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# Synthesis and reactivity of $[Pd_2L_2R_2(\mu\text{-}OH)_2]$-type complexes ($L = PEt_3$ or $PPh_3$; R = Me, $PhCH_2$ or Ph). Crystal structure of $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)(\mu\text{-}NHC_6H_4OMe\text{-}p)]$

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The metathesis of $Cl^-$ by $OH^-$ in $[Pd_2(PEt_3)_2R_2(\mu\text{-}Cl)_2]$ gave the binuclear hydroxo complexes $[Pd_2(PEt_3)_2R_2(\mu\text{-}OH)_2]$ (R = Me or $PhCH_2$) which in $CDCl_3$ solution exist as 1 : 1 mixtures of *syn* and *anti* isomers. They reacted with 3,5-dimethylpyrazole (Hdmpz) in 1 : 2 molar ratio to yield the corresponding azolate complexes *anti*-$[Pd_2(PEt_3)_2R_2(\mu\text{-}dmpz)_2]$ and with oxalic acid ($H_2ox$), in 1 : 1 molar ratio, to afford the corresponding oxalate complexes *anti*-$[Pd_2(PEt_3)_2R_2(\mu\text{-}ox)]$. The cleavage of the OH bridges of the di-μ-hydroxo complexes yields the mononuclear $[Pd(PEt_3)_2R(OH)]$ which in solution are present as 1 : 1 mixtures of *cis* and *trans* isomers. Binuclear μ-hydroxo-μ-amido palladium complexes $[Pd_2L_2R_2(\mu\text{-}OH)(\mu\text{-}NHR'')_2]$ (R = Me, $L = PEt_3$; R = Ph, $L = PPh_3$; R″ = Ph, $C_6H_4Me\text{-}p$, $C_6H_4OMe\text{-}p$, $C_6H_4Cl\text{-}p$ or $C_6H_4NO_2\text{-}p$) have been prepared by reaction of $[Pd_2L_2R_2(\mu\text{-}OH)_2]$ with the corresponding aromatic amine $R''NH_2$. The NMR data indicate that the isolated complexes are the *anti* isomers. The crystal structure of complex $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)(\mu\text{-}NHC_6H_4OMe\text{-}p)]$ has been established; the $Pd_2ON$ ring is severely bent.

Since the $OH^-$ ligand is an σ,π-electron donor there has been the deceptive perception that late transition-metal hydroxides are unstable because π donation to electron-rich metal centres should be unfavorable. Until recently the only reported organopalladium hydroxo complexes were of the type $[Pd(PPh_3)_2R(OH)]$, prepared by Yoshida *et al.*[1] Recent work, however, suggests that late metal–hydroxide bonds are not particularly weak relative to M–H or M–C bonds, but the presence of lone electron pairs gives these compounds modes of reactivity not normally available to metal alkyls and hydrides.[2] In fact, their reactivity and catalytic properties have stimulated the recent surge of interest in the chemistry of late-metal hydroxides.[2,3]

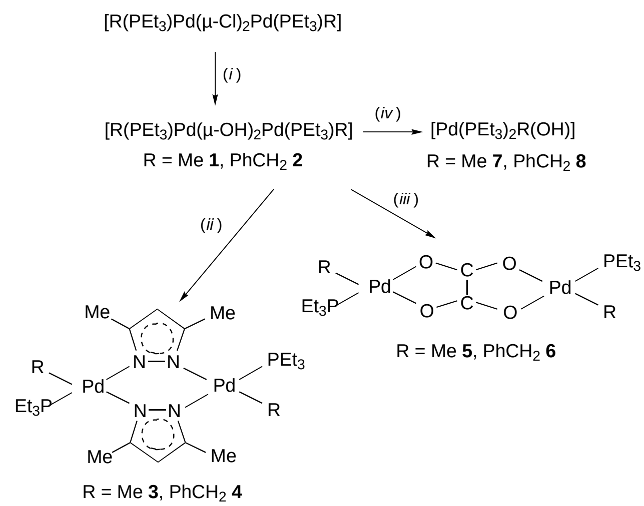
Binuclear organopalladium hydroxo complexes $[Pd_2R_4(\mu\text{-}OH)_2]^{2-}$ ($R = C_6F_5$,[4] $C_6Cl_5$,[5] or $C_6F_3H_2$-2,4,6[6]), $[Pd_2L_2R_2(\mu\text{-}OH)_2]$ ($L = PPh_3$; R = Me,[7] Ph,[8] $C_6F_5$ or $C_6Cl_5$[9]) and $[Pd_2(L\text{–}L^-)_2(\mu\text{-}X)(\mu\text{-}OH)]$ [$L\text{–}L^-$ = 8-quinolylmethyl, X = carboxylate;[10] $L\text{–}L^-$ = 2-(dimethylaminomethyl)phenyl, X = Br[11]] are known. The reaction of a labile precursor such as *cis*-$[MR_2(NCPh)_2]$ with $[NBu_4]OH$ or the metathesis of $X^-$ by $OH^-$ in a binuclear $M(\mu\text{-}X)_2M$ complex are the methods used for the preparation of hydroxo complexes.[12] The equilibrium between $[Pd(PR_3)_2R'(OH)]$ and $[Pd_2(PR_3)_2R'_2(\mu\text{-}OH)_2]$ has been investigated very recently.[13]

