Reactions of Palladium(II) Allyl Dimers with Palladium(II) Complexes containing σ-Bonded 1,2-Bis(imino)alkyl Groups. Crystal and Molecular Structure of the Zwitterionic Binuclear Compound [Pd(η^3-2-MeC_3H_4)-{$R^1N=C(PdCl_2L)-CMe=NR^2$}] ($L = PPh_3$, $R^1 = R^2 = C_6H_4OMe$-*p*)†

By **Bruno Crociani** * and **Roberta Bertani**, Istituto di Chimica Generale, Via Archirafi 26, University of Palermo, Italy
Tristano Boschi, Istituto di Chimica, Facolta di Ingegneria, University of Rome, Italy
Giuliano Bandoli, Istituto di Chimica e Tecnologia dei Radioelementi C.N.R., Area di Ricerca, Padova, Italy

The 1,2-bis(imino)alkylpalladium derivatives (A), $R^1N{=}CL'{-}CR^3{=}NR^2$ [$R^1 = R^2 = C_6H_4OMe$-*p*, R^3 = Me, L' = *trans*-$PdClL_2$ (L = *para*-substituted triarylphosphine or $AsPh_3$); $R^1 = R^2 = C_6H_4OMe$-*p*, R^3 = H or Ph, L' = *trans*-$PdCl(PPh_3)_2$; $R^1 = C_6H_4OMe$-*p*, $R^2 = R^3$ = Me, L' = *trans*-$PdCl(PPh_3)_2$] react with [{PdCl(η^3-2-$R^4C_3H_4$)}$_2$] (R^4 = H or Me) in the presence of $NaClO_4$ to yield the cationic binuclear complexes (B), [Pd(η^3-2-$R^4C_3H_4$)($R^1N{=}CL'{-}CR^3{=}NR^2$)][ClO_4], where the 1,2-bis(imino)alkyl group acts as σσ'-*NN'* chelating ligand. In the absence of $NaClO_4$, the reaction leads initially to the formation of the ionic compounds (C), [Pd(η^3-2-$R^4C_3H_4$)($R^1N{=}CL'{-}CR^3{=}NR^2$)][$PdCl_2$(η^3-2-$R^4C_3H_4$)], which in a subsequent slower stage reacts further with exchange of ancillary ligands between the cationic and anionic species, to give the zwitterionic binuclear complexes (D), [Pd(η^3-2-$R^4C_3H_4$)($R^1N{=}CL''{-}CR^3{=}NR^2$)] (L'' = *cis*-$PdCl_2L$), and [PdCl($\eta^3$-2-$R^4C_3H_4$)L]. A complex of type (C) [$R^1 = R^2 = C_6H_4OMe$-*p*, $R^3 = R^4$ = Me, L' = PdCl(dppe), dppe = 1,2-bis(diphenylphosphino)ethane] can be isolated from the reaction of the corresponding derivative (A) with [{PdCl(η^3-2-MeC_3H_4)}$_2$]. The rates of ligand exchange depend markedly on the substituents R^1, R^2, and R^3, on the nature of L, and on the solvent. Based on these effects and on ^1H n.m.r. spectral data, a mechanism is proposed, which essentially involves opening the five-membered 1,2-bis(imino) ring of the cation promoted by interaction with the anionic species in the intermediate (C). The ^1H n.m.r. spectra of (D) indicate the presence of diastereoisomers which interconvert more or less rapidly at room temperature depending on the substituents R^2 or R^3 and on the ligand L. The crystal and molecular structure of a typical complex (D) ($R^1 = R^2 = C_6H_4OMe$-*p*, $R^3 = R^4$ = Me, L = PPh_3) has been determined by *X*-ray diffraction analysis. Crystals are Orthorhombic, *a* = 20.224(5), *b* = 20.073(8), *c* = 19.829(9) Å, space group *Pbca*, and *Z* = 8. The structure has been solved by the heavy-atom method and refined by full-matrix least squares to *R* = 0.086 for 1 795 diffractometer data (Mo-K_α radiation). The structural data show that the η^3-allyl group is almost symmetrically bound to palladium and its plane forms a dihedral angle of 107.4° with the planar five-membered ring. The 1,2-bis(imino)propyl group is σσ'-*NN'* chelated to the Pd(η^3-2-MeC_3H_4) unit and the mean plane of the cycle makes a dihedral angle of 81.9° with the co-ordination mean plane of the *cis*-$PdCl_2(PPh_3)$ group. The major features of the structure are represented by a short Pd–C(imino) bond [1.92(3) Å], indicating a relevant π contribution, and by a close approach of the R^3 substituent to the metal centre of the *cis*-$PdCl_2(PPh_3)$ unit [Pd ··· C(methyl) 3.19 Å].

IN recent years the chemistry of polynuclear compounds has attracted considerable attention for the inherent theoretical interest and for the relevant catalytic implications. A general synthetic route to polynuclear non-cluster compounds involves the co-ordination reaction of metal complexes containing potentially ligating functions, such as *C*-bonded acetyl,[1] methoxy(imino)methyl,[2] and pentane-2,4-dione[3] groups or *N*-bonded pyrazolate[4] and *P*-bonded phosphinoyl ligands,[5] see following page. Due to our interest in this field, we have previously studied the syntheses[6] and the co-ordinating abilities[6c,7] of *C*-bonded 1,2-bis(imino)alkylpalladium(II) derivatives of type (A) (following page).

In general the reactions of (A) with transition metal substrates yield binuclear complexes in which the 1,2-bis(imino)alkyl group acts as a σσ'-*NN'* chelating bidentate ligand.

Only in a few cases, however, are trinuclear complexes obtained, which probably involve a σσ'-*NN'* bridging co-ordination mode of (A).[7d] In some binuclear compounds, migration of ancillary ligands between the metal centres is also observed.[7c,d]

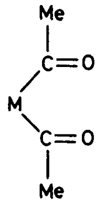
Following up this line of research and with a particular aim of elucidating the factors which affect the exchange of ancillary ligands, we have carried out an investigation of the reactions of (A) with palladium(II) allyl dimers, the results of which are reported herein.

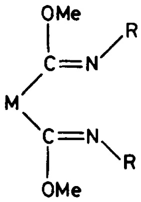
RESULTS AND DISCUSSION

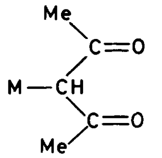
The reactions of various 1,2-bis(imino)alkylpalladium(II) derivatives with [{PdCl(η^3-2-$R^4C_3H_4$)}$_2$] (R^4 = H or Me) are reported in Schemes 1 and 2. When an excess of $NaClO_4$ is present, reactions (1) and (3) lead to the formation of intensely coloured (from deep yellow to red-orange) cationic binuclear complexes (B) and (28), which behave as mono-monovalent electrolytes in MeOH solutions (Table 1). The presence of an unco-ordinated perchlorate anion in the solid is confirmed by the occurrence of a strong broad band at *ca.* 1 090 cm^{-1} [ν(Cl–O)] and a sharp strong absorption at *ca.* 625 cm^{-1} [δ(Cl–O)]. Reaction (1) (Scheme 1) with compounds (5) or (6) yields

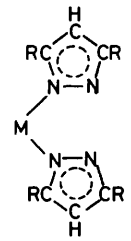
† μ-[1',2'-Bis(*p*-methoxyphenylimino)propyl-*C*1'(Pd^1):*NN'*-(Pd^2)]-1,1-dichloro-2-(1''—3''-η-2''-methylallyl)-1-triphenylphosphinedipalladium.

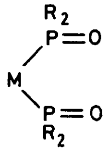
cationic complexes of type (B), contaminated by a certain amount of the products of types (D) and (E) of reaction (2). In the preparation of compound (14), the formation of the latter impurities can be minimized when the reaction mixture is worked-up as quick as possible (see Experimental section). The $\sigma\sigma'$-*NN'* chelation of the 1,2-bis(imino)alkyl group, indicated by the electronic and ^{1}H n.m.r. spectra, affects the characteristic i.r. bands, ν(C=N) and ν(Pd–Cl), of the free ligands (A) in the same way as previously observed[6c,7] for other types of binuclear complexes. In particular, the high-frequency shift of ν(Pd–Cl) in (B) is due to the reduced *trans*-influence of the σ-bonded organic moiety of (A) upon co-ordination, as can be inferred from the shortening of the Pd–Cl bond distance of compound (1) in its adducts with $CuCl_2$ [(1) 2.41; $CuCl_2\cdot(1)$ 2.36 Å].[6b,7b] On the other hand, the ν(Pd–Cl) band in compound (27) (294 or 283 cm^{-1}),[7a] in which the chloride ligand is *trans* to a phosphorus atom of the chelating group dppe [dppe = 1,2-bis(diphenylphosphino)ethane], is essentially unaffected by co-ordination [ν(Pd–Cl) = 297 or 285 cm^{-1} in (28)].

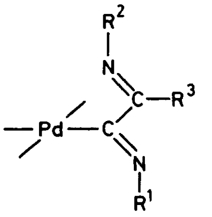










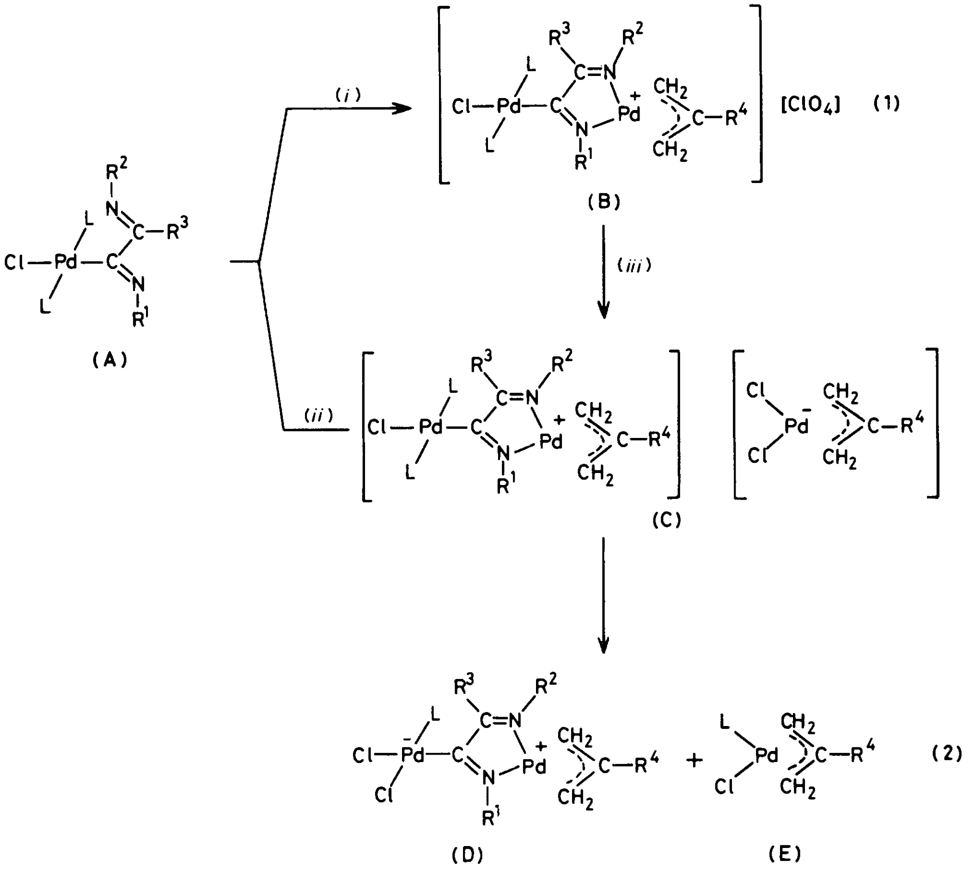


(A)

