.60 (s, 3 H, Me), 3.11 (s, 3 H, Me), 2.61 (d, 2 H, CH, $^2J_{PH}$ = 6), 7—9 (m, 15 H, py + Ph)	23.6s
(**3b**)	1 670vs,br	297s	0.68 (t, 3 H, Me, $^2J_{HH}$ = 7), 1.05 (t, 3 H, Me, $^2J_{HH}$ = 7), 2.49 (d, 1 H, CH, $^2J_{PH}$ = 2), 2.58 (d, 1 H, CH, $^2J_{PH}$ = 5), 3.56 (m, 2 H, CH_2), 4.05 (m, 2 H, CH_2), 7—9 (m, 15 H, py + Ph)	23.98s
(**4a**)	1 690vs 1 670vs	310m	3.67 (s, 3 H, Me), 3.1 (d, 1 H, $^2J_{PH}$ = 4), 3.0 (s, 3 H, Me), 1.73 (dd, 1 H, CH, $^2J_{PH}$ = 5, $^3J_{PH}$ = 2), 7.4—8.1 (m, 25 H, Ph)	21.87, 23.72 (AB) $^3J_{AB}$ = 15
(**4b**)	1 685vs 1 665vs	310s	0.64 (t, 3 H, Me, $^2J_{HH}$ = 7), 1.15 (t, 3 H, Me, $^2J_{HH}$ = 7), 1.66 (dd, 1 H, CH, $^2J_{PH}$ = 7, $^3J_{PH}$ = 2), 2.93 (dd, 1 H, CH, $^2J_{PH}$ = 11, $^3J_{PH}$ = 4), 3.52 (m, 2 H, CH_2), 4.11 (m, 2 H, CH_2), 7—8 (m, 25 H, Ph)	22.39, 23.70 (AB) $^3J_{AB}$ = 15
(**5a**)	1 690vs,br		3.46 (s, 6 H, Me), 2.72 (s, 2 H, CH), 7.5—9.5 (m, 18 H, bipy + Ph)	31.55s
(**6a**)	1 690vs 1 675vs,sh		2.88 (s, 6 H, Me), 2.74 (d, 2 H, CH, $^2J_{PH}$ = 5), 2.6 (m, 4 H, dppe), 7—8 (m, 30 H, Ph)	56.08 (d, dppe), 23.97 (t, ylide) $^3J_{PP}$ = 12
(**7b**)	1 680vs		0.71 (t, 6 H, Me, $^2J_{HH}$ = 7), 2.40 (d, 2 H, CH, $^2J_{PH}$ = 3), 3.64 (m, 4 H, CH_2), 7—9 (m, 20 H, Ph)	29.71s
(**8a**)	1 690vs 1 670vs		1.91 (s, 6 H, MeCO), 2.41 (d, 2 H, CH, $^2J_{PH}$ = 5), 3.47 (s, 6 H, $MeCO_2$), 5.24 (s, 1 H, CH), 7—8 (m, 10 H, Ph)	23.51s
(**9a**)	1 685vs		2.74 (d, 2 H, CH, $^2J_{PH}$ = 6), 3.44 (s, 6 H, Me), 5.63 (s, 5 H, cp), 7—8 (m, 10 H, Ph)	19.10s

* X and Y are isomers (see text).

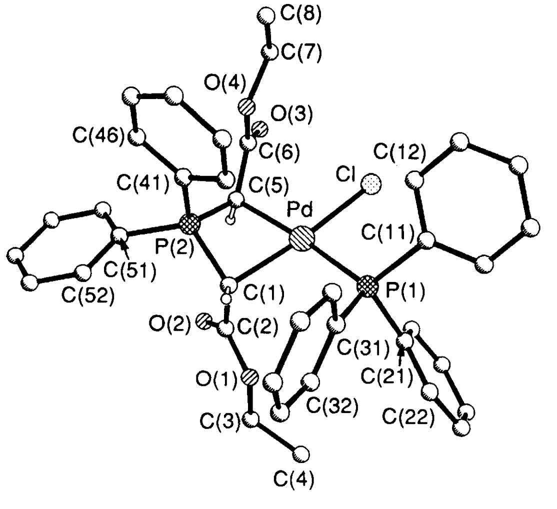


Figure 2. The structure of complex (**4b**) in the crystal, showing the atom numbering scheme. Radii are arbitrary; H atoms (except methine H) omitted for clarity

(**2a**) and (**2b**) would be mixtures of *RR*(Pd)Cl_2(Pd)*SS* and *RR*(Pd)Cl_2(Pd)*RR* + *SS*(Pd)Cl_2(Pd)*SS* with molar ratios for the isolated samples of 0.88:1 for (**2a**) and 1:1 for (**2b**), again from n.m.r. data. The addition of neutral ligands to these two complexes should give the pair of enantiomers *RR*(Pd)Cl(L)

