Cyclometallated complexes of palladium(II) with 1-methyl-2-phenylimidazole and tertiary diphosphines. Crystal and molecular structure of $[\{Pd[o\text{-}C_6H_4C=NC(H)=C(H)NMe]\}(Ph_2PCH(Me)PPh_2\text{-}P,P)][PF_6]$

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Abstract

Treatment of $Pd(AcO)_2$ with 1-methyl-2-phenylimidazole, and subsequent treatment with sodium chloride or sodium bromide gave the corresponding halide-bridged cyclometallated complexes $[Pd\{o\text{-}C_6H_4C=NC(H)=C(H)NMe\}(\mu\text{-}X)]_2$ (**2**, X = Cl; **3**, X = Br). Complexes **2** and **3** react with tertiary diphosphines in a 1:1 molar ratio to give dinuclear cyclometallated compounds with bridging diphosphine and halogen ligands $[Pd\{o\text{-}C_6H_4C=NC(H)=C(H)NMe\}(\mu\text{-}L\text{-}L)(\mu\text{-}X)]X$ (**4–9**) or with only bridging diphosphine ligands $[Pd\{o\text{-}C_6H_4C=NC(H)=C(H)NMe\}(\mu\text{-}L\text{-}L)(X)_2]$ (**10–17**), [X = Cl, Br; L-L = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PC(=CH_2)PPh_2$ (vdpp), $Ph_2PCH(CH_3)PPh_2$ (1,1-dppe), *trans*-$Ph_2P(CH=CH)PPh_2$ (*trans*-dppe), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp), $Ph_2P(CH_2)_4PPh_2$ (dppb), as appropriate]. When the reaction is carried out in a 1:2 molar ratio and in the presence of NH_4PF_6 or $NaClO_4$, mononuclear cyclometallated compounds with a chelating diphosphine ligand are obtained $[Pd\{o\text{-}C_6H_4C=NC(H)=C(H)NMe\}(L\text{-}L\text{-}P,P)][Y]$ (**18–27**) [Y = PF_6, ClO_4; L-L = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PC(=CH_2)PPh_2$ (vdpp), $Ph_2PCH(CH_3)PPh_2$ (1,1-dppe), $Ph_2PN(CH_3)PPh_2$ (dppma), *cis*-$Ph_2P(CH=CH)PPh_2$ (*cis*-dppe), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)PPh_2$ (dppp), $Ph_2P(CH_2)_4PPh_2$ (dppb)]. Compounds **18–22** and **25–27** could also be obtained by reaction of complexes **4–17** with the appropriate diphosphine and NH_4PF_6 or $NaClO_4$. The diphosphines dppma and *cis*-dppe failed to behave as bridging ligands and only gave mononuclear compounds. The complexes were characterized by their elemental analysis (C, H, N) and by IR and $^{31}P\text{-}\{^1H\}$ and ^1H NMR data. The X-ray crystal structure of complex **22** is described. © 1997 Elsevier Science S.A.

1. Introduction

Cyclometallation [1] is now widely accepted as part of organometallic chemistry and it involves compounds of the transition metals (although some main group metals have also been used) in which an organic substrate undergoes intramolecular metallation with the formation of a σ M–C bond and of a coordinative bond between the metal center and a donor atom; complexes with five-membered rings seem to be the

most favored [2]. Cyclometallated complexes have been extensively researched and reviews covering them have appeared [3–13]. The variety of organic ligands and of metals that produce cyclometallated complexes is such that it allows different approaches to these complexes adding a great versatility to cyclometallation chemistry; to name but a few we have, for instance, the synthesis of complexes with ligands having either one or more donor atoms [14–17], the reactivity of the bonds to the metal center [18], double cyclometallation [14–17], ligand exchange reactions [19,20]. Also, cyclometallated compounds are involved in other branches of chemistry

Table 1
^{31}P^a and ^{1}H^b NMR data^{c,d}

	δ(H2)	δ(H3)	δ(H4)	δ(H5)^f	δ(Ha)^g	δ(Hb)^g	δ(NMe)	δ(P)^h	Others
L	7.60dd ^3J(H2H3), 8.0		7.57–7.36m		7.09d	6.94d (1.1)	3.71s		δ(**H6**) = 7.60dd ^3J(H5H6), 8.0; ^4J(H2H6), 1.6
1	6.88d ^3J(H2H3), 7.6		6.79–6.61m		6.43d 6.54d	6.21d (1.4) 6.41d (1.4)	3.66s 3.49s		δ(**MeCO$_2$**) = 2.19s 2.24s, 2.12s
4	^{e}	6.90t ^3J(H2H3), 7.6 ^3J(H3H4), 7.6	6.40td ^3J(H4H5), 7.7 ^4J(H4H2), 1.3	6.19m ^4J(PH5), 6.4	^{e}	^{e}	4.05s	29.6s	δ(**PCH$_2$P**) = 4.44t, 4.32t ^2J(PH) = 12.2
5	^{e}	6.92t ^3J(H2H3), 7.5 ^3J(H3H4), 7.5	6.39td ^3J(H4H5), 7.5 ^4J(H4H2), 1.3	6.14m ^4J(PH5), 6.3	^{e}	^{e}	4.06s	29.8s	δ(**PCH$_2$P**) = 4.58t, 4.42t ^2J(PH) = 12.2
6	^{e}	6.90t ^3J(H2H3), 7.6 ^3J(H3H4), 7.6	6.37t ^3J(H4H5), 7.6	6.15m	^{e}	^{e}	4.09s	41.5s	δ(C=**CH$_2$**) = 6.09m
7	^{e}	6.91t ^3J(H2H3), 7.5 ^3J(H3H4), 7.5	6.38td ^3J(H4H5), 7.5 ^4J(H4H2), 1.4	6.12m	^{e}	^{e}	4.09s	41.4s	δ(C=**CH$_2$**) = 6.09m
8	^{e}	6.90t ^3J(H2H3), 7.5 ^3J(H3H4), 7.5	6.38t ^3J(H4H5), 7.5	6.20m ^4J(PH5), 6.4	^{e}	^{e}	4.07s	41.8s	δ(PCHP) = 4.41m δ(CHMe) = 1.08m
9	^{e}	6.92t ^3J(H2H3), 7.5 ^3J(H3H4), 7.5	6.40t ^3J(H4H5), 7.5	6.22m ^4J(PH5), 6.4	^{e}	^{e}	4.09s	37.9s	δ(PCHP) = 4.67m δ(CHMe) = 1.04m
10	^{e}	6.90t	6.45t	6.22m	^{e}	^{e}	3.94s	34.3s	δ(**CH=CH**) = 7.16t^i N = 38.2
11	^{e}	6.87t	6.43t	6.20m	^{e}	^{e}	3.95s	36.1s	δ(**CH=CH**) = 7.17t^i N = 38.0
12	^{e}	6.89t	6.48t	6.24m	^{e}	^{e}	3.94s	54.1s	
13	^{e}	6.88t	6.42t	6.20m	^{e}	^{e}	3.94s	59.5s	
14	^{e}	6.85t	6.52t	6.23m	^{e}	^{e}	3.94s	48.6s	
15	^{e}	6.86t	6.49t	6.21m	^{e}	^{e}	3.95s	34.1s	
16	^{e}	6.89t	6.54t	6.24m	^{e}	^{e}	3.96s	34.2s	
17	^{e}	6.90t	6.51t	6.22m	^{e}	^{e}	3.96s	36.7s	
18	^{e}	7.14td ^3J(H2H3), 7.9 ^3J(H3H4), 7.9 ^3J(H3H5), 1.4	6.97–6.84m		7.00d	6.82d (1.6)	4.07s	−12.6d −34.1d (69.9)	δ(**PCH$_2$P**) = 4.28dd ^2J(PH)^j = 11.1; 8.7 δ(**PF$_6$**) = −146.20h J(PF) = 712.1
19	^{e}	7.13t ^3J(H2H3), 7.9 ^3J(H3H4), 7.9	6.91–6.84m		7.07d	5.82d (1.6)	4.08s	−14.6d −31.1d (66.8)	(**PCH$_2$P**) = 4.34dd ^2J(PH)^j = 11.2; 8.6
20	^{e}	7.17t ^3J(H2H3), 7.6 ^3J(H3H4), 7.6	6.86td ^3J(H4H5), 7.6 ^4J(H2H4), 1.3	6.96m ^4J(PH5), 9.2, 7.1	7.01d	6.76d (1.6)	4.07s	9.39d −7.4d (8.7)	δ(C=**CH$_2$**) = 6.21m δ(**PF$_6$**) = −146.80h J(PF) = 713.2
21	^{e}	7.15t ^3J(H2H3), 7.5 ^3J(H3H4), 7.5	6.84td ^3J(H4H5), 7.5 ^4J(H2H4), 1.4	6.95m ^4J(PH5), 9.3, 7.2	7.10d	6.76d (1.6)	4.09s	7.2d −9.6d (8.0)	δ(C=**CH$_2$**) = 6.24m
22	^{e}	7.14td ^3J(H2H3), 7.6 ^3J(H3H4), 7.6 ^3J(H3H5), 1.5	6.88–6.80m		6.99d	6.74d (1.9)	4.08s	0.4d −21.7d (65.1)	δ(PCHP) = 4.67m δ(CHMe) = 1.16m δ(**PF$_6$**) = −146.01h J(PF) = 712.7
23	^{e}	7.11t ^3J(H2H3), 7.4 ^3J(H3H4), 7.4	7.00–6.87m		7.05d	6.68d (1.8)	4.03s	57.0d 48.4d (58.9)	δ(PNMeP) = 2.62dd ^3J(PH)^d = 9.7; 9.2
24	^{e}	7.35t ^3J(H2H3), 7.3 ^3J(H3H4), 7.3	6.80t ^3J(H4H5), 7.3	7.08m ^4J(PH5), 9.4, 7.1	6.98d	6.51d (1.7)	4.04s	61.6d 51.6d (51.4)	
25	^{e}	7.08t ^3J(H2H3), 7.4 ^3J(H3H4), 7.4	6.73t ^3J(H4H5), 7.4	6.82m ^4J(PH5), 9.6, 7.0	6.86d	6.17d (1.1)	4.05s	59.7d 42.6d (52.0)	
26	^{e}	6.98t ^3J(H2H3), 7.5 ^3J(H3H4), 7.5	6.35t ^3J(H4H5), 7.5	6.55m ^4J(PH5), 9.3, 7.1	6.62d	5.70d (1.7)	3.96s	23.7d −3.9d (54.8)	δ(**PF$_6$**) = −146.04h J(PF) = 712.2