$R^1 = R^2 = C_6H_{11}$ or C_6H_4X-*p* (X = H, Me, or OMe); R^3 = Me or Ph
$R^1 = R^2 = C_6H_4OMe$-*p*; R^3 = H
$R^1 = C_6H_{11}$; $R^2 = C_6H_4OMe$-*p*; R^3 = Me
$R^1 = C_6H_4OMe$-*p*; $R^2 = R^3$ = Me

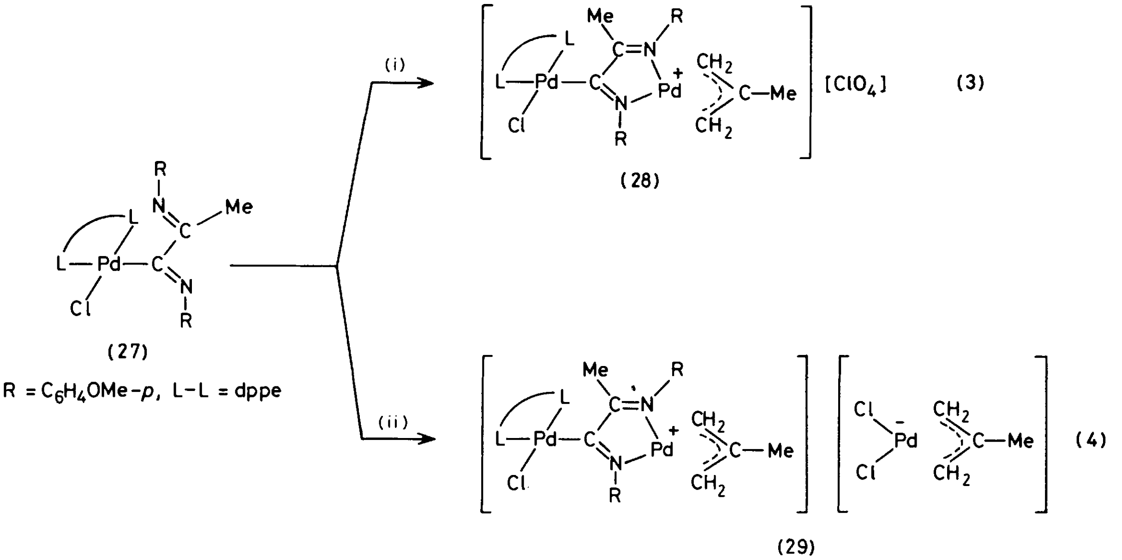
The ^{1}H n.m.r. spectra (Table 2) show that the allyl groups of (B) are η^3-bound to the palladium centre which is linked to the imino-nitrogen atoms and do not undergo any dynamic process at an appreciable rate in CD_2Cl_2 or $CDCl_3$ solutions at 35 °C. This result is in contrast with the fast *syn–syn,anti–anti* exchange of the allyl protons in the cationic mononuclear complexes, $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)Y]^+$ (R = H or Me; Y = *p*-$MeOC_6H_4N{=}CH{-}CMe{=}NC_6H_4$-OMe-*p*),[8] containing an asymmetric 1,2-bis(imino) ligand, and with the fast exchange of the non-equivalent terminal allyl carbons observed at 23 °C for CD_2Cl_2 solutions of $[Pd(\eta^3\text{-}C_3H_5)(aqa)]^+$ (aqa = 8-alkylquinoline-2-carbaldehyde-*N*-methylimine).[9] This is probably related to the presence of stronger Pd–N bonds in the binuclear cationic compounds (9)—(17) and (28), with a consequently higher activation energy for the formation of a monodentate *N*-ligand intermediate involved in the above dynamic processes.

In the absence of $NaClO_4$, the reaction of (A) with $[\{PdCl(\eta^3\text{-}2\text{-}R^4C_3H_4)\}_2]$ follows a quite different course, which eventually leads to the formation of the binuclear zwitterionic complexes (D) and the well known derivatives (E) [reaction (2)]. Upon mixing of the reactants (1 : 1 molar ratio), the ionic intermediates (C) are immediately and quantitatively formed, as indicated by the electronic spectra in methanol, characterized by the intense metal-to-ligand charge-transfer (m.l.c.t.) bands of the cationic complexes (B), and by the ^{1}H n.m.r. spectra in $CDCl_3$, which exhibit the typical signals of (B) and the anionic compounds $[PdCl_2(\eta^3\text{-}2\text{-}R^4C_3H_4)]^-$. The only relevant difference occurs in the dynamic behaviour (*syn–anti* exchange) of the allyl group of the cationic species. The same spectral features are observed when the independently prepared complexes (B) and $[AsPh_4][PdCl_2(\eta^3\text{-}2\text{-}R^4C_3H_4)]$ are mixed together in a 1 : 1 molar ratio, under comparable experimental conditions. A typical ^{1}H n.m.r. spectrum of the initial reaction mixtures (1)–$[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$, or (10)–$[AsPh_4][PdCl_2(\eta^3\text{-}C_3H_5)]$, is reported in Figure 1. The signals H_c, H_s, and H_a are due to the η^3-C_3H_5 group of the anion and compare well with those of the complex $[AsPh_4][PdCl_2(\eta^3\text{-}C_3H_5)]$ {$\delta(H_c)$ = 5.5—5.0 (central proton); $\delta(H_s)$ = 3.93 [*syn* protons, $^3J(H_c\text{–}H_s)$ = 7.3]; and $\delta(H_a)$ = 2.85 p.p.m. [*anti* protons, $^3J(H_c\text{–}H_a)$ = 12.3 Hz]}. The *syn* and *anti* protons of the allyl groups of the cationic derivative (10) undergo a rather fast exchange, indicated by their appearance as a doublet H′ at 3.14 p.p.m. [$^3J(H_c'\text{–}H')$ = 9.9 Hz], with a corresponding quintet H_c' at 5.70 p.p.m. for the central allylic proton. The same dynamic process is also apparent from the ^{1}H n.m.r. spectra of the equimolar mixtures (A)–$[\{PdCl(\eta^3\text{-}2\text{-}R^4C_3H_4)\}_2]$ {or (B)–$[AsPh_4][PdCl_2(\eta^3\text{-}2\text{-}R^4C_3H_4)]$}, if the subsequent ligand exchange reaction leading to (D) and (E) is sufficiently slow. For the initial mixture (1)–$[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2]$ {or (9)–$[AsPh_4][PdCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]$} in $CDCl_3$ at 35 °C, the *syn* and *anti* proton signals of the cationic species coalesce into a rather broad singlet at 2.93 p.p.m., whereas those of the anion occur as sharp singlets at 3.74 (*syn*) and 2.73 (*anti*), with the allyl methyl resonance at 2.02 p.p.m. {In $[AsPh_4][PdCl_2(\eta^3\text{-}2\text{-}$



(A)	L	$R^1 = R^2$	R^3	(B)	(D)	R^4
(1)	PPh_3	C_6H_4OMe-*p*	Me	(9)	(18)	Me
				(10)	(19)	H
(2)	$P(C_6H_4Cl$-*p*$)_3$	C_6H_4OMe-*p*	Me	(11)	(20)	Me
(3)	$P(C_6H_4Me$-*p*$)_3$	C_6H_4OMe-*p*	Me	(12)	(21)	Me
(4)	$P(C_6H_4OMe$-*p*$)_3$	C_6H_4OMe-*p*	Me	(13)	(22)	Me
(5)	$AsPh_3$	C_6H_4OMe-*p*	Me		(23)	Me
(6)	PPh_3	C_6H_4OMe-*p*	H	(14)	(24)	Me
(7)	PPh_3	C_6H_4OMe-*p*	Ph	(15)	(25)	Me
(8)	PPh_3	$R^1 = C_6H_4OMe$-*p*; R^2 = Me	Me	(16)	(26)	Me
				(17)		H

SCHEME 1 (*i*) [$\{PdCl(\eta^3\text{-}2\text{-}R^4C_3H_4)\}_2$], $NaClO_4$ (excess); (*ii*) [$\{PdCl(\eta^3\text{-}2\text{-}R^4C_3H_4)\}_2$]; (*iii*) [$AsPh_4$][$PdCl_2(\eta^3\text{-}2\text{-}R^4C_3H_4)$]



SCHEME 2 (*i*) $[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2]$, $NaClO_4$ (excess); (*ii*) $[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2]$