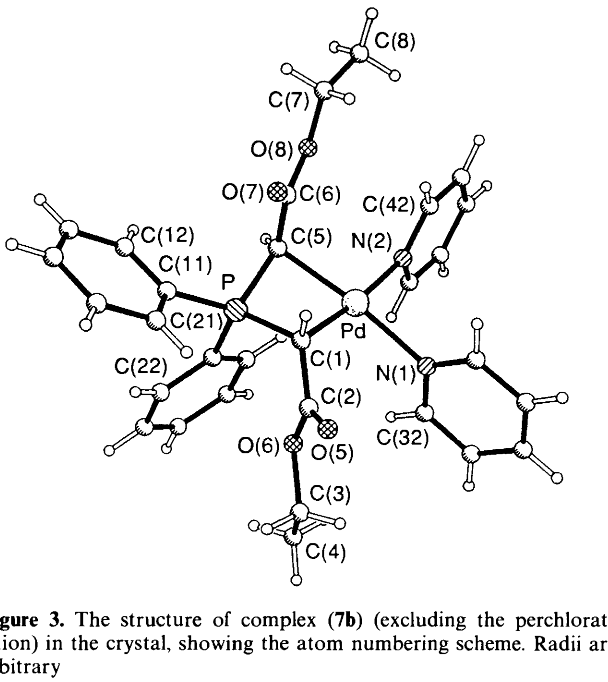


Figure 3. The structure of complex (**7b**) (excluding the perchlorate anion) in the crystal, showing the atom numbering scheme. Radii are arbitrary

Table 3. Crystal data

Compound	(**1b**)	(**4b**)	(**7b**)
Formula	$C_{40}H_{44}O_8P_2Pd$	$C_{38}H_{37}ClO_4P_2Pd$	$C_{30}H_{32}ClN_2O_8PPd$
M	821.15	761.47	721.40
Crystal habit	Pale yellow prism	Pale yellow prism	Colourless prism
Crystal size (mm)	0.75 × 0.2 × 0.2	0.65 × 0.4 × 0.15	0.5 × 0.45 × 0.2
Space group	*Pbca*	$P2_1/c$	$P2_1/n$
Temperature (°C)	20	−95	20
Diffractometer	Stoe	Siemens	Siemens
Cell contants			
a/Å	8.648(2)	19.656(7)	9.761(2)
b/Å	22.504(4)	9.806(4)	20.577(6)
c/Å	20.078(4)	18.167(7)	16.651(5)
β/°		94.35(3)	104.48(2)
U/Å^3	3 906	3 492	3 238
Z	4	4	4
D_c/Mg m^{-3}	1.40	1.45	1.48
F(000)	1 696	1 560	1 472
μ/mm^{-1}	0.6	0.7	0.7
$2\theta_{max.}$/°	50	50	50
Scan type	ω—θ	ω	ω
No. of reflections			
measured	4 360	5 826	7 782
independent	3 438	5 398	5 670
R_{int}	0.016	0.022	0.020
observed [$>4\sigma(F)$]	2 345	4 750	3 991
Absorption correction	ψ Scans	None	ψ Scans
Transmissions	0.74—0.76		0.84—0.93
R	0.038	0.029	0.039
R'	0.034	0.038	0.046
g	0.0001	0.0003	0.0003
No. of parameters	232	415	389
S	1.5	1.5	1.5
Maximum Δ/σ	0.08	0.001	0.002
Maximum Δρ/e Å^{-3}	0.3	0.3	0.9

Table 4. Atomic co-ordinates (× 10^4) for compound (**1b**)

Atom	*x*	*y*	*z*
Pd	5 000	5 000	5 000
P	4 763(1)	6 026.3(4)	4 337.0(5)
C(1)	5 974(4)	5 874(1)	5 022(2)
C(2)	5 862(5)	6 209(2)	5 641(2)
C(3)	7 128(6)	6 391(2)	6 669(2)
C(4)	8 594(7)	6 293(2)	6 981(2)
C(5)	4 519(4)	5 302(2)	4 012(2)
C(6)	5 693(5)	5 070(2)	3 554(2)
C(7)	8 357(5)	5 110(2)	3 252(2)
C(8)	9 794(5)	5 391(3)	3 498(3)
O(1)	4 843(3)	6 538(1)	5 817(1)
O(2)	7 115(3)	6 107(1)	6 022(1)
O(3)	5 458(3)	4 736(1)	3 098(1)
O(4)	7 119(3)	5 282(1)	3 695(1)
C(11)	5 535(5)	6 564(2)	3 754(2)
C(12)	6 413(5)	7 031(2)	3 982(2)
C(13)	7 042(6)	7 428(2)	3 535(3)
C(14)	6 799(8)	7 353(3)	2 869(3)
C(15)	5 920(8)	6 896(2)	2 644(3)
C(16)	5 280(6)	6 498(2)	3 081(2)
C(21)	2 869(4)	6 285(2)	4 592(2)
C(22)	2 279(5)	6 812(2)	4 334(2)
C(23)	827(6)	7 003(2)	4 523(3)
C(24)	− 15(6)	6 679(2)	4 970(2)
C(25)	549(5)	6 157(2)	5 220(2)
C(26)	1 985(5)	5 958(2)	5 033(2)

and *SS*(Pd)Cl(L) for the neutral complexes (**3a**), (**3b**), (**4a**), and (**4b**), *RR*(Pd)L_2 and *SS*(Pd)L_2 for the cationic complexes (**5a**), (**6a**), and (**7b**), and *RR*(Pd)X and *SS*(Pd)X for (**8a**) and (**9a**); thus only one isomer can be 'observed' by n.m.r. spectroscopy.