The basic character of these hydroxo complexes allows the preparation of a variety of mono- and bi-nuclear complexes by reaction with a protic electrophile ($M\text{–}OH + HX \longrightarrow M\text{–}X + H_2O$). For example, aryloxo[14] and amido[15,16] complexes of palladium have been prepared by reaction of a hydroxopalladium complex with phenols and amines, respectively. The binuclear complex $[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ is an efficient basic catalyst for the cyclotrimerization of malononitrile to 4,6-diamino-2-cyanomethylpyridine-3,5-dicarbonitrile.[17]

In this paper we report the preparation of hydroxopalladium complexes of the type $[Pd_2(PEt_3)_2R_2(\mu\text{-}OH)_2]$ and their reactions with 3,5-dimethylpyrazole, oxalic acid, triethylphosphine and a number of arylamines.

## Results and Discussion

In acetone or acetone–methanol the reaction of $[Pd_2(PEt_3)_2R_2(\mu\text{-}Cl)_2]$ with $[NBu_4]OH(aq)$ leads to the formation of the bis(μ-hydroxo) complexes **1** and **2** shown in Scheme 1. The metathesis of $Cl^-$ by $OH^-$ occurs smoothly at room temperature and the hydroxo complexes are isolated in *ca.* 90% yields. The presence of the hydroxo ligand is manifested by the observation of characteristic IR absorptions in the vicinity of 3500 $cm^{-1}$ and of high-field proton resonances at δ −1.4 (**1**) and −3.3 (**2**). The NMR data (Table 1) reveal that complexes **1** and **2** exist in $CDCl_3$ solution as 1 : 1 mixtures of *syn* and *anti* isomers: two $^{31}P$ resonances are found for the phosphines and two $^1H$ and $^{13}C$ resonances are also observed for the $CH_3Pd$ and $CH_2P$ groups. For the methyl nickel analogue $[Ni_2(PMe_3)_2$-