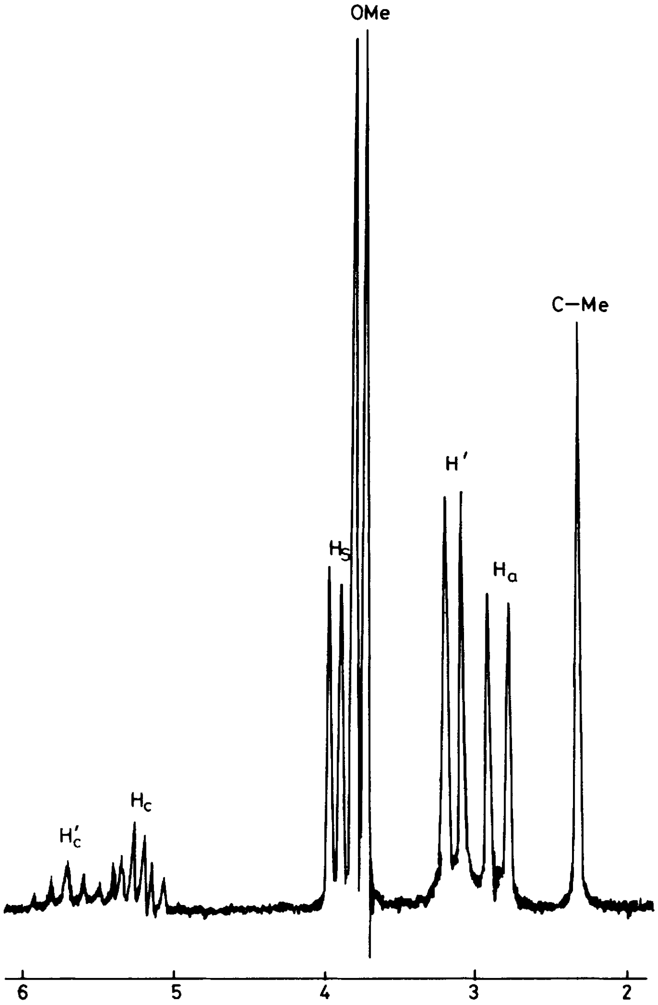


FIGURE 1 Proton n.m.r. spectrum in $CDCl_3$ at 35 °C of the system (1)–$[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$, or (10)–$[AsPh_4][PdCl_2(\eta^3\text{-}C_3H_5)]$, (1 : 1 molar ratio) after 10 min from mixing

MeC_3H_4)] the corresponding signals are at 3.70, 2.69, and 1.99 p.p.m., respectively.} The characteristic δ(O–Me) and δ(C–Me) resonances of the co-ordinated 1,2-bis-(imino)propyl group appear at 3.84, 3.74, and 2.38 p.p.m., respectively, in good agreement with the corresponding chemical shift values of compound (9) (Table 2). The intermediacy of the ionic compounds (C) in reaction (2) is further supported by the isolation of product (29) from reaction (4) (Scheme 2). This can be easily achieved because the exchange of ancillary ligands between the cation containing a chelating dppe ligand and the anion of (29), if it occurs, proceeds at a considerably much slower rate than the exchange of monodentate ligands in the intermediates (C) of reaction (2). No exchange of ligands was observed in the reaction of (27) with an equimolar amount of [{RhCl(cod)}$_2$] (cod = cyclo-octa-1,5-diene).[7d] The formulation of (29) is based on elemental analysis, conductivity, and spectral measurements. The i.r. spectrum in the solid shows two intense ν(Pd–Cl) bands of the anionic species at 270 and 255 cm^{-1}, which partly overlap with the ν(Pd–Cl) absorption of the cation. The electronic spectrum in MeOH at 25 °C is characterized by strong m.l.c.t. bands with a maximum at 25 900 (ε = 4 900 dm^3 mol^{-1} cm^{-1}) and shoulders at 22 500 and 20 900 cm^{-1}, and matches very well with the spectrum of (28) in the same solvent. The

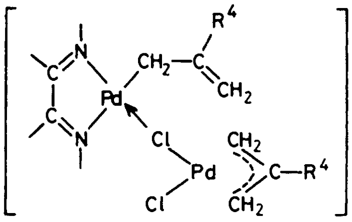
TABLE 1

Analytical, physical, conductivity, and characteristic i.r. data

Compd.	M.p.[a] (θ_c/°C)	Analysis[b] (%)				Λ[c] (Ω^{-1} cm^2 mol^{-1})	M[b,d]	I.r. absorption (cm^{-1})	
		C	H	N	Cl			ν(C=N)[e]	ν(Pd–Cl)
(2)	185	55.4 (55.15)	3.6 (3.60)	2.4 (2.45)	21.7 (21.50)		1 198 (1 154.4)	1 620ms, 1 564ms	270m
(3)	189—192	68.4 (68.65)	5.9 (5.75)	2.6 (2.70)	3.6 (3.45)		1 015 (1 031.9)	1 624s, 1 552s	265m
(4)	170	62.9 (62.80)	5.4 (5.25)	2.5 (2.50)	3.2 (3.15)		1 118 (1 127.9)	1 620ms, 1 565s	265m
(5)	160—164	60.5 (61.45)	4.6 (4.55)	2.6 (2.70)	3.6 (3.40)		1 040 (1 035.6)	1 620s, 1 560ms	274m
(9)	164	56.6 (56.65)	4.7 (4.50)	2.2 (2.30)	6.0 (5.85)	81.1		1 580m, 1 510 (sh)	309m
(10)	163	55.8 (56.30)	4.5 (4.40)	2.3 (2.35)	5.9 (5.95)	81.1		1 580m, 1 510 (sh)	308m
(11)	193	48.3 (48.35)	3.5 (3.40)	2.0 (2.0)	19.8 (20.05)	74.1		1 560m	312m
(12)	175	57.8 (58.50)	5.0 (5.15)	2.1 (2.15)	5.6 (5.50)	79.8		1 580 (sh)	315ms
(13)	167	54.2 (54.50)	4.6 (4.80)	1.9 (2.00)	5.1 (5.10)	75.6		1 568m	310m
(14)	159	55.2 (56.3)	4.3 (4.40)	2.3 (2.35)	6.1 (5.95)	84.9		1 552m	305mw
(15)	164—166	58.4 (58.60)	4.4 (4.45)	2.1 (2.20)	5.7 (5.60)	75.4		1 578m	302m
(16)	178	54.9 (54.85)	4.4 (4.50)	2.5 (2.50)	6.5 (6.35)	85.1		1 575m, 1 510 (sh)	300m
(17)	179	54.0 (54.45)	4.3 (4.40)	2.5 (2.55)	6.5 (6.45)	81.4		1 575m, 1 510 (sh)	302m
(28)	163	52.5 (52.15)	4.3 (4.45)	2.5 (2.60)	6.6 (6.55)	81.4		1 581m	297m or 285m
(18)	180	52.8 (53.10)	4.5 (4.45)	3.1 (3.15)	8.0 (8.05)	43.9 0.1[f]	869 (882.4)	1 580m, 1 515 (sh)	297ms, 280ms
(19)	179	52.4 (52.55)	4.2 (4.30)	3.2 (3.25)	8.2 (8.15)	42.6 0.2[f]	885 (868.4)	1 580m	300m, 280m
(20)	187—189	47.1 (47.50)	3.8 (3.70)	2.8 (2.85)	18.1 (18.0)	51.5		1 565m	300m, 284m
(21)	183—186	53.9 (54.55)	4.8 (4.90)	3.0 (3.05)	7.6 (7.65)	46.7	946 (924.5)	1 580m, 1 520 (sh)	295s, 280 (sh)
(22)	164	51.7 (51.85)	4.5 (4.65)	2.7 (2.90)	7.3 (7.30)			1 565m	294ms, 277ms
(23)	171	49.8 (50.55)	4.2 (4.25)	2.9 (3.00)	7.6 (7.65)	31.6 0.15[f]	954 (926.3)	1 580m, 1 510 (sh)	291s, 280 (sh)
(24)	179—181	52.3 (52.55)	4.4 (4.30)	3.2 (3.25)	8.2 (8.15)	39.7	893 (868.4)	1 560m	298ms, 276ms
(25)	145	55.7 (55.95)	4.3 (4.40)	2.8 (2.95)	7.5 (7.50)	47.6	926 (944.4)	1 575m	294ms, 272ms
(26)	160	49.8 (50.15)	4.4 (4.45)	3.4 (3.55)	9.1 (8.95)	44.1	792 (790.3)	1 575mw, 1 520 (sh)	298ms, 273ms
(29)	165	50.2 (50.40)	4.5 (4.55)	2.3 (2.30)	8.5 (8.75)	61.1		1 581m	298m, 270m, 255 (sh)

[a] Uncorrected values, all compounds decompose on melting. [b] Calculated values are given in parentheses. [c] Molar conductivities of 10^{-3} mol dm^{-3} MeOH solutions, 293 K. [d] Molecular weight determinations by osmometry in 1,2-dichloroethane. [e] The assignment of the ν(C=N) band of the binuclear complexes is tentative because of the occurrence of strong absorptions of the *para*-substituted phenyl groups around 1 600 and 1 500 cm^{-1}. [f] Molar conductivities of 10^{-3} mol dm^{-3} 1,2-dichloroethane solutions, 293 K.

^1H n.m.r. spectrum in $CDCl_3$ confirms the presence of both the cationic and anionic species. Also in this case, the *syn* and *anti* allyl protons of the binuclear cation are rapidly exchanging so as to give rise to a slightly broad singlet at 2.92 p.p.m., whereas the η^3-2-MeC_3H_4 system of the anion remains essentially unchanged. The dynamic behaviour of the allyl groups of the cation in the intermediates (C), as well as in compound (29), may be reasonably accounted for by an interaction with the anion, $[PdCl_2(\eta^3\text{-}2\text{-}R^4C_3H_4)]^-$, probably through bridging chlorides, whereby a short lived σ-allyl is formed [10] (see below).