Table 5. Bond lengths (Å) for compound (**1b**)

Pd–C(1)	2.140(3)	Pd–C(5)	2.139(3)
Pd • • • P	2.674(2)	P–C(1)	1.762(4)
P–C(5)	1.769(3)	P–C(11)	1.811(4)
P–C(21)	1.811(4)	C(1)–C(2)	1.457(5)
C(2)–O(1)	1.205(5)	C(2)–O(2)	1.345(5)
C(3)–C(4)	1.430(7)	C(3)–O(2)	1.448(5)
C(5)–C(6)	1.465(5)	C(6)–O(3)	1.202(5)
C(6)–O(4)	1.351(5)	C(7)–C(8)	1.478(6)
C(7)–O(4)	1.443(5)	C(11)–C(12)	1.375(6)
C(11)–C(16)	1.377(6)	C(12)–C(13)	1.379(7)
C(13)–C(14)	1.364(9)	C(14)–C(15)	1.355(9)
C(15)–C(16)	1.371(7)	C(21)–C(22)	1.391(5)
C(21)–C(26)	1.382(5)	C(22)–C(23)	1.380(6)
C(23)–C(24)	1.366(7)	C(24)–C(25)	1.368(6)
C(25)–C(26)	1.372(6)		

All three structures show the expected planar co-ordination at palladium; (**1b**) is exactly planar because the Pd atom occupies a crystallographic symmetry centre, whereas the mean deviations from planarity for (**4b**) and (**7b**) are 0.05 Å (best planes through five atoms). The co-ordination cannot be described as *square* planar because of the restricted bite of the ylide ligands (C–P–C angles 77.2—78.7°). The ylide P–C bond lengths lie in the range 1.762—1.783 Å. The four-membered rings are non-planar, with the ylide P atom lying 0.62, 0.76, and 0.74 Å (respectively) out of the PdCC planes of (**1b**), (**4b**), and (**7b**). The short transannular Pd • • • P contacts [2.674, 2.672, and 2.670 Å, *cf.* 2.304 Å for the true Pd–P bond in (**4b**)] are clearly to some extent imposed by the small rings, but may indicate some phospha-allyl bonding character, as was suggested [5b] for the nickel complex mentioned above, which has similar geometry (the chelate ring is non-planar, in contrast to the planar cobalt complex). However, it was also noted[5b] that the P–M interaction would not be of major proportions. It is unlikely that crystallographic studies alone can resolve this problem, and we thus feel that there is much to be said for the simple representation of the bonding as type (**B**) (see above) with metal–carbon σ bonds.

The Pd–C bond lengths reflect the differing *trans* influences of the ligands *trans* to C. The longest bonds are observed in (**1b**) (2.139 and 2.140 Å), where the ligand is *trans* to its symmetry equivalent. In (**4b**) the values are 2.111 Å *trans* to Cl and 2.160 Å *trans* to P, and in (**7b**) 2.084 and 2.104 Å, both *trans* to N.

The i.r. spectra of complexes (**1**)—(**9**) show one or two very strong bands in the 1 700—1 640 cm^{-1} region, assignable to $\nu_{asym.}(CO_2)$ modes. The lowering of energy of these bands (by *ca.* 20—50 cm^{-1}) from the corresponding bands of the parent phosphonium salts is in accordance with previous observations.[7]

Experimental

The i.r. spectra, the C, H, and N analyses, conductance measurements, melting-point determinations, and n.m.r. spectra were recorded as described elsewhere.[8]

$[Pd\{(CHCO_2R)_2PPh_2\}_2]$ [R = Me, (**1a**); *or* Et, (**1b**)].—The reaction of equimolar amounts of *trans*-$[PdCl_2(NCPh)_2]$ and $[Ag_2\{\mu\text{-}(CHCO_2R)_2PPh_2\}_2]$ (R = Me or Et) in CH_2Cl_2 (room temperature, 4 h, in the dark) leads to suspensions that were filtered over $MgSO_4$ to give yellow solutions. Concentration to

Table 6. Bond angles (°) for compound (**1b**)