Table 1 (continued)

	δ(H2)	δ(H3)	δ(H4)	δ(H5)^f	δ(Ha)^g	δ(Hb)^g	δ(NMe)	δ(P)^h	Others
27	e	6.97t ^3J(H2H3), 7.6 ^3J(H3H4), 7.6	6.54t ^3J(H4H5), 7.6	6.77m ^4J(PH5), 9.6, 7.1	6.64d	5.82d (1.8)	3.96s	38.0d 12.0d (34.3)	

^{a} In CDCl$_3$. Measured at 100.6 MHz (ca. +20°C); chemical shifts (δ) in ppm ($\pm$0.1) to high frequency of 85% H$_3$PO$_4$.
^{b} In CDCl$_3$, unless otherwise stated. Measured at 250 MHz (ca. +20°C); chemical shifts (δ) in ppm ($\pm$0.01) to high frequency of SiMe$_4$.
^{c} Coupling constants in Hz.
^{d} s, singlet; d, doublet; dd, doublet of doublets; t, triplet; h, heptuplet; m, multiplet.
^{e} Not assigned, occluded by the phosphine resonances.
^{f} trans-^4J(PH5) > cis-^4J(PH5); ^nJ(PP) values in parenthesis.
^{g} ^3J(HH) values in parenthesis.
^{h} δ(P)$_{trans\ to\ N}$ > δ(P)$_{trans\ to\ C6}$.
^{i} Apparent triplet of an AA'XX' spin system.
^{j} ^2J(PH)$_{P\ trans\ to\ N}$ > ^2J(PH)$_{P\ trans\ to\ C6}$.

such as regiospecific organic and organometallic synthesis [21–23], asymmetric synthesis with optically active cyclometallated compounds [24], catalytic materials [25] and liquid crystals [26].

We have studied cyclometallated complexes derived from differently substituted Schiff bases quite extensively, and our more recent research in this field was involved with the synthesis of cyclometallated complexes of bidentate Schiff base ligands derived from diamines [27], where metallation takes place at different aromatic rings, or terephthalaldehyde [28] and isophthalaldehyde [29], where metallation is induced at the same phenyl ring. In the latter case, complexes where one of the C=N double bonds was cleaved giving a free formyl group on the aromatic ring were synthesized; the imine moiety may be regenerated by treatment with primary amines. We [30–32] and others [33] have also performed metallation of ligands with the nitrogen-donor atom being part of an imidazole ring; the donor atom in this case is shared by the coordination and the heterocyclic rings.

In the compounds with Schiff bases reactions with tertiary mono- and diphosphine ligands were tested, among others. In the resulting complexes, diphosphine ligands may bridge two metal centers in dinuclear compounds or behave as chelating ligands in the mononuclear ones; this is mainly dependent on the length and nature of the carbon chain between the phosphorus atoms. With small 'bite' diphosphines, a second bridging ligand is present in the compounds, i.e., an acetato or halogen ligand [34,35]. In some of these cases, a possible equilibrium between two geometrical conformations has also been proposed [36]. However, similar reactions with diphosphines in compounds bearing ligands with donor atoms in heterocyclic rings, in particular imidazole ligands, are scarce.

In the present paper, we report the synthesis and characterization of a new series of mono- and dinuclear cyclopalladated complexes derived from a phenylimida-

zole ligand containing either bridging or chelating diphosphines.