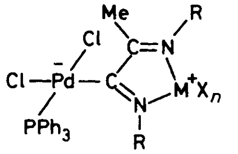


This is also supported by the fact that the static η^3-allyl group of the binuclear cationic complex (28) is promptly turned into a dynamic system, identical to that of (29), upon addition of Cl^- ions (see Table 2). The cation–anion interaction in (C) and in (29) does not involve exchange of the $Pd(2\text{-}R^4C_3H_4)$ unit between the two allyl species at a significant rate on the n.m.r. time-scale, at variance with the behaviour of the systems Y–$[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2]$ and $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)Y][ClO_4]$–$[AsPh_4][PdCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]$, where Y is an α-di-imine ligand of the type RN=CH–CH=NR (R = Bu^t or C_6H_4OMe-*p*) or RN=CMe–CMe=NR (R = C_6H_4-OMe-*p*) [8] [see reaction (5)]. In this case, the ^1H n.m.r. spectra showed a fast scrambling of the $Pd(\eta^3\text{-}2\text{-}MeC_3H_4)$ group among the different allyl complexes, but gave no evidence of any *syn–anti* exchange of the allylic protons in $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)Y]^+$. Such a difference may be related to the presence of stronger Pd–N bonds in the binuclear complexes (B) (as earlier discussed), which would make the exchange of the $Pd(\eta^3\text{-}2\text{-}R^4C_3H_4)$ unit between the cation and the anion of (C) energetically less favourable than the dynamic process involving *syn–anti* exchange in the allyl cation.

$$\begin{tikzcd}
Y + [\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2] \arrow[rr, shift left] \arrow[dr, shift left] & & \{[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2Y\} \arrow[ll, shift left] \arrow[dl, shift left] \\
& {[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)Y]^+[PdCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]^-} \arrow[ul, shift left] \arrow[ur, shift left] &
\end{tikzcd} \qquad (5)$$

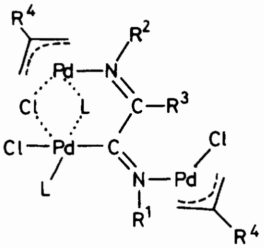
Both products (D) and (E) of reaction (2) have been isolated and characterized. The compounds (E) are easily identified by elemental analysis and by comparison of their i.r. and ^1H n.m.r. spectra with those of authentic samples prepared by bridge-splitting reactions of the dimers $[\{PdCl(\eta^3\text{-}2\text{-}R^4C_3H_4)\}_2]$ with L. The zwitterionic binuclear complexes (D) are monomers in 1,2-dichloroethane, where they are essentially non-conducting. In MeOH solution, however, an appreciable electrical conductivity is observed, which probably arises from ionic dissociation of the Pd–Cl bonds weakened by the *trans*-influence of L and of the σ-bonded 1,2-bis(imino)-alkyl group, and by the presence of a formal negative charge on the palladium atom. The formulation of (D), suggested by spectral data, was confirmed by an *X*-ray structural analysis of complex (18), which will be discussed later on.

The i.r. spectra in the metal–chloride stretching frequencies region show two ν(Pd–Cl) bands in the ranges 300—291 and the 284—272 cm^{-1} respectively, due to the mutually *cis* chloride ligands of the unit $PdCl_2L$. The same spectral feature was observed for the related derivatives (see below) [R = C_6H_4OMe-*p*; MX_n = $Rh(CO)_2$, Rh(cod),[7d] $Pd(S_2C_2NMe_2)$ and $Pt(S_2C_2NMe_2)$,[7c] and Pd(pd) and Cu(pd) (pd = pentane-2,4-dionate) [11]] and appears to be diagnostic for this class of zwitterionic binuclear complexes containing the *cis*-$PdCl_2L$ group.



The course of reaction (2) can be monitored either by ^1H n.m.r. or by visible electronic spectra. The formation of the products (D) and (E) in a 1 : 1 molar ratio is clearly indicated by the integration of the ^1H n.m.r. spectra of the mixtures when reaction (2) is completed. The rates are markedly influenced by the nature of the solvent in the order: benzene > chlorinated solvents (CH_2Cl_2, $CHCl_3$, 1,2-dichloroethane) ≫ alcohols (MeOH, EtOH); by the neutral ligand L and the R^2, R^3 substituents in the order: L = $AsPh_3$ ≫ $P(C_6H_4Cl\text{-}p)_3$ > PPh_3 > $P(C_6H_4Me\text{-}p)_3$ > $P(C_6H_4OMe\text{-}p)_3$ (when $R^1 = R^2 = C_6H_4OMe$-*p* and R^3 = Me); R^3 = H > Ph ≫ Me (when L = PPh_3 and $R^1 = R^2 = C_6H_4OMe$-*p*); $R^2 = C_6H_4$-OMe-*p* ≫ Me (when L = PPh_3, $R^1 = C_6H_4OMe$-*p*, and R^3 = Me).

While the influence of L essentially reflects the different strength of the Pd–L bonds, the effects of the substituents on the α-di-imine moiety are mainly related to the stability of the five-membered ring of (B) [8,12] and imply that a Pd–N bond breaking (*i.e.* opening of the ring) is involved in the step (C)→(D) + (E) of reaction (2). According to the reaction mechanism which will be reported in detail in a forthcoming paper,[13] the exchange of ligands occurs preferentially *via* a trinuclear transition state, arising from the slow opening of the five-membered ring of the cationic substrate (B) upon interaction with the anion (see below). An analogous trinuclear transition state (or transient) was proposed for the transfer of ancillary ligands occurring in the reaction of (1) or (8) with $[\{RhCl(cod)\}_2]$.[7d]



Electronic Spectra.—The electronic spectra of the complexes (B) and (D) are characterized by a series of overlapping bands in the range 20 000—30 000 cm^{-1}, which give rise to a rather broad absorption with a maximum surrounded by one or more shoulders and with molar absorption coefficients varying from 3 500 to 10 500 dm^3 mol^{-1} cm^{-1} (Figure 2). These bands have essentially a metal-to-ligand charge-transfer character ($d_{Pd} \longrightarrow \pi^*_{\alpha\text{-di-imine}}$), as indicated by their dependence on the nature of the C- and N-substituents of the 1,2-bis(imino)alkyl groups and by solvatochromic effects.[8,14] Whereas the neutral ligand L has only a little influence on the position of the band maxima in both compounds (B) and (D), on passing from the cationic complexes (B) to the zwitterionic derivatives (D) [*i.e.* replacing the *trans*-$PdClL_2$ by the *cis*-$PdCl_2L$ group] the m.l.c.t. bands undergo a shift to higher frequency of *ca.* 1 500—2 000 cm^{-1}, as can be seen from the spectra of the pairs (9), (18) and (14), (24) in Figure 2. A high-frequency shift is also observed; when the R^3 substituent is changed in the order: Ph, H, Me [for example, the $\tilde{\nu}_{max.}$ of (25), (24), and (18) occur at 24 200, 24 900, and 25 500 cm^{-1}, respectively, in 1,2-dichloroethane]; when the C_6H_4OMe-*p* group as R^2 substituent is replaced by a methyl group [$\tilde{\nu}_{max.}$ of (9) and (16) at 23 500 and 25 700 cm^{-1}, respectively, in 1,2-dichloroethane]; and when the polarity of solvent is increased [$\tilde{\nu}_{max.}$ of (28), 25 800 in 1,2-dichloroethane and 26 400 cm^{-1} in methanol]. Except for the higher intensity of the m.l.c.t. bands of (14) and (24), due to the presence of a proton as R^3 substituent, the spectra of the binuclear complexes in Figure 2 are quite similar to that of the mononuclear compound $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)Y][ClO_4]$ (Y = *p*-$MeOC_6H_4N{=}CMe{-}CMe{=}NC_6H_4OMe$-*p*), which was shown to contain a $\sigma\sigma'$-*NN'* chelating α-di-imine ligand.[8] This indicates that the same five-membered metallocycle chromophore is also present in derivatives of type (B) and (D), as was confirmed by the *X*-ray structural analysis of (18).

Proton N.m.r. Spectra.—The ^1H n.m.r. spectra of some representative complexes are reported in Table 2. In general, the signals of the C- and N-substituents of the 1,2-bis(imino)alkyl moieties are shifted downfield on co-ordination. This effect is particularly evident for the R^3 group, when R^3 = Me, since for $R^1 = R^2 = C_6H_4$-OMe-*p* and/or R^3 = Ph, the aromatic proton signals are partially masked by the intense phenyl resonances of L. In the complexes (A) with R^3 = Me, $\delta(R^3)$ occurs at rather high field, 1.29—1.01 p.p.m. [the $\delta(R^3)$ values of compounds (1), 1.29, and (8), 1.01 p.p.m., are taken from refs. 7(*a*) and 6(*c*)], owing to the through-space shielding effect of the phenyl ring current of the two mutually *trans*-L ligands,[6b] whereas in the corresponding cationic derivatives (B) they are detected in the range 2.42—2.35 p.p.m. Such a marked downfield shift can be ascribed in part to a σ-*N* ligating mode of the imino-nitrogens {in the mononuclear compound $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)Y]^+$ (Y = *p*-$MeOC_6H_4{-}N{=}CMe{-}CMe{=}N{-}C_6H_4OMe$-*p*) the δ(C–Me) signal of the $\sigma\sigma'$-*NN'* chelating α-di-imine at 2.33 p.p.m. is only 0.23 p.p.m. to lower field from that of the free ligand[8]} and, to greater extent, to the change of configuration (*trans*→*cis*) of the 1,2-bis(imino)alkyl unit upon chelation, which brings the methyl protons into a position very close to the palladium centre of the *trans*-$PdClL_2$ group above its co-ordination plane [Pd···C(methyl) distances of 3.37 and 3.19 Å have been observed in $CuCl_2{\cdot}(1)$[7b] and (18), respectively]. It is well established that protons closely approaching d^8 square planar metal centres above the co-ordination plane undergo large downfield shifts, resulting from the anisotropy in the magnetic susceptibility of the metal.[9,15]

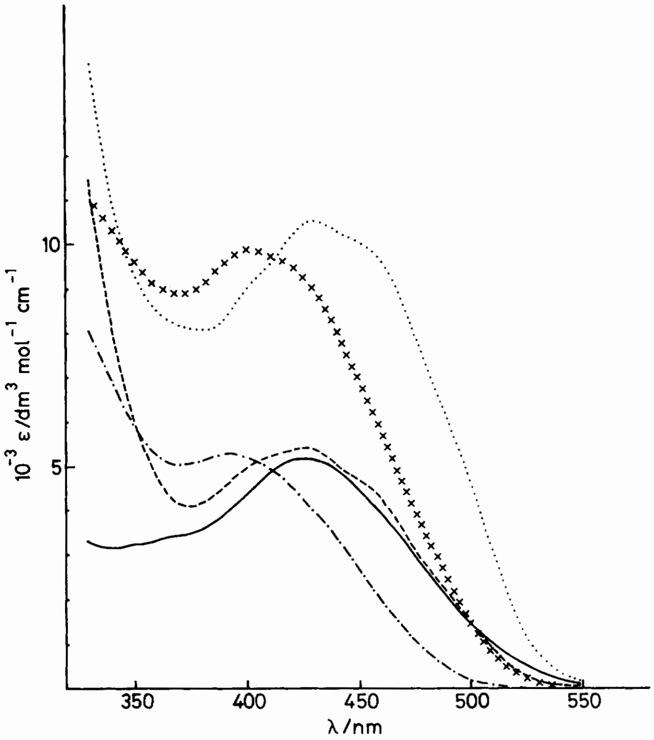


FIGURE 2 Electronic spectra in 1,2-dichloroethane at 25 °C of complexes $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(p\text{-}MeOC_6H_4N{=}CMe{-}CMe{=}NC_6H_4\text{-}OMe\text{-}p)][ClO_4]$ (——); (9) (– – – –); (14) (· · · ·); (18) (— · — · —); and (24) (× × × ×)