C(1)–Pd–C(5)	78.7(1)	C(5)–Pd–C(1a)	101.3(1)
C(1)–P–C(5)	100.4(2)	C(1)–P–C(11)	114.6(2)
C(5)–P–C(11)	114.9(2)	C(1)–P–C(21)	112.2(2)
C(5)–P–C(21)	107.1(2)	C(11)–P–C(21)	107.5(2)
Pd–C(1)–P	85.9(1)	Pd–C(1)–C(2)	117.9(2)
P–C(1)–C(2)	121.8(3)	C(1)–C(2)–O(1)	128.0(4)
C(1)–C(2)–O(2)	110.2(3)	O(1)–C(2)–O(2)	121.8(3)
C(4)–C(3)–O(2)	109.3(4)	Pd–C(5)–P	85.8(1)
Pd–C(5)–C(6)	109.5(2)	P–C(5)–C(6)	118.5(3)
C(5)–C(6)–O(3)	125.7(4)	C(5)–C(6)–O(4)	112.0(3)
O(3)–C(6)–O(4)	122.3(4)	C(8)–C(7)–O(4)	107.6(4)
C(2)–O(2)–C(3)	116.2(3)	C(6)–O(4)–C(7)	116.9(3)
P–C(11)–C(12)	119.9(3)	P–C(11)–C(16)	120.2(3)
C(12)–C(11)–C(16)	119.8(4)	C(11)–C(12)–C(13)	119.7(4)
C(12)–C(13)–C(14)	119.9(5)	C(13)–C(14)–C(15)	120.4(6)
C(14)–C(15)–C(16)	120.6(5)	C(11)–C(16)–C(15)	119.6(4)
P–C(21)–C(22)	120.0(3)	P–C(21)–C(26)	120.6(3)
C(22)–C(21)–C(26)	119.4(4)	C(21)–C(22)–C(23)	119.7(4)
C(22)–C(23)–C(24)	119.9(4)	C(23)–C(24)–C(25)	120.7(4)
C(24)–C(25)–C(26)	120.2(4)	C(21)–C(26)–C(25)	120.0(4)

Symmetry operator: (a) $1 - x, 1 - y, 1 - z$.

Table 8. Bond lengths (Å) for compound (**4b**)

Pd–P(1)	2.304(2)	Pd • • • P(2)	2.672(2)
Pd–Cl	2.342(2)	Pd–C(1)	2.111(2)
Pd–C(5)	2.160(3)	P(1)–C(11)	1.827(3)
P(1)–C(21)	1.818(2)	P(1)–C(31)	1.837(3)
P(2)–C(41)	1.803(3)	P(2)–C(51)	1.813(3)
P(2)–C(1)	1.779(3)	P(2)–C(5)	1.769(3)
C(11)–C(12)	1.390(4)	C(11)–C(16)	1.390(4)
C(12)–C(13)	1.386(5)	C(13)–C(14)	1.378(5)
C(14)–C(15)	1.383(5)	C(15)–C(16)	1.386(4)
C(21)–C(22)	1.394(4)	C(21)–C(26)	1.392(4)
C(22)–C(23)	1.392(4)	C(23)–C(24)	1.377(4)
C(24)–C(25)	1.376(4)	C(25)–C(26)	1.393(4)
C(31)–C(32)	1.384(4)	C(31)–C(36)	1.402(4)
C(32)–C(33)	1.390(5)	C(33)–C(34)	1.380(6)
C(34)–C(35)	1.368(7)	C(35)–C(36)	1.394(5)
C(41)–C(42)	1.393(4)	C(41)–C(46)	1.390(4)
C(42)–C(43)	1.388(4)	C(43)–C(44)	1.379(4)
C(44)–C(45)	1.377(4)	C(45)–C(46)	1.382(4)
C(51)–C(52)	1.388(4)	C(51)–C(56)	1.389(4)
C(52)–C(53)	1.381(4)	C(53)–C(54)	1.380(5)
C(54)–C(55)	1.385(5)	C(55)–C(56)	1.388(4)
C(1)–C(2)	1.474(4)	C(2)–O(1)	1.339(3)
C(2)–O(2)	1.212(3)	C(3)–C(4)	1.488(4)
C(3)–O(1)	1.447(4)	C(5)–C(6)	1.464(4)
C(6)–O(3)	1.203(4)	C(6)–O(4)	1.352(3)
C(7)–C(8)	1.504(6)	C(7)–O(4)	1.446(4)

Table 7. Atomic co-ordinates (× 10^4) for compound (**4b**)