2. Results and discussion

2.1. Cyclometallation of 1-methyl-2-phenylimidazole, L

In a previous paper [30], we reported the synthesis of compounds 1–3. The dinuclear chloride-bridged complex was made from the direct reaction of the ligand N-(methyl)-2-phenylimidazole, L, with lithium tetrachloropalladate. Complex 3 was synthesized by treatment of 2 with lithium bromide; subsequent treatment of either 2 or 3 with silver acetate afforded the dinuclear acetato-bridged complex 1. In the present paper, the need of compounds 2 and 3 as starting materials led us to revisit the synthetic method previously employed in order to obtain improved yields. We have now used the standard procedure reported in more recent papers [28]. Thus, treatment of L with palladium(II) acetate in glacial acetic acid for 4 h under reflux gave 1 in ca. 76% yield; previously [30], no NMR data was given, now 1 was fully characterized. The ν_{as}(COO) and ν_s(COO) values were consistent with bridging acetato groups [37]; the singlet resonance at δ 2.19 was assigned to the methyl acetate protons, consistent with a trans geometry of the cyclometallated moieties [38]; two weak resonances also appeared at δ 2.24 and 2.12 ppm, which were assigned to the inequivalent MeCOO groups of the isomer with a cis arrangement of the imidazole ligands; the trans/cis isomer ratio was estimated to be ca. 10:1 (see Section 4 and Tables 1 and 2). For the NMe, Ha and Hb protons, two signals were observed in each case; the weaker resonances were ascribed to the isomer with the cyclometallated groups in a cis arrangement. Reaction of 1 with an aqueous solution of sodium chloride or sodium bromide gave the halide-bridged complexes 2 and 3 (Scheme 1). Complexes 2 and 3 were too insoluble for

Table 2
^{31}P parameters

	P^a	P$_a$	Δ_R
18	43.08	− 12.58	− 55.66
19	43.08	− 14.61	− 57.69
20	43.08	9.39	− 33.69
21	43.08	7.20	− 35.88
22	43.08	0.36	− 42.72
23	43.08	56.99	13.91
24	43.08	61.64	18.56
25	43.08	59.68	16.60
26	43.08	23.69	− 19.39
27	43.08	37.98	− 5.10

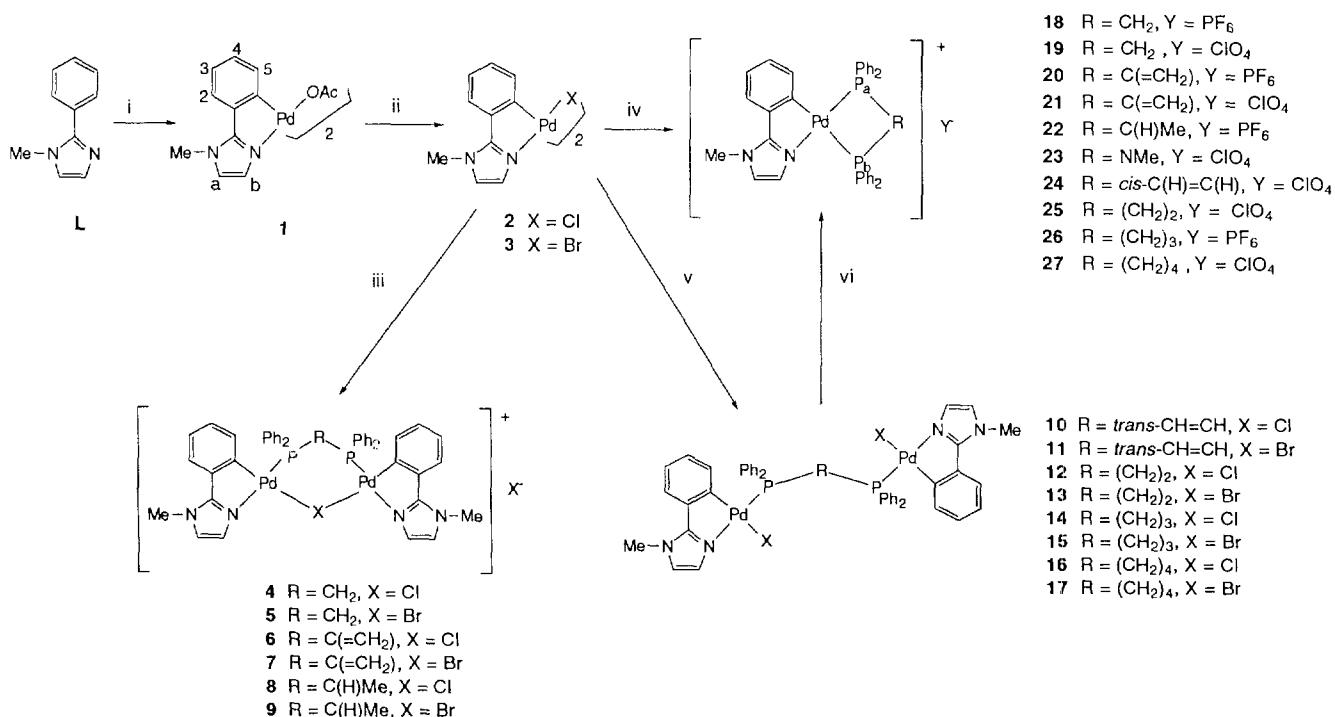^{a}Equivalent phosphorus (PPh$_3$) in a non-chelated analogue (Ref. [57]).

their ^{1}H NMR determination; thus, it was not possible to verify the presence of two isomers for these complexes from their ^{1}H NMR spectra. However, upon reaction of the latter with tertiary diphosphines, only one isomer was obtained (vide infra). Compounds **2** and **3** were characterized by elemental analysis and by the subsequent diphosphine derivatives.

2.2. Synthesis of dinuclear cyclometallated diphosphine-bridged compounds 4–17

The reaction of [{Pd[o-C$_6$H$_4$C=NC(H)=C(H)NMe]}(μ-X)]$_2$ (**2, 3**) with ter-

tiary diphosphines, in 1:1 molar ratio, in acetone at room temperature gave the dinuclear cyclometallated compounds **4–9** and **10–17**, respectively (Scheme 1).

The new compounds obtained are air-stable and soluble in the more common organic solvents, such as chloroform, ethanol, benzene, or tetrahydrofuran. They were characterized by elemental analysis, infrared spectra, ^{1}H and ^{31}P-{^{1}H} NMR in CDCl$_3$ (Section 4 and Table 1). The values of the conductivity data for **4–9** (130–155 Ω^{-1} cm^2 mol^{-1} in 10^{-3} mol dm^{-3} solutions in dry acetonitrile) indicate the compounds to be 1:1 electrolytes [42]. The larger 'bite' diphosphine impedes any possibility of a bridging halogen ligand between the metal atoms in compounds **10–17**. The ^{1}H NMR spectra of the compounds have been fully assigned. Selective proton decoupling allowed the correct identification of the aromatic protons; the H2 and the imidazole proton signals are occluded by the phosphine proton resonances (Table 1). The NMe group of the imidazole ring appears low-field shifted by ca. 0.3 ppm. This shift can be explained by the deshielding effect of the metallated phenyl ring and shows that both rings adopt a close-to-planar disposition. In the free ligand, the NMe value is close to the one found for 1-methylimidazole [43], suggesting the imidazole ring is tilted ca. 45° in this case. The ^{31}P-{^{1}H} NMR spectra display a singlet, suggesting the two phosphorus nuclei to be equivalent. For compounds **4–9**, these results are in accordance with a parallel disposition of the imidazole

18 R = CH$_2$, Y = PF$_6$
19 R = CH$_2$, Y = ClO$_4$
20 R = C(=CH$_2$), Y = PF$_6$
21 R = C(=CH$_2$), Y = ClO$_4$
22 R = C(H)Me, Y = PF$_6$
23 R = NMe, Y = ClO$_4$
24 R = cis-C(H)=C(H), Y = ClO$_4$
25 R = (CH$_2$)$_2$, Y = ClO$_4$
26 R = (CH$_2$)$_3$, Y = PF$_6$
27 R = (CH$_2$)$_4$, Y = ClO$_4$