A further deshielding of the R^1, R^2, and R^3 protons is observed on going from (B) to (D) (*i.e.* upon replacement of L by Cl^-), which is essentially due to the reduced

TABLE 2

Proton n.m.r. data [a]

		1,2-Bis(imino)alkyl group					Allyl group	
Compound	Solvent	P–C_6H_5 or P–C_6H_4–	N–C_6H_4–	OCH_3	C–R^3		CH_2	C–R^4
(9)	CD_2Cl_2	7.7—7.2 (m) [30]	7.2—6.2 (m) [8]	3.85 (s) [3] 3.75 (s) [3]	2.42 (s) [3]		2.93 (s, br) [1] 2.86 (s) [1] 2.76 (s, br) [2]	1.94 (s) [3]
(18)	$CDCl_3$	7.8—7.0 (m) [17]	6.9—6.7 (m) [6] [b]	3.88 (s) [3] 3.79 (s) [3]	2.96 (s) [3]		2.80 (s, br) [2] [c] 2.68 (s) [1] 2.60 (s) [1]	1.96 (s, br) 1.82 (s, br) } [3] [c,d]
(18)–$AsPh_4Cl$ [e]	$CDCl_3$			3.89 (s) [3] 3.80 (s) [3]	2.97 (s) [3]		2.83 (s) [2] 2.69 (s) [1] 2.61 (s) [1]	1.90 (s) [3]
(2)	$CDCl_3$	7.7—7.1 (m) [26]	6.9—5.9 (m) [6] [b]	3.81 (s) 3.79 (s) } [6]	1.28 (s) [3] [f]			
(11)	$CDCl_3$	7.7—7.0 (m) [26]	7.0—6.2 (m) [6] [b]	3.89 (s) [3] 3.81 (s) [3]	2.35 (s) [3]		3.14 (sh) 3.10 (s) } [2] 3.01 (s) [1] 2.91 (s, br) [1]	2.07 (s) [3]
(20)	CD_2Cl_2	7.7—7.0 (m) [14]	7.0—6.8 (m) [6] [b]	3.88 (s) [3] 3.78 (s) [3]	2.87 (s) [5] [g]		2.92 (sh) [g] 2.80 (s, br) [1] 2.69 (s) [1]	2.0 (s, br) 1.87 (s, br) } [3] [d]
(13)	$CDCl_3$	7.8—6.5 (m) [30] [g]	6.4—6.2 (m) [2] [g]	3.86 (s) 3.81 (s) } [24]	2.40 (s) [3]		3.04 (s, br) [1] 2.91 (s) [1] 2.83 (s, br) [2]	2.01 (s) [3]
(22)	$CDCl_3$	7.8—6.5 (m) [20]		3.85 (s) 3.76 (s) } [15]	2.90 (s) [3]		2.76 (s, br) [2] 2.67 (s) [1] 2.59 (s, br) [1]	1.95 (s, br) 1.79 (s, br) } [3] [d]
(23)	$CDCl_3$	7.8—7.0 (m) [17] [h]	6.9—6.6 (m) [6] [b]	3.84 (s) [3] 3.78 (s) [3]	2.99 (s) [3]		2.81 (s, br) [2] 2.64 (s) [1] 2.57 (s) [1]	1.87 (s, br) [3]
(14)	CD_2Cl_2	7.8—7.0 (m) [32]	6.9—6.5 (m) [6] [b]	3.87 (s) [3] 3.79 (s) [3]	7.80 (s) [1]		3.42 (s, br) [1] 3.13 (s, br) [1] 2.94 (s) [1] 2.86 (s) [1]	1.99 (s) [3]
(24)	CD_2Cl_2	7.7—7.1 (m) [17]	7.1—6.8 (m) [6] [b]	3.94 (s) [3] 3.89 (s) [3]	8.88 (s) [1]		3.31 (s, br) [2] 2.95 (s) [1] 2.86 (s) [1]	2.01 (s) [3]
(15)	$CDCl_3$	7.8—6.3 (m) [43]		3.82 (s) [3] 3.65 (s) [3]	[i]		3.22 (s) [1] 3.15 (s, br) [1] 2.91 (sh) 2.94 (s, br) } [2]	2.02 (s) [3]
(25)	$CDCl_3$	7.9—6.4 (m) [28]		3.82 (s) [3] 3.65 (s) [3]	[i]		2.93 (s, br) [2] 2.84 (s) 2.79 (s) } [2]	1.98 (s) [3]
(26)	$CDCl_3$	7.6—7.0 (m) [17]	6.8—6.6 (m) [2]	3.84 (s) [3]	2.98 (s) [3]	3.39 (s) [3] (N–CH_3)	3.30 (br) [1] [j] 2.79 (br) 2.65 (br) } [3]	1.98 (s, br) 1.85 (s, br) } [3] [d,j]
(28)	$CDCl_3$	8.0—6.4 (m)		3.79 (s) 3.75 (s)	2.33 (s) [d] 2.30 (s) [d]	3.2—2.0 (m, br) [g] (P–CH_2–)	3.1—2.7 [g]	2.08 (s, br) [d] 1.81 (s, br) [d]
(28)–$AsPh_4Cl$ [e]	$CDCl_3$			3.80 (s) 3.76 (s)	2.32 (s)	3.2—2.0 (m, br) (P–CH_2–)	2.91 (s, br)	1.93 (s)
(29)	$CDCl_3$	8.0—6.4 (m)		3.81 (s) 3.77 (s)	2.34 (s)	3.2—2.0 (m, br) (P–CH_2–)	3.70 (s) [k] 2.69 (s) [k] 2.92 (s, br)	1.99 (s) [k] 1.94 (s)

[a] Chemical shift δ/p.p.m., spectra recorded at 35 °C unless stated otherwise; s = singlet, m = multiplet, br = broad. Integration values are given in square brackets. [b] Overlapping AA′BB′ signals of the C_6H_4OMe-*p* groups (R^1 and R^2 substituents), the *ortho* protons of R^1 being masked by the intense phenyl protons resonances of L. [c] At 100 °C in 1,1,2,2-tetrachloroethane, the allyl group signals occur at 2.82 (s) [2], 2.70 (s) [1], 2.62 (s) [1], δ(CH_2); and at 1.89 (s) [3], δ(C–R^4). [d] Two diastereoisomers are present (see text). [e] Molar ratio (compound) : $AsPh_4Cl \geqslant 20:1$. [f] The δ(C–R^3) signal of the new complexes (3), (4), and (5) occurs at 1.17, 1.22, and 1.21 p.p.m., respectively. [g] Overlapping signals. [h] As–C_6H_5 + N–C_6H_4– protons. [i] Masked by the P–C_6H_5 + N–C_6H_4– signals. [j] In CD_2Cl_2 at −40 °C, the allylic CH_2 signals occur at 3.45 (sh), 3.41 (s), 2.97 (sh), 2.92 (s), 2.85 (s), 2.77 (s), and 2.69 (s), and are partially masked by the δ(N–CH_3) and δ(C–R^3) resonances at 3.53 and 3.05 p.p.m. respectively. The allylic methyl protons are detected as two sharp singlets at 2.06 and 1.92 p.p.m. [k] Signals of the $[PdCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]^-$ anion.

shielding effect of the phenyl ring current of the single L ligand in the *cis*-$PdCl_2L$ unit,[6b] and probably also to a different charge distribution in the zwitterionic binuclear complexes. Such a downfield shift is of *ca.* 0.5 p.p.m. for R^3 = Me and becomes remarkably large (1.08 p.p.m.) for R^3 = H. The change in chemical shift of the R^2 protons (when R^2 = Me) is illustrated by the sequence: (8) 3.02,[6c] (16) 3.10, (26) 3.39 p.p.m.

In general, the ^1H n.m.r. spectra of both types of binuclear complexes (B) and (D) indicate the presence of η^3-allyl groups, characterized by distinct resonances for the *syn* and *anti* protons, even though in most cases (for η^3-2-MeC_3H_4) the assignment proved to be rather difficult for the following reasons.

(*a*) The *syn* and *anti* protons have chemical shifts rather close to each other so that overlapping often occurs.

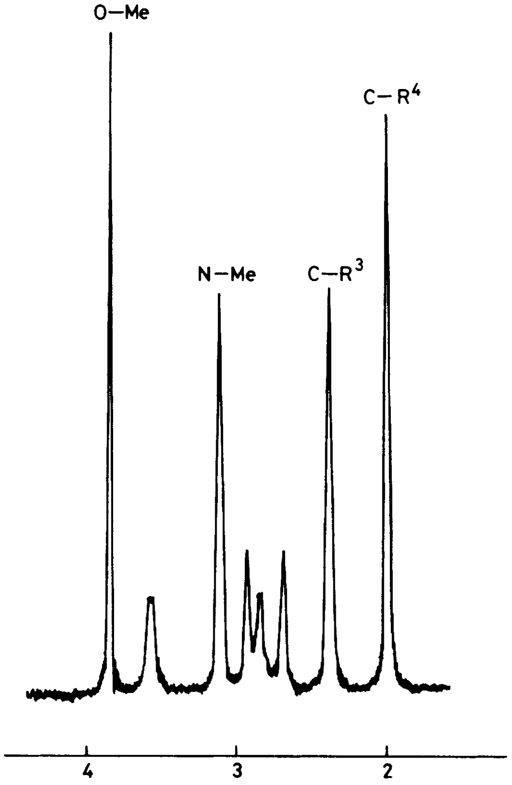
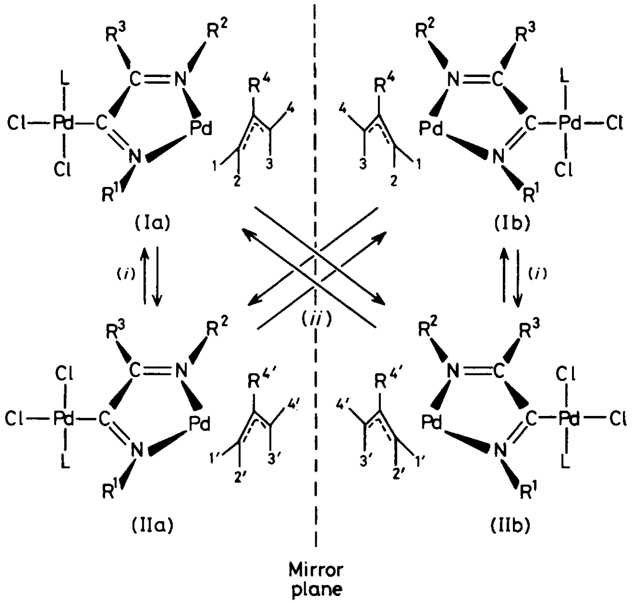