Atom	*x*	*y*	*z*
Pd	2 343.3(1)	1 936.4(2)	3 962.2(1)
P(1)	1 451.9(3)	2 863.8(7)	4 547.5(4)
P(2)	3 677.4(3)	2 498.1(7)	4 080.4(4)
Cl	1 747.4(3)	−87.4(7)	3 679.4(4)
C(11)	1 015(1)	1 672(3)	5 124(2)
C(12)	1 376(2)	580(3)	5 448(2)
C(13)	1 070(2)	−267(3)	5 936(2)
C(14)	404(2)	−46(3)	6 094(2)
C(15)	37(2)	1 022(3)	5 764(2)
C(16)	343(1)	1 886(3)	5 283(2)
C(21)	787(1)	3 547(3)	3 901(1)
C(22)	347(1)	4 592(3)	4 078(2)
C(23)	−187(1)	4 991(3)	3 576(2)
C(24)	−285(1)	4 348(3)	2 903(2)
C(25)	146(2)	3 317(3)	2 721(2)
C(26)	688(1)	2 919(3)	3 214(2)
C(31)	1 691(1)	4 236(3)	5 206(2)
C(32)	1 747(1)	5 570(3)	4 970(2)
C(33)	1 978(2)	6 583(4)	5 462(2)
C(34)	2 127(2)	6 244(5)	6 186(2)
C(35)	2 117(2)	4 931(5)	6 430(2)
C(36)	1 878(1)	3 908(4)	5 944(2)
C(41)	3 880(1)	1 947(3)	5 018(1)
C(42)	3 386(2)	1 968(3)	5 528(2)
C(43)	3 541(2)	1 519(4)	6 245(2)
C(44)	4 187(2)	1 054(3)	6 462(2)
C(45)	4 681(2)	1 051(3)	5 963(2)
C(46)	4 533(1)	1 495(3)	5 247(2)
C(51)	4 459(1)	3 178(3)	3 757(2)
C(52)	4 692(1)	4 446(3)	4 003(2)
C(53)	5 278(2)	4 988(3)	3 747(2)
C(54)	5 638(2)	4 264(3)	3 253(2)
C(55)	5 410(2)	2 995(3)	3 008(2)
C(56)	4 816(1)	2 453(3)	3 255(2)
C(1)	2 984(1)	3 663(3)	4 084(1)
C(2)	2 860(1)	4 423(3)	3 387(2)
C(3)	2 193(2)	6 173(3)	2 773(2)
C(4)	1 474(2)	6 628(3)	2 807(2)
C(5)	3 265(1)	1 254(3)	3 500(1)
C(6)	3 360(1)	−226(3)	3 545(2)
C(7)	3 462(2)	−2 115(3)	4 359(2)
C(8)	3 612(2)	−2 364(4)	5 172(2)
O(1)	2 382(1)	5 386(2)	3 431(1)
O(2)	3 149(1)	4 214(2)	2 832(1)
O(3)	3 298(1)	−989(2)	3 026(1)
O(4)	3 500(1)	−658(2)	4 246(1)

1 cm^3 and addition of diethyl ether or n-hexane (15 cm^3) gave pale yellow complexes (**1a**) and (**1b**). Complex (**1a**) can be obtained in better yield by treating (**2a**) with $[Ag_2\{\mu\text{-}(CHCO_2Me)_2PPh_2\}_2]$ (1:1) in dichloromethane (6 h, room temperature, in the dark). The resulting suspension was treated with dichloromethane (3 × 15 cm^3) and filtered, the solution concentrated to 2 cm^3, and diethyl ether (15 cm^3) added to precipitate complex (**1a**).

Table 9. Bond angles (°) for compound (**4b**)