4 R = CH$_2$, X = Cl
5 R = CH$_2$, X = Br
6 R = C(=CH$_2$), X = Cl
7 R = C(=CH$_2$), X = Br
8 R = C(H)Me, X = Cl
9 R = C(H)Me, X = Br

10 R = trans-CH=CH, X = Cl
11 R = trans-CH=CH, X = Br
12 R = (CH$_2$)$_2$, X = Cl
13 R = (CH$_2$)$_2$, X = Br
14 R = (CH$_2$)$_3$, X = Cl
15 R = (CH$_2$)$_3$, X = Br
16 R = (CH$_2$)$_4$, X = Cl
17 R = (CH$_2$)$_4$, X = Br

Scheme 1. Legend: (i) Pd(AcO)$_2$, HAcO, reflux, 3 h; (ii) NaCl or NaBr in aqueous acetone; (iii) 1 equiv. of Ph$_2$PRPPh$_2$ in acetone; (iv) 2 equiv. of Ph$_2$PRPPh$_2$ in acetone + NH$_4$PF$_6$ or NaClO$_4$; (v) 1 equiv. of Ph$_2$PRPPh$_2$ in acetone; (vi) 1 (only for **12–17**) equiv. of Ph$_2$PRPPh$_2$ in acetone + NH$_4$PF$_6$ + NaClO$_4$.

ligands (Scheme 1), i.e., each phosphorus atom is *trans* to the nitrogen atom and *cis* to the phenyl carbon atom of the organic ligand; in an antiparallel arrangement (one of the phosphorus atoms is *trans* to the phenyl carbon and *cis* to the nitrogen atom), the phosphorus resonances would appear as two doublets, a pattern arising from the presence of two nonequivalent phosphorus atoms. Similarly, the NMR results show that in compounds **10–17** the cyclometallated imidazole ligands are in an antiparallel disposition, with both phosphorus atoms *trans* to the nitrogen atoms. We may conclude that compounds **4–9** are symmetric across a two-fold axis and that compounds **10–17** are centrosymmetric. The aromatic protons of the metallated ring H3, H4 and H5 are high-field shifted, due to shielding caused by the phosphine phenyl rings, showing a *cis* geometry of the phosphorus atom and the metallated ring, as mentioned above, with the H5 resonance appearing at higher field than the H4 resonance. However, when one compares the NMR data for the free ligand and the acetato-bridged complex, a multiplet shifted to high field is observed for the latter; this shielding of the aromatic protons has been attributed to the flow of charge from the electron-rich metal atom into the aromatic ring (π-back bonding) [44]. In complexes **4** and **5**, no geminal coupling is observed for the methylene protons of the diphosphine, they are triplets due to coupling to the two equivalent phosphorus nuclei. In compounds **10** and **11**, the apparent triplet ca. 7.0 ppm was assigned to the PCH=CHP proton resonances (AA′XX′ spin system) with *N* ca. 38 Hz.

2.3. Synthesis of mononuclear cyclometallated compounds 18–27

The reaction of [{Pd[*o*-C₆H₄C=NC(H)=C(H)NMe]}(μ-X)]₂ (**2**, **3**) with tertiary diphosphines in 1:2 molar ratio, and ammonium hexafluorophosphate or sodium perchlorate as appropriate, in acetone at room temperature, gave the dinuclear cyclometallated compounds **18–27** (Scheme 1). The new compounds prepared are air-stable and soluble in chloroform, ethanol, benzene, or tetrahydrofuran. They were characterized by elemental analyses, infrared spectra, ¹H and ³¹P-{¹H} NMR in CDCl₃ (Section 4 and Table 1). The final products are the same whichever halide dimer is used in the reaction, as the halogen is exchanged by the hexafluorophosphate or perchlorate ion. The values of the conductivity data for **18–27** (130–155 Ω⁻¹ cm² mol⁻¹ in 10⁻³ mol dm⁻³ solutions in dry acetonitrile) indicate the compounds to be 1:1 electrolytes [42]. Compounds **25**, **26** and **27** could also be made by reaction of compounds **12–17** with the diphosphine in 1:1 molar ratio and ammonium hexafluorophosphate or sodium perchlorate as is the case. Analogously, compounds **18–22** were also synthesized

from **4–9** as appropriate. The aromatic protons were assigned as mentioned above, except H2 which was occluded by the phosphine resonances; they show the high-field shift observed in compounds **4–17**. However, in the ¹H NMR spectra of the mononuclear compounds, the H4 and H5 resonances appear in the inverse order as before, i.e., with the H5 signal at lower field than the H4 signal. This could be due to the different orientation of the phenyl rings on phosphorus, when the diphosphine ligand is bridging or chelating. The imidazole proton signals appear as doublets with ²*J*(HH) 1–2 ppm. The Hb proton signal is shifted to high field, the shift being most noticeable in compounds **19**, **24–27**; proton Ha is only significantly shifted to high field in compounds **25–27**. The ³¹P-{¹H} NMR spectra show the expected pair of doublets arising from a simple AX system for the two inequivalent phosphorus atoms. The assignment of the doublets was made on the assumption that a ligand of greater *trans* influence shifts the resonance of the phosphorus atoms *trans* to it to lower frequency [45]. This was confirmed by selective decoupling experiments. Selective irradiation at Pₐ yields a value of ⁴*J*(PH5) 9.2–9.6 Hz, while irradiating at P_b gives a value of ⁴*J*(PH5) ca. 7.1 Hz. Thus, based on the assumption that *trans*-⁴*J*(PH5) > *cis*-⁴*J*(PH5), we may assign P_b as being *trans* to the phenyl carbon atom and Pₐ to the nitrogen atom.

Garrou [46] has proposed that the ³¹P chemical shift is influenced by ring size. The data for compounds **18–27** are summarized in Table 2. The effect of unsaturation in the phosphine backbone in **24** gives only a slight variation of Δ_R. The four-membered ring compound **23** gives a positive Δ_R, similar to the values of the five-membered ring compounds, due to the presence
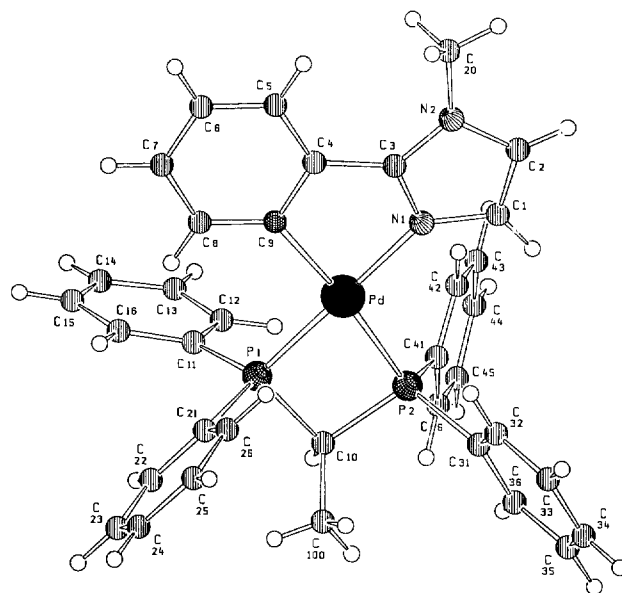

Fig. 1.

of the more electronegative nitrogen heteroatom in the phosphine ligand.