FIGURE 3 Proton n.m.r. spectrum in $CDCl_3$ at 35 °C of complex (16)

(*b*) The asymmetric nature of the 1,2-bis(imino)alkyl group (when $R^1 = R^2 = C_6H_4OMe$-*p* and R^3 = Me) does not appreciably affect the two CH_2 ends of the η^3-2-MeC_3H_4 system. For complexes (B) with a ' rigid ' η^3-2-MeC_3H_4 group, one would expect four signals, one for each allyl proton, which may exhibit a fine structure resulting from coupling between non-equivalent protons (ABCD spectrum). Spectra of this type have been observed for compounds (14) and (15), where R^3 = H and Ph respectively, and also for complexes (16), where R^1 = C_6H_4OMe-*p* and R^2 = Me (see Figure 3). A common feature of these spectra is represented by the presence of two broader bands [at 3.55 and 2.82 p.p.m. for (16)], which upon accurate examination appear as unresolved doublets and are tentatively assigned to the *syn* protons on the basis of coupling constant considerations (it is generally observed that the more significant coupling in allylic systems is that between the two *syn* protons [16]). In the analogue (17) the *syn*, *anti* assignment results from the different coupling constants with the central allyl proton [δ/p.p.m. (^3J/Hz) in CD_2Cl_2, 3.76 (6.4) and 3.19 (6.1) *syn* protons; 3.07 (13.3) and 2.90 (12.9) *anti* protons].



SCHEME 3 (*i*) Interchange of diastereoisomers (I) $\rightleftarrows$ (II) either through loss of configuration of the *cis*-$PdCl_2L$ unit or through rotation about the Pd–C bond; (*ii*) interchange of diastereoisomers (Ia) $\rightleftarrows$ (IIb) and (Ib) $\rightleftarrows$ (IIa) through dynamic processes of the allyl group (see text)

(*c*) Because of restricted rotation about the Pd–C σ bond of the 1,2-bis(imino)alkyl group in the zwitterionic complexes (D), as can be inferred from the structural data of (18) on the basis of steric and electronic (relevant π contribution in the Pd–C bond) considerations, four diastereoisomers may be present in solution (Scheme 3). Due to the asymmetry of the PdCl(dppe) unit relative to the co-ordination plane of the chelating α-di-imine, similar diastereoisomers may also occur for complex (28), whereas for derivatives (B), containing the *trans*-$PdClL_2$ group, only two enantiomers are possible, which are not distinguished by ^1H n.m.r. spectra. The presence of both diastereoisomers (I) and (II) in solution is generally indicated by the occurrence of two signals for the methyl protons of the 2-MeC_3H_4 ligand and, in a few cases, by two very close δ(C–R^3) resonances [δ(C–Me) 2.33 and 2.30 p.p.m. for (28) in $CDCl_3$ at 35 °C; δ(C–H) 8.89 and 8.87 p.p.m. for (24) in CD_2Cl_2 at −50 °C]. The integration and the broadness of the two allylic methyl bands of (18), (20), (22), (26), and (28) show that isomers (I) and (II) are present in *ca.* 1 : 1 ratio and interconvert rather rapidly on the n.m.r. time-scale at 35 °C. For complex (18) a coalescence temperature of *ca.* 70 °C has been observed in 1,1,2,2-tetrachloroethane. For the binuclear derivatives (23), (24), or (25), however, the interconversion rate is much higher as to give rise to a single $\delta(C-R^4)$ at 35 °C. At a lower temperature (−50 °C) the allylic methyl signal of (24) at 2.01 p.p.m. splits into two signals of equal intensity at 2.08 and 1.86 p.p.m., with a concomitant splitting of $\delta(C-R^3)$. Qualitatively, the rates depend on the substituent R^3 in the order Ph $\simeq$ H > Me, and on the ancillary ligand L in the order $AsPh_3 > P(C_6H_4Cl\text{-}p)_3 > PPh_3$, all other things being equal. In the fast exchange limit, the terminal allylic protons of the 2-MeC_3H_4 group appear as three separate resonances (singlets) of relative intensity 2 : 1 : 1, the more intense of which being slightly broad. This may be interpreted either as an ABCD spectrum with two coincident signals or as two overlapping AA′BB′ spectra. In any case, the (I) $\rightleftharpoons$ (II) interconversion does not involve any $\eta^3 \rightleftharpoons \sigma$ rearrangement of the allyl moiety. In the slow exchange limit, one would expect two more or less superimposed ABCD patterns, one for each $Pd(\eta^3\text{-}2\text{-}MeC_3H_4)$ group linked to the asymmetric chelating ligands which are not mirror images. This has been observed for complex (26) ($R^1 = C_6H_4OMe\text{-}p$, R^2 = Me) in CD_2Cl_2 at −40 °C, whereas, for the other derivatives with $R^1 = R^2 = C_6H_4OMe\text{-}p$, the differences in chemical shift are so small that large overlapping occurs. The rate of (I) $\rightleftharpoons$ (II) interconversion is very much increased by a small amount of Cl^- ions. As discussed earlier, in the system (28)–$AsPh_4Cl$ this proceeds *via* a fast $\eta^3 \rightleftharpoons \sigma$ dynamic process of the allyl group so that the *syn* and *anti* protons, and those of the R^3 and R^4 groups of the binuclear cationic complex, coalesce into singlets at 2.91, 2.32, and 1.93 p.p.m., respectively. In the mixture (18)–$AsPh_4Cl$, however, a different mechanism is operating, since its spectrum at 35 °C (Table 2) is very similar to that obtained for (18) in 1,1,2,2-tetrachloroethane at high temperature. Various mechanisms can be proposed in order to account for the above spectral observations. The (I) $\rightleftharpoons$ (II) interconversion *via* path (*i*) of Scheme 3 may involve either rotation of the chelated 1,2-bis(imino)alkyl group about the Pd–C σ bond or loss of configuration of the *cis*-$PdCl_2L$ unit probably through a Pd–Cl bond dissociation equilibrium (see previous discussion). The (I) $\rightleftharpoons$ (II) interconversion *via* path (*ii*) may involve either rotation of the allyl group around its bond axis to palladium, or *cis-trans* isomerization of the asymmetric 1,2-bis(imino) ligand through cleavage of one Pd–N bond, or a ' flipping ' motion of the allyl ligand. Mechanisms involving complete dissociation of the $Pd(\eta^3\text{-}2\text{-}R^4C_3H_4)$ unit or simultaneous occurrence of both path (*i*) and (*ii*) at comparable rate can be ruled out as they would lead to one AA′BB′ pattern. The catalytic activity of added Cl^- ions may take place either by path (*i*) (attack of Cl^- on the *cis*-$PdCl_2L$ unit with loss of configuration at the Pd centre) or by path (*ii*) [cleavage of one Pd–N bond upon attack of Cl^- on the $Pd(\eta^3\text{-}2\text{-}R^4C_3H_4)$ unit, followed by *cis-trans* isomerization].

Crystal and Molecular Structure of Complex (18).—In order to establish definitely the formulation of the zwitterionic binuclear complexes (D), a single-crystal *X*-ray diffraction study of a typical representative compound, (18), was carried out.

A PLUTO drawing [17] of the molecule is shown in Figure 4, which also gives the labelling scheme. Selected intramolecular distances and angles with their estimated standard deviations are listed in Table 3. The standard deviations for all the distances and angles between light atoms are rather high and reflect the low precision of the positional parameters (see Experimental section), owing to the disorder at $MeOH-H_2O$ positions (in the unit cell there are four MeOH and four H_2O molecules of crystallization per eight molecules of complex), the relatively poor quality of the diffraction data, and the limited number of observed reflections. Because of the large uncertainties, comparison of lengths and angles is restricted to the ' inner core ' of the complex. Although both diastereoisomers (I) and (II) of complex (18) are observed in solution (see Scheme 3 and Table 2), only the enantiomers (I) precipitate during the crystallization process. The geometry around the Pd(1) atom is approximately square planar and the five-membered chelate ring, including the Pd(2) atom, shows only very small deviations from planarity. The Pd(2) co-ordination sphere also includes a non-planar 2-methylallyl unit, with C(5)

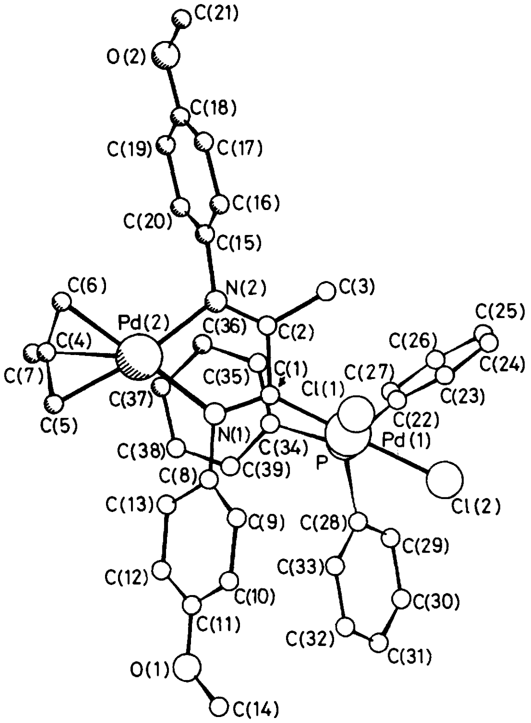


FIGURE 4 Projection of complex (18) viewed along the normal to the five-membered chelate ring including Pd(2)

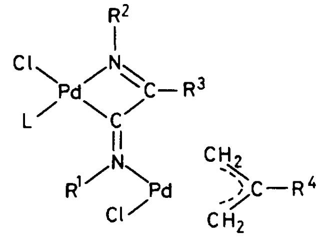
TABLE 3

Selected intramolecular distances (Å) and angles (°) for complex (18) with estimated standard deviations in parentheses