P(1)–Pd–Cl	92.9(1)	P(1)–Pd–C(1)	95.9(1)
Cl–Pd–C(1)	170.7(1)	P(1)–Pd–C(5)	172.4(1)
Cl–Pd–C(5)	94.1(1)	C(1)–Pd–C(5)	77.2(1)
Pd–P(1)–C(11)	114.8(1)	Pd–P(1)–C(21)	112.5(1)
C(11)–P(1)–C(21)	105.1(1)	Pd–P(1)–C(31)	115.1(1)
C(11)–P(1)–C(31)	101.7(1)	C(21)–P(1)–C(31)	106.7(1)
C(41)–P(2)–C(51)	106.5(1)	C(41)–P(2)–C(1)	107.7(1)
C(51)–P(2)–C(1)	115.7(1)	C(41)–P(2)–C(5)	114.5(1)
C(51)–P(2)–C(5)	115.0(1)	C(1)–P(2)–C(5)	97.4(1)
P(1)–C(11)–C(12)	119.2(2)	P(1)–C(11)–C(16)	121.2(2)
C(12)–C(11)–C(16)	119.4(3)	C(11)–C(12)–C(13)	120.0(3)
C(12)–C(13)–C(14)	120.3(3)	C(13)–C(14)–C(15)	120.0(3)
C(14)–C(15)–C(16)	120.0(3)	C(11)–C(16)–C(15)	120.2(3)
P(1)–C(21)–C(22)	123.4(2)	P(1)–C(21)–C(26)	117.4(2)
C(22)–C(21)–C(26)	119.0(2)	C(21)–C(22)–C(23)	120.4(3)
C(22)–C(23)–C(24)	120.1(3)	C(23)–C(24)–C(25)	120.1(3)
C(24)–C(25)–C(26)	120.5(3)	C(21)–C(26)–C(25)	119.9(3)
P(1)–C(31)–C(32)	120.9(2)	P(1)–C(31)–C(36)	119.4(2)
C(32)–C(31)–C(36)	119.4(3)	C(31)–C(32)–C(33)	120.4(3)
C(32)–C(33)–C(34)	119.6(4)	C(33)–C(34)–C(35)	120.8(4)
C(34)–C(35)–C(36)	120.2(3)	C(31)–C(36)–C(35)	119.5(3)
P(2)–C(41)–C(42)	120.5(2)	P(2)–C(41)–C(46)	120.7(2)
C(42)–C(41)–C(46)	118.8(2)	C(41)–C(42)–C(43)	120.3(3)
C(42)–C(43)–C(44)	120.3(3)	C(43)–C(44)–C(45)	119.5(3)
C(44)–C(45)–C(46)	120.7(3)	C(41)–C(46)–C(45)	120.4(3)
P(2)–C(51)–C(52)	119.5(2)	P(2)–C(51)–C(56)	120.5(2)
C(52)–C(51)–C(56)	119.9(3)	C(51)–C(52)–C(53)	120.0(3)
C(52)–C(53)–C(54)	120.2(3)	C(53)–C(54)–C(55)	120.1(3)
C(54)–C(55)–C(56)	120.0(3)	C(51)–C(56)–C(55)	119.8(3)
Pd–C(1)–P(2)	86.3(1)	Pd–C(1)–C(2)	104.9(2)
P(2)–C(1)–C(2)	113.4(2)	C(1)–C(2)–O(1)	112.1(2)
C(1)–C(2)–O(2)	124.9(2)	O(1)–C(2)–O(2)	123.0(2)
C(4)–C(3)–O(1)	108.1(2)	Pd–C(5)–P(2)	85.1(1)
Pd–C(5)–C(6)	113.1(2)	P(2)–C(5)–C(6)	126.9(2)
C(5)–C(6)–O(3)	124.6(3)	C(5)–C(6)–O(4)	112.2(2)
O(3)–C(6)–O(4)	123.1(3)	C(8)–C(7)–O(4)	107.0(3)
C(2)–O(1)–C(3)	117.6(2)	C(6)–O(4)–C(7)	115.7(2)

$[Pd_2\{(CHCO_2Me)_2PPh_2\}_2(\mu\text{-}Cl)_2]$ (**2a**).—The complexes $[Ag_2\{\mu\text{-}(CHCO_2Me)_2PPh_2\}_2]$ and $[PdCl_2(NCMe)_2]$ (1:2) were refluxed in MeCN (3 h in the dark). The reaction mixture was then filtered over Celite, the yellow solution concentrated to 2 cm^3, and diethyl ether (15 cm^3) added to precipitate the orange-yellow complex (**2a**), which was recrystallized from dichloromethane–diethyl ether.

$[Pd_2\{(CHCO_2Et)_2PPh_2\}_2(\mu\text{-}Cl)_2]$ (**2b**).—A suspension of (**1b**) was treated with $PdCl_2$ (1:1) in refluxing acetone for 2 h. A deep yellow solution was obtained, which was filtered over

Table 11. Bond lengths (Å) for compound (**7b**)

Pd–C(1)	2.084(4)	Pd–C(5)	2.104(4)
Pd–N(1)	2.090(4)	Pd–N(2)	2.096(3)
Pd ··· P	2.670(2)	P–C(1)	1.771(4)
P–C(5)	1.783(4)	P–C(11)	1.802(5)
P–C(21)	1.794(4)	C(1)–C(2)	1.465(7)
C(2)–O(5)	1.196(6)	C(2)–O(6)	1.320(7)
C(3)–C(4)	1.415(13)	C(3)–O(6)	1.466(9)
C(5)–C(6)	1.461(7)	C(6)–O(7)	1.216(6)
C(6)–O(8)	1.336(6)	C(7)–C(8)	1.499(8)
C(7)–O(8)	1.453(7)	C(11)–C(12)	1.375(7)
C(11)–C(16)	1.373(6)	C(12)–C(13)	1.390(8)
C(13)–C(14)	1.359(8)	C(14)–C(15)	1.358(9)
C(15)–C(16)	1.398(8)	C(21)–C(22)	1.387(6)
C(21)–C(26)	1.388(6)	C(22)–C(23)	1.371(8)
C(23)–C(24)	1.376(8)	C(24)–C(25)	1.360(8)
C(25)–C(26)	1.386(7)	N(1)–C(32)	1.328(7)
N(1)–C(36)	1.338(6)	C(32)–C(33)	1.376(8)
C(33)–C(34)	1.360(8)	C(34)–C(35)	1.362(9)
C(35)–C(36)	1.350(7)	N(2)–C(42)	1.341(7)
N(2)–C(46)	1.330(7)	C(42)–C(43)	1.368(7)
C(43)–C(44)	1.347(11)	C(44)–C(45)	1.388(10)
C(45)–C(46)	1.363(7)	Cl–O(1)	1.351(8)
Cl–O(2)	1.309(8)	Cl–O(3)	1.410(5)
Cl–O(4)	1.418(6)		