2.4. Structure of compound 22

Suitable crystals were grown by slowly evaporating a chloroform solution of the complex. Fig. 1 shows the molecular structure of **22** together with the numbering scheme, fractional coordinates and isotropic thermal parameters are listed in Table 3, while selected bond lengths and bond angles with estimated standard deviations are listed in Table 4.

The four coordinate palladium(II) atom is bonded to four atoms: two phosphorus atoms from a bidentate 1,1-bis(diphenylphosphino)ethane, and one nitrogen and the adjacent *ortho*-carbon of a *N*-(methyl)-2-phenylimidazole ligand in a square-planar coordination with a tetrahedral distortion. Thus, displacement from the least-squares plane of the coordination sphere (the plane formed by palladium and atoms directly bonded to it, P(1), P(2), N(1), C(9)) are as follows: Pd, 0.0406 Å; P(1), 0.0142 Å; P(2), −0.0133 Å; N(1), 0.0138 Å; C(9), −0.0147 Å. The metallacycle is essentially planar; the largest deviation from the mean plane determined by Pd, N(1), C(3), C(4), C(9) is 0.0007 Å for N(1) and −0.0005 Å for Pd. The torsion angles P(1)–Pd–P(2)–C(10), 4.09° and P(2)–Pd–P(1)–C(10), 4.11° show the planarity of the PdP$_2$C moiety. The five- and six-membered rings of the imidazole ligand are planar (r.m.s. deviations less than 0.0103 Å; deviation of C(20) from the five-membered ring by 0.0259 Å). The angle between the rings is 3.74° and they are approximately coplanar (2.40° and 1.81°) with the adjacent five-membered PdC$_3$N chelate ring. The four phenyl rings on the terminal phosphine are each planar (r.m.s. deviations 0.026, 0.003; 0.008, 0.002; 0.007, 0.001 and 0.020, 0.002 Å; deviations of phosphorus atoms by up to 0.13 Å) and the pairs are inclined at 55.43° and 59.88°. The donor atoms of the chelating imidazole occupy *cis* sites with a somewhat reduced bond angle [C(9)–Pd–N(1) 80.2(3)°] consequent upon chelation. This is reflected in the value of the C(8)–C(9)–Pd, 133.1(8)° angle. The sum of angles about the palladium atom is 359.9°. The Pd–C bond length, 2.056(9) Å, is within the expected value of 2.081 Å based on the sum of the covalent radii for carbon and palladium, 0.771 and 1.31 Å, respectively [47]. However, they are longer than those found in related complexes [38–41] where partial multiple-bond character of the Pd–C bond was assumed; in the present case, the *trans* influence of the phosphine ligand accounts for the observed lengthening. The Pd–N bond length, 2.056(9), which is longer than the single bond value of 2.01 Å calculated from the covalent radii of N (sp^2) 0.70 Å and palladium 1.31 Å, reflects the

Table 3
Final atomic coordinates (1×10^4) and isotropic thermal parameters (Å^2) for **22**

Atom	x	y	z	B (Å^2)
Pd	0.19662(6)	0.19374(6)	0.02793(4)	3.42(1)
P(1)	0.2155(2)	0.2942(2)	0.1199(1)	3.71(5)
P(2)	0.3714(2)	0.2099(2)	0.0561(1)	3.88(6)
N(1)	0.1800(6)	0.0987(6)	−0.0547(4)	3.8(2)
N(2)	0.0831(7)	0.0114(6)	−0.1298(4)	4.3(2)
C(1)	0.2434(8)	0.0464(9)	−0.0939(6)	4.9(3)
C(2)	0.1848(9)	−0.0097(9)	−0.1406(5)	5.0(3)
C(3)	0.0844(8)	0.0769(7)	−0.0760(5)	3.7(2)
C(4)	0.0054(7)	0.1216(7)	−0.0394(5)	3.5(2)
C(5)	−0.0987(7)	0.1055(8)	−0.0526(6)	4.4(2)
C(6)	−0.1656(8)	0.1493(9)	−0.0138(6)	5.3(3)
C(7)	−0.1322(8)	0.2103(9)	0.0398(6)	5.1(3)
C(8)	−0.0289(7)	0.2284(7)	0.0533(5)	4.0(2)
C(9)	0.0413(7)	0.1841(7)	0.0155(5	3.6(2)
C(10)	0.3571(7)	0.3006(8)	0.1256(6)	4.6(3)
C(11)	0.1804(7)	0.2496(7)	0.2045(5)	3.6(2)
C(12)	0.2310(9)	0.1715(8)	0.2346(6)	5.0(3)
C(13)	0.199(1)	0.1315(9)	0.2956(7)	6.5(3)
C(14)	0.119(1)	0.1700(9)	0.3272(6)	5.9(3)
C(15)	0.0656(9)	0.2466(8)	0.2949(7)	5.4(3)
C(16)	0.0956(8)	0.2863(8)	0.2338(6)	4.5(2)
C(20)	−0.003(1)	−0.0313(9)	−0.1692(7)	6.3(3)
C(21)	0.1712(7)	0.4159(7)	0.1099(5)	3.5(2)
C(22)	0.1803(9)	0.4790(8)	0.1656(6)	4.7(3)
C(23)	0.1567(9)	0.5743(8)	0.1554(6)	5.3(3)
C(24)	0.1255(9)	0.6065(8)	0.0887(7)	5.6(3)
C(25)	0.1175(9)	0.5452(9)	0.0317(7)	5.7(3)
C(26)	0.1410(8)	0.4480(8)	0.0427(6)	4.7(3)
C(31)	0.4535(7)	0.2578(8)	−0.0063(6)	4.3(2)
C(32)	0.4119(9)	0.282(1)	−0.0713(7)	5.9(3)
C(33)	0.469(1)	0.323(1)	−0.1205(8)	8.5(4)
C(34)	0.5710(9)	0.338(1)	−0.1038(7)	6.7(3)
C(35)	0.6140(9)	0.314(1)	−0.0403(7)	6.8(3)
C(36)	0.5559(8)	0.2743(9)	0.0100(7)	5.7(3)
C(41)	0.4345(7)	0.1103(8)	0.1028(6)	4.2(2)
C(42)	0.398(1)	0.0204(8)	0.0868(7)	5.9(3)
C(43)	0.441(1)	−0.057(1)	0.1237(7)	7.4(4)
C(44)	0.515(1)	−0.046(1)	0.1755(7)	7.2(4)
C(45)	0.555(1)	0.042(1)	0.1910(7)	6.3(3)
C(46)	0.5141(9)	0.1208(9)	0.1541(6)	5.1(3)
C(100)	0.405(1)	0.393(1)	0.121(1)	9.8(5)
P(3)	0.2533(3)	0.6699(3)	0.7743(2)	6.17(9)
F(19)	0.377	0.683	0.771	10.2(5)*
F(11)	0.335	0.722	0.737	9.9(5)*
F(2)	0.150	0.634	0.795	12.4(4)*
F(21)	0.197	0.615	0.838	9.9(8)*
F(3)	0.247	0.775	0.803	8.7(4)*
F(31)	0.173	0.757	0.786	12.9(7)*
F(4)	0.262	0.570	0.735	9.2(3)*
F(41)	0.314	0.578	0.778	13.0(8)*
F(5)	0.301	0.643	0.849	12.4(5)*
F(51)	0.295	0.720	0.844	12.1(9)*
F(6)	0.245	0.713	0.694	9.7(6)*
F(61)	0.179	0.681	0.707	14.3(6)*

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \cdot [a^2 \cdot B_{11} + b^2 \cdot B_{22} + c^2 \cdot B_{33} + ab(\cos\gamma) \cdot B_{12} + ac(\cos\beta) \cdot A_{13} + bc(\cos\alpha) \cdot B_{23}]$.

trans influence of the phosphine ligands. The distinct Pd–P bond lengths [Pd–P(1) 2.241(3), Pd–P(2) 2.342(3) Å] put forward the differing *trans* influences of the phenyl carbon and nitrogen atoms of the organic ligand; they are shorter than the sum of the single bond radii for palladium and phosphorus, 2.41 Å, suggesting some partial double bond between the palladium and phosphorus atoms may exist and is similar to others found earlier [48] (Table 5).