Pd(1)–Cl(1)	2.36(1)
Pd(1)–Cl(2)	2.37(1)
Pd(1)–P	2.26(1)
Pd(1)–C(1)	1.92(3)
Pd(2)–C(4)	2.15(3)
Pd(2)–C(5)	2.16(3)
Pd(2)–C(6)	2.11(3)
Pd(2)–N(1)	2.07(3)
Pd(2)–N(2)	2.08(2)
N(1)–C(1)	1.29(3)
C(1)–C(2)	1.55(4)
C(2)–N(2)	1.25(3)
C(2)–C(3)	1.51(3)
N(1)–C(8)	1.48(3)
C(11)–O(1)	1.34(4)
O(1)–C(14)	1.45(4)
N(2)–C(15)	1.51(3)
C(4)–C(5)	1.43(4)
C(4)–C(6)	1.36(4)
C(18)–O(2)	1.39(4)
C(2)–C(21)	1.48(3)
C(4)–C(7)	1.53(4)
P–C mean	1.82(2)
C–C(phenyl) mean	1.40(3)
N(1) · · · N(2)	2.50(3)
Pd(1) · · · Pd(2)	4.88(1)
Pd(2) · · · C(1)	2.98(3)
Cl(1)–Pd(1)–Cl(2)	91.2(3)
Cl(2)–Pd(1)–P	89.2(3)
P–Pd(1)–C(1)	92(1)
C(1)–Pd(1)–Cl(1)	88(1)
Cl(1)–Pd(1)–P	175.3(3)
Cl(2)–Pd(1)–C(1)	179(1)
N(1)–Pd(2)–C(4)	143(1)
N(1)–Pd(2)–C(5)	114(1)
N(1)–Pd(2)–C(6)	177(1)
N(1)–Pd(2)–N(2)	74(1)
N(2)–Pd(2)–C(4)	137(1)
N(2)–Pd(2)–C(5)	170(1)
N(2)–Pd(2)–C(6)	107(1)
C(4)–Pd(2)–C(5)	39(1)
C(4)–Pd(2)–C(6)	37(1)
C(5)–Pd(2)–C(6)	65(1)
Pd(2)–C(4)–C(7)	116(2)
C(5)–C(4)–C(7)	124(3)
Pd(2)–C(6)–C(4)	73(1)
Pd(2)–C(5)–C(4)	70(1)
C(5)–C(4)–C(6)	110(2)
C(6)–C(4)–C(7)	125(3)
Pd(2)–N(1)–C(1)	124(2)
Pd(2)–N(1)–C(8)	123(2)
C(1)–N(1)–C(8)	114(2)
Pd(2)–N(2)–C(2)	118(2)
Pd(2)–N(2)–C(15)	119(2)
C(2)–N(2)–C(15)	123(2)
N(1)–C(1)–Pd(1)	135(2)
N(1)–C(1)–C(2)	106(2)
Pd(1)–C(1)–C(2)	119(2)
C(1)–C(2)–N(2)	118(2)
C(1)–C(2)–C(3)	118(2)
N(2)–C(2)–C(3)	125(2)
C(11)–O(1)–C(14)	120(2)
C(18)–O(2)–C(21)	118(2)
Pd(1)–C(1) · · · Pd(2)	169.4(7)
C–C–C(phenyl) mean	120(2)
C(phenyl)–P–C(phenyl) mean	104(2)

(0.09 Å) above the chelate ring plane and C(4), C(6) (−0.73, −0.02 Å, respectively) below it. The plane of the allyl group makes an angle of 107.4° with the Pd(2) co-ordinative plane, so that C(4) is tilted away from Pd(2). These structural features are normal for η^3-2-methylallyl complexes of palladium.[18] The Pd(1) and Pd(2) co-ordination planes are roughly normal (81.9°) and C(1) links the two planes. The distance between the palladium atoms is 4.88 Å, with a Pd(1)–C(1) · · · Pd(2) angle of 169.4°. Within the allyl group the bond lengths and angles are similar to those found in the previous 2-methylallyl palladium structures,[18,19] and the geometry of the groups out of the ' inner core ' of the complex is normal. The two rings of the *p*-methoxyphenyl units are at a dihedral angle of 24.4° and make angles of 53.5 and 71.7° with the chelating ring, in line with the values observed in the adduct $CuCl_2\cdot(1)$.[7b] The allyl moiety is η^3-bonded to Pd(2) in an essentially symmetrical manner. The 1,2-bis(imino)propyl group acts as a $\sigma\sigma'$-*NN'* chelating ligand, with Pd(2)–N(sp^2) bond lengths of 2.07 and 2.08 Å, which are rather longer than the predicted value of 2.01 Å [based upon $r(\mathrm{Pd^{II}}) = 1.31$ and $r(\mathrm{N}) = 0.70$ Å (Pauling radii)].[20] However, the difference (*ca.* 2σ) is not significant and the observed distances are very close to those reported for other palladium–imino-nitrogen bonds.[9,18c] The PPh_3 ligand and the chelated 1,2-bis(imino)propyl group have essentially the same structural *trans*-influence, as indicated by the close Pd(1)–Cl(1) and Pd(1)–Cl(2) distances (2.36 and 2.37 Å, respectively). The Pd(1)–C(1) length [1.92(3) Å] is considerably shorter than the sum of covalent radii for a Pd–C(sp^2) bond [20] and the values observed in other complexes containing a Pd–C(sp^2) σ-bond.[6b,7d] This may be ascribed to a relevant π contribution ($d \longrightarrow \pi^*_{\mathrm{imino}}$) which would reduce the formal negative charge on the *cis*-$PdCl_2(PPh_3)$ metal centre. In this structure short range palladium–hydrogen interactions are likely to occur, as can be inferred from the Pd(1) · · · C(9) (3.25 Å) and Pd(1) · · · C(3) (3.19 Å) distances above and below the mean co-ordination plane. In particular, the interaction of the C(3) methyl protons (which may reach a minimum calculated distance of 2.5 Å) is reflected in the rather low-field chemical shift (2.96 p.p.m.) of this group in the ^{1}H n.m.r. spectrum of (18).

This study rules out the alternative formulation of complexes (D) (see below) which does not require any



separation of electrical charges and can be related to the structures of other compounds with four-membered *N,C*-chelating 1,2-bis(imino)alkyl groups.[21,22]

EXPERIMENTAL

Physical Measurements.—The molecular weights were determined using a Knauer osmometer in 1,2-dichloroethane at 37 °C. Conductivity measurements were carried out with a Philips PR9500 bridge at 20 °C. Proton n.m.r. spectra were recorded on a Varian EM-390 90 MHz spectrometer with $SiMe_4$ as internal standard. Electronic spectra in solution were recorded with a Bausch–Lomb Spectronic 210UV spectrophotometer in the range 650—250 nm at 25 °C, using quartz cells of 1 cm path length. Infrared spectra were recorded with a Perkin-Elmer 597 instrument, using hexachlorobutadiene mulls and NaCl plates in the range 4 000—1 300 cm^{-1}, and Nujol mulls and CsI plates in the range 1 700—250 cm^{-1}. Microanalyses were performed by A. Berton and G. Biasioli of the Microanalytical Laboratory, Instituto Radioelementi C.N.R., Padua.

Preparation of the 1,2-*Bis(imino)alkylpalladium Derivatives* (A), (1)—(8) *and* (27).—The complexes (1), (6)—(8), and (27) have been prepared by previously described methods.[6a,6c,6d,7a] The new compounds (2)—(5), all containing the 1,2-bis(*p*-methoxyphenylimino)propyl group, have been obtained by the same synthetic procedure as for (1), using the appropriate ligand L instead of PPh_3. For complex (5) (L = $AsPh_3$), the reaction takes *ca.* 12 h for completion, after addition of $AsPh_3$ to the mixture resulting from the initial reaction between *cis*-$[PdCl_2(CNC_6H_4OMe\text{-}p)_2]$ and $HgMe_2$ (molar ratio $\simeq 1 : 1.5$, 7 h).

Due to the high solubility of (2) in benzene or CH_2Cl_2, n-hexane was added for precipitation. In all cases, after elimination of the residual HgMeCl by sublimation, the products were conveniently purified by dissolving in the minimum volume of benzene (or CH_2Cl_2, depending on solubility) and adding a double volume of ethanol. The mixture was concentrated at reduced pressure until the compounds began to precipitate, and stored at −20 °C to complete the crystallization. [Yields based on theoretical amount: (2) 70; (3) 83; (4) 68; (5) 60%.]

Preparation of the Binuclear Cationic Complexes (B), (9)—(17) *and* (28).—All these compounds have been prepared by a general method, which is described in detail for compound (9). The dimer $[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2]$ (0.1 g, 0.25 mmol) dissolved in dichloromethane (*ca.* 40 cm^3) was treated with (1) (0.48 g, 0.5 mmol) and then with a solution of $NaClO_4 \cdot H_2O$ (0.140 g, 1 mmol) in methanol (5 cm^3). A white precipitate of NaCl was immediately formed and the solution became red-orange. After stirring for 15 min the reaction mixture was evaporated to dryness and the residue treated with dichloromethane and charcoal. After filtration, the clear solution was concentrated to a small volume at reduced pressure and the product was precipitated by addition of diethyl ether. The complex was purified by recrystallization * from dichloromethane–diethyl ether (0.46 g, 76%). High yields (75—90%) were also obtained for the other cationic compounds. In the reaction with (6), the reactants were initially mixed together at 0 °C. After stirring for 5 min, the mixture was worked-up at room temperature as quick as possible to give a satisfactorily pure product, (14), in 65% yield.

Preparation of the Binuclear Zwitterionic Complexes (D), (18)—(26).—These compounds can be prepared in good yields from the reactions of the 1,2-bis(imino)alkylpalladium derivatives (A) with $[\{PdCl(\eta^3\text{-}2\text{-}R^4C_3H_4)\}_2]$ (R^4 = H or Me; 1 : 1 molar ratio) either in chlorinated solvents (usually 1,2-dichloroethane, but also dichloromethane, and chloroform) or in benzene at room temperature. Since the reaction rates are much higher in benzene, the use of this solvent is particularly convenient for reactions which are exceedingly slow in 1,2-dichloroethane. For instance, the reactions of (4), (8), and (3) require 8, 4, and 3 d respectively for completion in 1,2-dichloroethane, whereas in benzene the reaction times are reduced to 48, 24, and 24 h, respectively. Another advantage of benzene is that the products (D) precipitate on forming. The two general methods will be described in detail for the preparation of compound (18).