Table 10. Atomic co-ordinates (× 10^4) for compound (**7b**)

Atom	*x*	*y*	*z*
Pd	6 053.7(3)	6 043.2(1)	2 271.1(2)
P	5 406(1)	7 131.3(5)	1 384.1(7)
C(1)	6 591(5)	7 025(2)	2 372(3)
C(2)	6 506(5)	7 378(2)	3 121(3)
C(3)	5 003(8)	7 789(4)	3 935(4)
C(4)	3 608(9)	7 686(4)	4 012(5)
C(5)	5 614(5)	6 332(2)	1 020(3)
C(6)	6 895(5)	6 224(2)	735(3)
C(7)	8 119(6)	5 476(3)	88(4)
C(8)	7 975(7)	4 772(3)	−149(4)
O(5)	7 510(4)	7 598(2)	3 612(2)
O(6)	5 205(4)	7 431(2)	3 212(2)
O(7)	7 898(3)	6 593(2)	850(2)
O(8)	6 851(3)	5 655(2)	343(2)
C(11)	5 868(4)	7 791(2)	790(3)
C(12)	5 384(5)	7 793(2)	−59(3)
C(13)	5 761(6)	8 293(3)	−522(3)
C(14)	6 590(7)	8 789(3)	−135(4)
C(15)	7 056(6)	8 793(3)	705(4)
C(16)	6 707(5)	8 290(2)	1 183(3)
C(21)	3 598(4)	7 242(2)	1 419(3)
C(22)	3 002(5)	7 858(2)	1 334(3)
C(23)	1 629(6)	7 945(3)	1 375(4)
C(24)	812(6)	7 426(3)	1 494(4)
C(25)	1 385(5)	6 820(3)	1 586(3)
C(26)	2 779(5)	6 724(2)	1 562(3)
N(1)	6 421(4)	5 877(2)	3 546(2)
C(32)	5 355(5)	5 909(2)	3 907(3)
C(33)	5 544(7)	5 781(3)	4 739(4)
C(34)	6 847(7)	5 615(2)	5 209(3)
C(35)	7 943(6)	5 589(2)	4 839(3)
C(36)	7 697(5)	5 717(2)	4 019(3)
N(2)	5 578(4)	5 056(2)	2 045(2)
C(42)	6 499(5)	4 666(2)	1 803(3)
C(43)	6 273(7)	4 012(3)	1 686(4)
C(44)	5 081(8)	3 744(3)	1 804(4)
C(45)	4 123(7)	4 141(3)	2 063(4)
C(46)	4 410(5)	4 788(2)	2 172(3)
Cl	600(2)	5 041(1)	2 658(1)
O(1)	126(7)	4 677(4)	3 209(4)
O(2)	615(8)	4 775(5)	1 946(4)
O(3)	1 894(5)	5 341(3)	3 047(3)
O(4)	−444(6)	5 533(3)	2 436(5)

Table 12. Bond angles (°) for compound (**7b**)

C(1)–Pd–C(5)	77.9(2)	C(1)–Pd–N(1)	95.8(1)
C(5)–Pd–N(1)	172.7(1)	C(1)–Pd–N(2)	173.7(2)
C(5)–Pd–N(2)	96.6(2)	N(1)–Pd–N(2)	89.8(1)
C(1)–P–C(5)	95.6(2)	C(1)–P–C(11)	114.0(2)
C(5)–P–C(11)	116.3(2)	C(1)–P–C(21)	113.9(2)
C(5)–P–C(21)	109.0(2)	C(11)–P–C(21)	107.8(2)
Pd–C(1)–P	87.3(2)	Pd–C(1)–C(2)	118.9(3)
P–C(1)–C(2)	124.5(3)	C(1)–C(2)–O(5)	123.9(5)
C(1)–C(2)–O(6)	113.5(4)	O(5)–C(2)–O(6)	122.5(5)
C(4)–C(3)–O(6)	109.2(6)	Pd–C(5)–P	86.3(2)
Pd–C(5)–C(6)	107.5(3)	P–C(5)–C(6)	115.5(3)
C(5)–C(6)–O(7)	125.0(4)	C(5)–C(6)–O(8)	111.5(4)
O(7)–C(6)–O(8)	123.5(5)	C(8)–C(7)–O(8)	106.9(5)
C(2)–O(6)–C(3)	117.7(4)	C(6)–O(8)–C(7)	116.0(4)
P–C(11)–C(12)	119.9(3)	P–C(11)–C(16)	120.2(4)
C(12)–C(11)–C(16)	119.9(4)	C(11)–C(12)–C(13)	120.2(4)
C(12)–C(13)–C(14)	120.0(5)	C(13)–C(14)–C(15)	120.0(6)
C(14)–C(15)–C(16)	121.0(5)	C(11)–C(16)–C(15)	118.9(5)
P–C(21)–C(22)	120.2(4)	P–C(21)–C(26)	121.4(3)
C(22)–C(21)–C(26)	118.3(4)	C(21)–C(22)–C(23)	120.3(5)
C(22)–C(23)–C(24)	120.9(5)	C(23)–C(24)–C(25)	119.4(5)
C(24)–C(25)–C(26)	120.4(5)	C(21)–C(26)–C(25)	120.5(4)
Pd–N(1)–C(32)	119.8(3)	Pd–N(1)–C(36)	122.4(4)
C(32)–N(1)–C(36)	117.7(4)	N(1)–C(32)–C(33)	121.6(5)
C(32)–C(33)–C(34)	119.8(6)	C(33)–C(34)–C(35)	118.5(5)
C(34)–C(35)–C(36)	119.2(5)	N(1)–C(36)–C(35)	123.2(5)
Pd–N(2)–C(42)	119.9(3)	Pd–N(2)–C(46)	122.3(3)
C(42)–N(2)–C(46)	117.7(4)	N(2)–C(42)–C(43)	122.3(5)
C(42)–C(43)–C(44)	119.8(6)	C(43)–C(44)–C(45)	118.5(5)
C(44)–C(45)–C(46)	119.0(6)	N(2)–C(46)–C(45)	122.6(5)
O(1)–Cl–O(2)	117.9(5)	O(1)–Cl–O(3)	110.5(4)
O(2)–Cl–O(3)	112.8(4)	O(1)–Cl–O(4)	103.1(4)
O(2)–Cl–O(4)	103.4(5)	O(3)–Cl–O(4)	108.0(3)