3. Conclusions

We have found that the cyclometallated Pd(II) dimer complexes readily react with tertiary diphosphines to give mononuclear 1:1 electrolyte compounds, dinuclear 1:1 electrolyte species, which are symmetric across a two-fold axis, and dinuclear molecular compounds, which are centrosymmetric; the dinuclear compounds may react further with more diphosphine to yield mononuclear species. Some diphoshine ligands such as

Table 4
Selected bond distances (Å) and angles (deg) for **22**

Bond distances			
Pd–P(1)	2.241(3)	N(2)–C(2)	1.41(1)
Pd–P(2)	2.342(3)	N(2)–C(3)	1.37(1)
Pd–N(1)	2.056(9)	C(7)–C(8)	1.39(1)
Pd–C(9)	2.056(9)	C(8)–C(9)	1.38(1)
P(1)–C(10)	1.87(1)	N(2)–C(20)	1.44(2)
P(1)–C(11)	1.82(2)	C(1)–C(2)	1.37(2)
P(1)–C(21)	1.81(1)	C(3)–C(4)	1.45(1)
P(2)–C(10)	1.86(1)	C(4)–C(5)	1.40(1)
P(2)–C(31)	1.80(1)	C(4)–C(9)	1.41(1)
P(2)–C(41)	1.82(2)	C(5)–C(6)	1.35(2)
N(1)–C(1)	1.38(1)	C(6)–C(7)	1.37(2)
N(1)–C(3)	1.33(1)	C(10)–C(100)	1.45(2)
Bond angles			
P(1)–Pd–P(2)	73.7(1)	N(2)–C(2)–C(1)	106(1)
P(1)–Pd–N(1)	178.6(2)	N(1)–C(3)–C(4)	117.5(8)
P(1)–Pd–C(9)	100.0(3)	C(2)–N(2)–C(20)	125(1)
P(2)–Pd–N(1)	106.0(2)	C(3)–C(4)–C(9)	114.3(8)
P(2)–Pd–C(9)	173.2(3)	C(5)–C(4)–C(9)	120(1)
N(1)–Pd–C(9)	80.2(3)	C(4)–C(5)–C(6)	121(1)
P(1)–C(10)–P(2)	95.1(5)	C(5)–C(6)–C(7)	120(1)
P(1)–C(10)–C(100)	118.8(9)	C(6)–C(7)–C(8)	120(2)
P(2)–C(10)–C(100)	120(1)	C(7)–C(8)–C(9)	121.4(9)
C(10)–P(1)–C(11)	107.2(5)	C(7)–C(8)–C(9)	121.4(9)
C(10)–P(1)–C(21)	106.0(5)	C(7)–C(8)–C(9)	121.4(9)
C(11)–P(1)–C(21)	108.1(5)	C(4)–C(9)–C(8)	117.8(8)
C(10)–P(2)–C(31)	108.4(6)	C(0)–C(4)–C(5)	125.8(9)
C(10)–P(2)–C(41)	104.4(5)	P(1)–C(11)–C(12)	119.1(9)
C(31)–P(2)–C(41)	109.2(5)	P(1)–C(11)–C(16)	120.0(7)
C(1)–N(1)–C(3)	108.7(8)	P(1)–C(21)–C(22)	121.3(7)
C(2)–N(2)–C(3)	107.3(8)	P(1)–C(21)–C(26)	118.1(8)
C(3)–N(2)–C(20)	129(1)	P(2)–C(31)–C(32)	118.1(8)
N(1)–C(1)–C(2)	108(1)	P(2)–C(31)–C(36)	123.4(9)
N(1)–C(3)–N(2)	109.3(9)	P(2)–C(41)–C(42)	117.3(8)
N(2)–C(3)–C(4)	133(1)	P(2)–C(41)–C(46)	123.7(9)

Table 5
Selected angles (deg) between normals to planes for **22**

Planes	Angle
1 and 2	1.66
1 and 3	2.40
1 and 4	1.81
1 and 5	0.99
2 and 3	2.81
2 and 4	3.35
2 and 5	2.58
3 and 4	3.74
3 and 5	2.25
4 and 5	1.49

Definition of planes
1	Pd, N(1), C(3), C(4), C(9)
2	P(1), P(2), N(1), C(9)
3	N(1), C(1), C(2), N(2), C(3)
4	C(4), C(5), C(6), C(7), C(8), C(9)
5	N(1), C(1), C(2), N(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9)

dppma and *cis*-dppe failed to give dinuclear compounds; we suggest this may be due to the *gem*-dimethyl effect in the former case, and to the *cis* geometry of the ligand in the latter one. The ^{31}P chemical shift of the chelated diphosphines is in agreement with ring size. The bonds at palladium, for compound **22**, reflect the differing *trans* influence of the carbon, nitrogen and phosphorus atoms.

4. Experimental

4.1. Materials and instrumentation

All the reactions were carried out in an atmosphere of dry nitrogen. Solvents were purified by the standard methods [49]. Palladium(II) acetate and the diphosphines $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp), and $Ph_2P(CH_2)_4PPh_2$ (dppb) were purchased from Aldrich-Chemie; $Ph_2PC(=CH_2)PPh_2$ (vdpp) [50], *cis*-$Ph_2PCH=CHPPh_2$ (*cis*-dppe) and *trans*-$Ph_2PCH=CHPPh_2$ (*trans*-dppe) [51], $Ph_2PC(H)(Me)PPh_2$ (1,1-dppe), and $Ph_2PN(Me)PPh_2$ (dppma) (Barrett and Shaw, private communication) were prepared according to procedures described elsewhere. Elemental analyses were carried out on a Carlo-Erba elemental analyzer, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs on a Perkin-Elmer 1330 spectrophotometer. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (1H) or 85% H_3PO_4 (^{31}P-{^{1}H}) and were recorded on a Bruker WM-250 spectrometer. All chemical shifts were reported downfield from standards.

Extreme **caution** should be taken when handling perchlorate salts.