(*a*) *Reaction in* 1,2-*dichloroethane*. Compound (1) (0.48 g, 0.5 mmol) dissolved in 1,2-dichloroethane (*ca.* 40 cm^3) was reacted with $[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2]$ (0.2 g, 0.5 mmol). After 24 h, the reaction mixture was treated with activated charcoal, filtered off, and the resulting orange solution concentrated to a small volume at reduced pressure. The product (18) was precipitated almost quantitatively by addition of diethyl ether. Because of the presence of a small amount of the second product, $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ (indicated by the ^1H n.m.r. spectrum), complex (18) was recrystallized twice from the same solvents (0.32 g, 72%). The mother-liquor from the first precipitation was concentrated to small volume. Upon addition of n-hexane, a yellow precipitate was obtained which was recrystallized from 1,2-dichloroethane–n-hexane to give an analytically pure sample of $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ (0.23 g, 50%, based on the theoretical amount) (Found: C, 57.3; H, 4.7; Cl, 7.9. $C_{22}H_{22}ClPPd$ requires C, 57.55; H, 4.85; Cl, 7.70). This compound was further identified by comparing its i.r. and ^1H n.m.r. spectra with those of an authentic sample prepared by the bridge-splitting reaction of $[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2]$ with PPh_3. The same procedure was used for the preparation of (19) (reaction time 24 h, yield 75%); (20) (8 h, 84%); (23) (1 h, 70%); (24) (2 h, 76%); and (25) (5 h, 68%). In all cases, the second product (E) of reaction (2), $[PdCl(\eta^3\text{-}2\text{-}R^4C_3H_4)L]$, was isolated and identified *e.g.*, analysis of $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\{P(C_6H_4Cl\text{-}p)_3\}]$ (Found: C, 46.8; H, 3.3; Cl, 25.0. $C_{22}H_{19}Cl_4PPd$ requires C, 46.95; H, 3.40; Cl, 25.20). The binuclear complex (18) can also be prepared from the reaction of the cationic compound (9) (0.6 g, 0.5 mmol) with $[AsPh_4][PdCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]$ (0.31 g, 0.5 mmol) in 1,2-dichloroethane (20 cm^3). After filtration of the sparingly soluble salt $[AsPh_4][ClO_4]$, the reaction mixture was worked-up as described above.

(*b*) *Reaction in benzene*. Complex (1) (0.48 g, 0.5 mmol) was reacted with $[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2]$ (0.2 g, 0.5 mmol) in benzene (40 cm^3). A red-orange solution was initially obtained, from which yellow microcrystals of $(18) \cdot C_6H_6$ began to separate after a few minutes. The presence of a molecule of benzene of crystallization was indicated by elemental analysis (Found: C, 56.5; H, 4.8; N, 2.9; Cl, 7.4. $C_{45}H_{43}Cl_2N_2O_2PPd$ requires C, 56.25; H, 4.70; N, 2.90; Cl, 7.40%) and by g.l.c. analysis (gas liquid chromatography) of a dichloromethane solution. The reaction mixture was set aside for 6 h and then diethyl ether (20 cm^3) added in order to complete the precipitation. After filtration, the product was recrystallized twice from 1,2-dichloroethane–diethyl ether, whereupon the benzene of crystallization is lost (0.33 g, 75%). The mother-liquor from the first precipitation was worked-up in the same way as for the reaction in 1,2-dichloroethane to yield 0.25 g of $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$.

The same procedure was followed for the preparation of (21) (reaction time 24 h, yield 80%); (22) (48 h, 78%); and (26) (24 h, 75%).

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* General procedure: compounds were dissolved in the minimum volume of chlorinated solvent, the second solvent added until incipient precipitation (stirring), and set aside for 12—24 h.

Preparation of the Ionic Compound (29).—Complex (27) (0.21 g, 0.25 mmol) was reacted with [{PdCl(η^3-2-MeC$_3$H$_4$)}$_2$] (0.1 g, 0.25 mmol) in benzene (*ca.* 20 cm^3). An immediate change from yellow to orange occurred. After stirring for 10 min, the yellow product (29) began to precipitate. The mixture was set aside (without stirring) for 30 min, and then the solid was filtered off and washed with cold benzene (0.16 g, 53%). No further purification was required.

TABLE 4

Atomic co-ordinates ($\times 10^4$) for complex (18), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pd(1)	2 949(1)	8 071(1)	7 487(2)
Pd(2)	2 957(1)	6 320(1)	9 196(2)
Cl(1)	2 376(5)	8 771(5)	8 244(5)
Cl(2)	3 054(5)	8 950(4)	6 698(5)
P	3 416(4)	7 374(4)	6 732(5)
O(1)	5 857(12)	8 090(13)	8 608(13)
O(2)	−120(12)	5 005(11)	9 135(12)
O(3) *	4 616(18)	4 731(19)	975(21)
O(4) *	3 574(24)	4 204(24)	1 209(26)
N(1)	3 233(13)	7 109(12)	8 585(14)
N(2)	2 131(12)	6 546(11)	8 612(13)
C(1)	2 854(15)	7 371(14)	8 136(17)
C(2)	2 183(14)	6 998(14)	8 181(16)
C(3)	1 638(15)	7 212(14)	7 710(16)
C(4)	3 335(20)	5 474(19)	9 734(21)
C(5)	3 693(16)	6 057(17)	9 938(19)
C(6)	2 681(18)	5 551(17)	9 868(21)
C(7)	3 627(19)	4 913(19)	9 306(22)
C(8)	3 899(16)	7 413(16)	8 614(17)
C(9)	4 029(16)	8 080(17)	8 703(17)
C(10)	4 676(17)	8 351(15)	8 736(18)
C(11)	5 206(20)	7 889(20)	8 664(20)
C(12)	5 114(16)	7 218(17)	8 598(17)
C(13)	4 451(16)	6 941(16)	8 591(17)
C(14)	5 997(21)	8 792(23)	8 635(22)
C(15)	1 509(16)	6 144(16)	8 711(17)
C(16)	981(17)	6 462(16)	9 025(18)
C(17)	421(16)	6 059(17)	9 186(19)
C(18)	418(18)	5 416(19)	8 998(20)
C(19)	930(15)	5 107(15)	8 705(17)
C(20)	1 502(17)	5 482(17)	8 531(18)
C(21)	−722(17)	5 310(16)	9 431(18)
C(22)	2 920(17)	7 224(15)	6 006(17)
C(23)	2 389(17)	7 647(16)	5 870(20)
C(24)	2 011(19)	7 553(19)	5 290(21)
C(25)	2 163(18)	7 037(18)	4 845(21)
C(26)	2 694(18)	6 614(17)	4 981(22)
C(27)	3 073(20)	6 708(19)	5 561(22)
C(28)	4 202(17)	7 698(17)	6 410(20)
C(29)	4 410(18)	7 641(18)	5 742(22)
C(30)	5 006(22)	7 928(19)	5 539(21)
C(31)	5 394(18)	8 272(18)	6 005(22)
C(32)	5 186(21)	8 329(20)	6 674(25)
C(33)	4 590(18)	8 042(18)	6 876(20)
C(34)	3 613(16)	6 514(16)	7 001(18)
C(35)	3 080(19)	6 085(19)	7 107(21)
C(36)	3 190(20)	5 440(20)	7 345(23)
C(37)	3 833(21)	5 225(19)	7 477(24)
C(38)	4 366(20)	5 653(20)	7 371(23)
C(39)	4 256(19)	6 298(19)	7 133(20)
C(40) *	3 830(28)	4 484(29)	1 778(33)

* Occupancy factor: 0.5.

X-*Ray Crystallography of* (18).—Crystals of compound (18) were grown by very slow evaporation of a solution in MeOH–CH$_2$Cl$_2$ (3 : 1 v/v). The plates showed a strong tendency to crack and to twin. Eventually a cubic-shaped crystal was found which was not cracked or twinned which was used for the structural determination [C$_{39}$H$_{39}$Cl$_2$N$_2$O$_2$PPd$_2$(0.5MeOH·0.5H$_2$O), orthorhombic, $a = 20.224(5)$, $b = 20.073(8)$, $c = 19.829(9)$ Å, $U = 8\,050$ Å^3, $Z = 8$, $D_c = 1.50$ g cm^{-3}, $\mu = 10.9$ cm^{-1} for Mo-K_α radiation ($\lambda = 0.7107$ Å), space group *Pbca*]. The cell parameters were obtained with a Philips PW1100 computer-controlled diffractometer from 25 strong reflections at $20 \leqslant 2\theta \leqslant 27°$. Intensities were collected from the crystal of dimensions $0.18 \times 0.20 \times 0.18$ mm with graphite monochromated Mo-K_α radiation. An unique data set was collected out of $2\theta = 36°$ by the ω-scan technique with a scan range of $1.4 \pm 0.3 \tan\theta$ and a scan rate of 0.04° s^{-1}; no reflection was sufficiently strong to require the insertion of an attenuator filter. The intensities of 3 256 independent reflections were measured; of these only 1 795 obeyed the condition $I > 3\sigma(I)$ and were used in subsequent calculations. The intensities were processed in the usual manner.[23] No extinction or absorption corrections were applied. The structure was solved by the heavy-atom method. In the least-squares refinement the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, with unit weight to each reflection.

A weighting scheme based on counter statistics was unsuccessful, probably owing to systematic errors. In particular, inspection of F_o/F_c values showed a rather poor agreement among weak reflections attributable to an unsound signal-to-noise ratio of the scintillation counter. The scattering factors used were those of ref. 24. The major calculations for the analysis were made with the SHELX 76 program.[25] Calçulations were all performed on the Consorzio Interuniversitario Italia Nord-Orientale CDC 7600 computer system. A number of cycles of block-diagonal least-squares refinement with isotropic thermal parameters, followed by difference syntheses, enabled location of all the non-hydrogen atoms and led to convergence with $R = 0.12$. A difference synthesis at this stage showed evidence of anisotropy in the motion of the heavy atoms together with three unexpected peaks of 1.27, 1.15, and 0.98 e Å^{-3}. These peaks were attributed to MeOH and H$_2$O from the recrystallization mixture and the occupation factors for these sites were fixed at 0.5 in the successive refinement procedure. Thermal motions for these atoms are no greater than those observed in the core of the complex. Further full-matrix refinement, with anisotropic thermal parameters only for the heavy atoms and with the phenyl carbon atoms of the PPh$_3$ group constrained to fit a rigid regular hexagon to achieve a better 'observations–parameters' ratio, converged to $R = 0.086$. A final difference synthesis showed maxima no greater than 0.58 e Å^{-3}.

Table 4 shows the final position parameters of the atoms; thermal parameters and the observed and calculated structure factors are listed in Supplementary Publication No. SUP 23297 (14 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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