Celite and concentrated to 1 cm^3. The addition of n-hexane (15 cm^3) precipitated complex (**2b**).

[Pd{(CHCO$_2$R)$_2$PPh$_2$}ClL] [R = Me, L = py, (**3a**), *or* PPh$_3$, (**4a**); R = Et, L = py, (**3b**), *or* PPh$_3$, (**4b**)].—When complex (**2a**) reacts with py or PPh$_3$ (1:2) in CH$_2$Cl$_2$ (1.5 or 4.5 h, respectively) yellow solutions were obtained. Concentration to 1 cm^3 and addition of diethyl ether or n-hexane (15 cm^3) gave the yellow complex (**3a**) or (**4a**), respectively. Analogously, (**2b**) and py or PPh$_3$ react (1:2, 30 min, in acetone) to give solutions that upon concentration to 2 cm^3 and addition of diethyl ether–n-hexane (1:1, 15 cm^3) precipitated complexes (**3b**) or (**4b**) as pale yellow solids.

[Pd{(CHCO$_2$R)$_2$PPh$_2$}L$_2$]ClO$_4$ [R = Me, L$_2$ = bipy, (**5a**), *or* dppe, (**6a**); R = Et, L$_2$ = py, (**7b**)].—2,2′-Bipyridine and NaClO$_4$·H$_2$O (1:2:2) were successively added to an acetone suspension of complex (**2a**). The resulting suspension was stirred for 3 h and the solvent removed. The residue was extracted with dichloromethane (15 cm^3) and filtered. Concentration of the solution to 2 cm^3 and addition of diethyl ether (15 cm^3) precipitated yellow complex (**5a**), which was recrystallized from dichloromethane–diethyl ether. The analogous procedure using (**2a**)–dppe–NaClO$_4$·H$_2$O (1:2:2) or (**2b**)–py–NaClO$_4$·H$_2$O (1:4:2) gave complex (**6a**) or (**7b**), respectively.

[Pd{(CHCO$_2$Me)$_2$PPh$_2$}X] [X = acac, (**8a**), *or* cp, (**9a**)].—The salt TlX (X = acac or cp) was added (1:2) to a dichloromethane solution of complex (**2a**). The resulting suspension was stirred for 2.5 or 3.5 h, respectively and then filtered over Celite. Concentration of the solutions to 2 cm^3 and addition of n-hexane (15 cm^3) precipitated yellow complex (**8a**) or brown (**9a**), respectively.

X-Ray Structure Determinations.—Single crystals were obtained by diffusion of diethyl ether into dichloromethane solutions of the complexes. Diffractometer measurements were performed using monochromated Mo-K_α radiation. Cell constants were refined from setting angles [(**4b**), (**7b**)] or 2θ angles [(**1b**)] of *ca.* 50 reflections in the 2θ range 20—24°. Structures were solved with the heavy-atom method and subjected to full-matrix least-squares refinement on *F*. Hydrogen atoms were located in difference syntheses and included in the refinements using a riding model. Weighting schemes of the form $w^{-1} = \sigma^2(F) + gF^2$ were employed. The program system was Siemens SHELXTL PLUS. Crystal data are listed in Table 3, atomic co-ordinates, bond lengths and angles in Tables 4—12.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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