4.2. Preparations

4.2.1. [Pd{o-C₆H₄C = NC(H) = C(H)NMe}(μ-O₂CMe)]₂ 1

1-Methyl-2-phenyl-imidazole, L, (0.23 g, 1.47 mmol) and palladium(II) acetate (0.3 g, 1.34 mmol) were added to 40 cm³ of glacial acetic acid to give a red solution, which was heated under reflux for 4 h. After cooling to room temperature, the acetic acid was removed under vacuum. The residue was diluted with water and extracted with dichloromethane. The combined extracts were dried over anhydrous sodium sulfate, filtered and concentrated in vacuo to give a yellow solid. This was chromatographed on a column packed with silica gel. Elution with dichloromethane/ethanol (1%) afforded product 1 as a yellow solid after concentration, which was recrystallized from dichloromethane/hexane. Yield: 76%. (Found: 1, C, 44.9; H, 3.9; N, 8.9. C₂₄H₂₄N₄O₄Pd₂ requires C, 44.6; H, 3.7; N, 8.7%.) IR: v_{as}(COO) 1570s, v_s(COO) 1410s cm⁻¹.

4.2.2. [Pd{o-C₆H₄C = NC(H) = C(H)NMe}(μ-Cl)]₂ 2

An aqueous solution of NaCl (ca. 10⁻² M) was added dropwise to 1 (0.1 g, 0.13 mmol) in acetone (ca. 5 cm³). The mixture was stirred for 1 h after which a yellow solid precipitated which was filtered off, washed with dichloromethane and dried in vacuo. Yield: > 95%. (Found: C, 40.3; H, 3.2; N, 9.7. C₂₀H₁₈N₄Cl₂Pd₂ requires C, 40.1; H, 3.0; N, 9.3%.) IR: v(Pd–Cl) 262, 242 cm⁻¹. Compound 3 was made in a similar fashion. Yield: > 95%. (Found: C, 35.2; H, 2.9; N, 8.4. C₂₀H₁₈N₄Br₂Pd₂ requires C, 34.9; H, 2.6; N, 8.1%.)

4.2.3. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe]}₂{μ-Ph₂PCH₂PPh₂}(μ-Cl)]Cl 4

To a suspension of 2 (0.050 g, 0.083 mmol) in acetone (ca. 15 cm³), Ph₂PCH₂PPh₂ (0.032 g, 0.083 mmol) was added. The mixture was stirred for 12 h at room temperature, after which a precipitate formed, which was filtered off, dried in vacuo, and recrystallized from dichloromethane/hexane. Yield: 76%. (Found: C, 55.1; H, 4.1; N, 6.0. C₄₅H₄₀Cl₂N₄P₂Pd requires C, 55.0; H, 4.1; N, 5.7%.) IR: v(Pd–Cl) 290, 235 cm⁻¹.

Similarly, the following cyclometallated complexes were prepared and isolated as solids.

4.2.4. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe]}₂{μ-Ph₂PCH₂PPh₂}(μ-Br)]Br 5

Yield 77%. (Found: C, 50.0; H, 3.9; N, 5.4. C₄₅H₄₀Br₂N₄P₂Pd₂ requires C, 50.4; H, 3.7; N, 5.2%.)

4.2.5. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe]}₂{μ-Ph₂PC(= CH₂)PPh₂}(μ-Cl)]Cl 6

Yield 76%. (Found: C, 56.0; H, 4.2; N, 5.9. C₄₆H₄₀Cl₂N₄P₂Pd₂ requires C, 55.5; H, 4.0; N, 5.6%.) IR: v(Pd–Cl) 282, 235 cm⁻¹.

4.2.6. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe]}₂{μ-Ph₂PC(= CH₂)PPh₂}(μ-Br)]Br 7

Yield 92%. (Found: C, 51.3; H, 4.0; N, 5.2. C₄₆H₄₀Br₂N₄P₂Pd₂ requires C, 50.9; H, 3.7; N, 5.1%.)

4.2.7. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe]}₂{μ-Ph₂PCH(Me)PPh₂}(μ-Cl)]Cl 8

Yield 74%. (Found: C, 55.3; H, 4.4; N, 5.8. C₄₆H₄₂Cl₂N₄P₂Pd₂ requires C, 55.4; H, 4.2; N, 5.6%.) IR: v(Pd–Cl) 275 cm⁻¹.

4.2.8. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe]}₂{μ-Ph₂PCH(Me)PPh₂}(μ-Br)]Br 9

Yield 80%. (Found: C, 51.0; H, 4.2; N, 5.0. C₄₆H₄₂Br₂N₄P₂Pd₂ requires C, 50.9; H, 3.9; N, 5.1%.)

4.2.9. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe](Cl)}₂{μ-Ph₂PCH = CHPPh₂}] 10

To a suspension of 2 (0.050 g, 0.083 mmol) in acetone (ca. 15 cm³), trans-Ph₂PCH=CHPPh₂ (0.033 g, 0.083 mmol) was added. The mixture was stirred for 2 h at room temperature, after which a precipitate formed, which was filtered off and dried in vacuo. Yield: 85%. (Found: C, 55.6; H, 5.3; N, 4.3. C₄₆H₄₀Cl₂N₄P₂Pd₂ requires C, 55.5; H, 5.6; N, 4.0%.)

Similarly, the following cyclometallated complexes were prepared and isolated as solids.

4.2.10. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe](Br)}₂{μ-Ph₂PCH = CHPPh₂}] 11

Yield 91%. (Found: C, 51.4; H, 5.4; N, 3.8. C₄₆H₄₀Br₂N₄P₂Pd₂ requires C, 50.9; H, 5.1; N, 3.7%.)

4.2.11. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe](Cl)}₂{μ-Ph₂P(CH₂)₂PPh₂}] 12

Yield 80%. (Found: C, 55.6; H, 4.3; N, 5.6. C₄₆H₄₂Cl₂N₄P₂Pd₂ requires C, 55.4; H, 4.2; N, 5.6%.) IR: v(Pd–Cl) 280 cm⁻¹.

4.2.12. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe](Br)}₂{μ-Ph₂P(CH₂)₂PPh₂}] 13

Yield 53%. (Found: C, 51.0; H, 4.2; N, 5.3. C₄₆H₄₂Br₂N₄P₂Pd₂ requires C, 50.9; H, 3.9; N, 5.1%.)

4.2.13. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe](Cl)}₂{μ-Ph₂P(CH₂)₃PPh₂}] 14

Yield 79%. (Found: C, 56.1; H, 4.6; N, 5.6. C₄₇H₄₄Cl₂N₄P₂Pd₂ requires C, 55.8; H, 4.3; N, 5.5%.) IR: v(Pd–Cl) 275 cm⁻¹.

4.2.14. [{Pd[o-C₆H₄C = NC(H) = C(H)NMe](Br)}₂{μ-Ph₂P(CH₂)₃PPh₂}] 15

Yield 75%. (Found: C, 51.5; H, 4.3; N, 5.4. C₄₇H₄₄Br₂N₄P₂Pd₂ requires C, 51.3; H, 4.0; N, 5.0%.)

4.2.15. [{Pd[o-C_6H_4C= NC(H)= C(H)NMe](Cl)}$_2${μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$}] 16

Yield 86%. (Found: C, 56.0; H, 4.7; N, 5.6. C$_{48}$H$_{46}$Cl$_2$N$_4$P$_2$Pd$_2$ requires C, 56.2; H, 4.5; N, 5.4%.) IR: ν(Pd–Cl) 275 cm^{-1}.

4.2.16. [{Pd[o-C_6H_4C = NC(H)= C(H)NMe](Br)}$_2${μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$}] 17

Yield 73%. (Found: C, 52.1; H, 4.3; N, 5.1. C$_{48}$H$_{46}$Br$_2$N$_4$P$_2$Pd$_2$ requires C, 51.9; H, 4.1; N, 5.0%.)

4.2.17. [{Pd[o-C_6H_4C = NC(H)= C(H)NMe]}(Ph$_2$-PCH$_2$PPh$_2$-P,P)][PF$_6$] 18

To a suspension of **2** (0.050 g, 0.083 mmol) in acetone (ca. 15 cm^3), Ph$_2$PCH$_2$PPh$_2$ (0.033 g, 0.083 mmol) was added. The mixture was stirred for 2 h at room temperature, after which ammonium hexafluorophosphate was added and the mixture was stirred for another 2 h; water (ca. 15 cm^3) was added and stirring continued for another 4 h and the precipitate formed was filtered off, dried in vacuo and recrystallized from dichloromethane/*n*-hexane.

Yield 96%. (Found: C, 53.1; H, 4.1; N, 3.3. C$_{35}$H$_{31}$F$_6$N$_2$P$_3$Pd requires C, 53.0; H, 3.9; N, 3.0%.)

Similarly, the following cyclometallated complexes were prepared and isolated as solids, using ammonium hexafluorophosphate or sodium perchlorate, as appropriate.

4.2.18. [{Pd[o-C_6H_4C = NC(H)= C(H)NMe]}(Ph$_2$-PCH$_2$PPh$_2$-P,P)][ClO$_4$] 19

Yield 90%. (Found: C, 56.2; H, 4.3; N, 3.9. C$_{36}$H$_{31}$ClN$_2$O$_4$P$_2$Pd requires C, 56.2; H, 4.1; N, 3.7%.)

4.2.19. [{Pd[o-C_6H_4C = NC(H)= C(H)NMe]}(Ph$_2$PC-(= CH$_2$)PPh$_2$-P,P)][PF$_6$] 20

Yield 83%. (Found: C, 54.0; H, 3.9; N, 3.5. C$_{35}$H$_{31}$F$_6$N$_2$P$_3$Pd requires C, 53.7; H, 3.8; N, 3.4%.)

4.2.20. [{Pd[o-C_6H_4C = NC(H)= C(H)NMe]}(Ph$_2$PC-(= CH$_2$)PPh$_2$-P,P)][ClO$_4$] 21

Yield 93%. (Found: C, 56.7; H, 4.2; N, 3.8. C$_{36}$H$_{33}$ClN$_2$O$_4$P$_2$Pd requires C, 56.9; H, 4.1; N, 3.6%.)

4.2.21. [{Pd[o-C_6H_4C = NC(H)= C(H)NMe]}(Ph$_2$-PCH(Me)PPh$_2$-P,P)][PF$_6$] 22

Yield 86%. (Found: C, 54.0; H, 4.2; N, 3.5. C$_{35}$H$_{33}$F$_6$N$_2$P$_3$Pd requires C, 53.5; H, 4.1; N, 3.4%.)

4.2.22. [{Pd[o-C_6H_4C = NC(H)= C(H)NMe]}(Ph$_2$PN-(Me)PPh$_2$-P,P)][PF$_6$] 23

Yield 95%. (Found: C, 55.5; H, 4.5; N, 5.5. C$_{36}$H$_{31}$F$_6$N$_2$P$_3$Pd requires C, 55.1; H, 4.2; N, 5.5%.)

4.2.23. [{Pd[o-C_6H_4C = NC(H)= C(H)NMe]}(Ph$_2$-PCH = CHPPh$_2$-P,P)][ClO$_4$] 24

Yield 96%. (Found: C, 56.8; H, 3.9; N, 3.7. C$_{37}$H$_{32}$ClN$_3$O$_4$P$_2$Pd requires C, 56.9; H, 4.1; N, 3.6%.)

4.2.24. [{Pd[o-C_6H_4C = NC(H)= C(H)NMe]}(Ph$_2$P-(CH$_2$)$_2$PPh$_2$-P,P)][ClO$_4$] 25

Yield 90%. (Found: C, 56.9; H, 4.0; N, 3.5. C$_{37}$H$_{34}$ClN$_3$O$_4$P$_2$Pd requires C, 56.7; H, 4.3; N, 3.6%.)

4.2.25. [{Pd[o-C_6H_4C = NC(H)= C(H)NMe]}(Ph$_2$P-(CH$_2$)$_3$PPh$_2$-P,P)][PF$_6$] 26

Yield 95%. (Found: C, 54.1; H, 4.4; N, 3.6. C$_{38}$H$_{35}$F$_6$N$_2$P$_3$Pd requires C, 54.1; H, 4.2; N, 3.4%.)

4.2.26. [{Pd[o-C_6H_4C = NC(H)= C(H)NMe]}(Ph$_2$P-(CH$_2$)$_4$PPh$_2$-P,P)][ClO$_4$] 27

Yield 97%. (Found: C, 57.6; H, 5.0; N, 3.7. C$_{39}$H$_{38}$ClN$_3$O$_4$P$_2$Pd requires C, 57.8; H, 4.7; N, 3.5%.)

4.3. X-ray diffraction analysis

A suitable crystal for X-ray diffraction study of **22** was mounted on a glass fiber in an Enraf-Nonius CAD4 diffractometer for data collection. Cell constants were obtained by least-squares refinement of the data for 25 reflections in the range $8.48 < \theta < 11.90°$. Data were

Table 6
Summary of crystallographic data for **22**

Crystal size (mm)	0.20×0.25×0.30
Formula	C$_{36}$H$_{33}$F$_6$N$_2$P$_3$Pd
Formula weight	806.99
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	13.247(2) Å
b, Å	14.025(3) Å
c, Å	18.995(2) Å
β, (°)	94.94(1)°
Volume (Å^3)	3515.7(9)
Z	4
Density (calculated) (g cm^{-3})	1.525
$F(000)$	1632
Absorption coefficient (cm^{-1})	7.134
θ range for data collection	3 to 27°
No. of reflections collected	8379
No. of independent reflections	7543 [R_{int} = 0.030]
No. of reflections with $I > 3.0\sigma(I)$	3171
No. of parameters refined	404
R	0.060
R_w	0.063
Ratio of max. LS shift to e.s.d. (Δ/σ)	0.001
Max. residual elect. dens. (e Å^{-3})	0.671
Error in an observation of unit weight	3.597
Secondary extinction coefficient	9.476×10^{-9}

collected at room temperature by the $\omega/2\theta$ scan technique using graphite monochromatized MoK_α ($\lambda = 0.7093$ Å) radiation and were corrected for Lorentz and polarization effects. An empirical absorption correction was also made [52]. A summary of the crystal data, experimental details and refinement results is shown in Table 6.

The structure was solved by direct methods and refined on F by a full-matrix least-squares procedure. Anisotropic displacement parameters were used for all non-hydrogen atoms except those of the PF_6 anion. The PF_6 geometry is not clearly resolved; the best configuration around the phosphorus position gives a statistical disorder with twelve F positions with partial occupancy. Atoms of the disordered PF_6 unit were refined isotropically with positional parameters fixed, and the multiplicities for the twelve peaks also were refined. The hydrogen atoms were calculated at idealized positions and added to the structure factors calculations as fixed contributions ($B_{iso} = 5.0$ Å^2) but their positional parameters were not refined. Computations were performed by means of VAX-SDP [53], SHELXS86 [54], and SCHAKAL [55] programs on a DEX MICROVAXII computer. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography [56].

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