**Scheme 1** (*i*) $OH^-$; (*ii*) Hdmpz (3,5-dimethylpyrazole); (*iii*) $H_2ox$ (oxalic acid); (*iv*) $PEt_3$

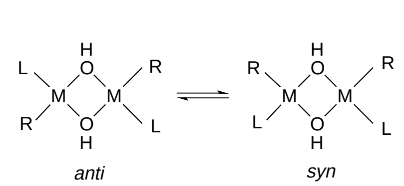


**Table 1** The NMR data ($J$ in Hz) for the palladium complexes **1**–**8** (in $CDCl_3$)

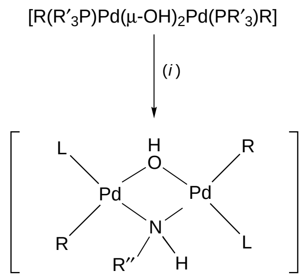
| Complex | $^1H$ δ($SiMe_4$) | $^{13}C$ δ($SiMe_4$) | $^{31}P$ δ($H_3PO_4$) |
|---|---|---|---|
| **1** | 1.6 (m, 24 H, $CH_2P$) | 16.1 (d, $CH_2P$, $J_{CP}$ 27.7) | 28.71 (s) |
| | 1.3 (m, 36 H, $CH_3CH_2P$) | 15.5 (d, $CH_2P$, $J_{CP}$ 29.4) | 28.60 (s) |
| | 0.46 (s, 6 H, $CH_3Pd$) | 8.1 (s, $CH_3CH_2P$) | |
| | 0.39 (s, 6 H, $CH_3Pd$) | −0.2 (br, $CH_3Pd$) | |
| | −1.4 (br, OH) | −3.1 (br, $CH_3Pd$) | |
| **2** | 7.0 (m, 20 H, $C_6H_5$) | 128.4 (br s, CH of $PhCH_2$) | 28.49 (s) |
| | 2.52 (d, 4 H, $CH_2Pd$, $J_{PH}$ 3.8) | 128.1 (br s, CH of $PhCH_2$) | 28.18 (s) |
| | 2.47 (d, 4 H, $CH_2Pd$, $J_{PH}$ 4.0) | 123.6 (br s, CH of $PhCH_2$) | |
| | 1.6 (m, 24 H, $CH_2P$) | 23.5 (br, $CH_2Pd$) | |
| | 1.0 (m, 36 H, $CH_3CH_2P$) | 20.6 (br, $CH_2Pd$) | |
| | −2.3 (br, OH) | 16.0 (br, $CH_2P$) | |
| | −2.4 (br, OH) | 15.4 (br, $CH_2P$) | |
| | −3.3 (br, OH) | 8.1 (s, $CH_3CH_2P$) | |
| **3** | 5.46 (s, 2 H, 4-H of dmpz) | 145.4 (s, 3-C of dmpz) | 25.07 (s) |
| | 2.17 (s, 6 H, Me of dmpz) | 144.7 (s, 5-C of dmpz) | |
| | 2.08 (s, 6 H, Me of dmpz) | 101.4 (s, 4-C of dmpz) | |
| | 1.56 (m, 12 H, $CH_2P$) | 15.8 (d, $CH_2P$, $J_{CP}$ 27.7) | |
| | 1.07 (m, 18 H, $CH_3CH_2P$) | 14.2 (s, Me of dmpz) | |
| | 0.15 (d, 6 H, $CH_3Pd$, $J_{PH}$ 4.1) | 13.7 (s, Me of dmpz) | |
| | | 8.2 (s, $CH_3CH_2P$) | |
| | | −8.8 (br, $CH_3Pd$) | |
| **4** | 7.0 (m, 10 H, $C_6H_5$) | 171.7 (s, $CCH_2$ of $PhCH_2$) | 22.43 (s) |
| | 5.33 (s, 2 H, 4-H of dmpz) | 145.6 (s, 3- and 5-C of dmpz) | |
| | 3.00 (d, 2 H, $CH_APd$, $J_{HH}$ 8.9) | 128.7 (s, CH of $PhCH_2$) | |
| | 2.44 (dd, 2 H, $CH_BPd$, $J_{HH} = J_{PH}$ 8.9) | 127.6 (s, CH of $PhCH_2$) | |
| | 2.19 (s, 6 H, Me of dmpz) | 122.3 (s, CH of $PhCH_2$) | |
| | 1.75 (s, 6 H, Me of dmpz) | 101.8 (d, 4-C of dmpz, $J_{CP}$ 3.2) | |
| | 1.57 (m, 12 H, $CH_2P$) | 17.0 (d, $CH_2Pd$, $J_{CP}$ 6.1) | |
| | 1.09 (m, 18 H, $CH_3CH_2P$) | 15.5 (d, $CH_2P$, $J_{CP}$ 27.3) | |
| | | 14.5 (s, Me of dmpz) | |
| | | 13.4 (s, Me of dmpz) | |
| | | 8.7 (s, $CH_3CH_2P$) | |
| **5** | 1.65 (m, 12 H, $CH_2P$) | 15.7 (d, $CH_2P$, $J_{CP}$ 30.7) | 37.22 (s) |
| | 1.11 (m, 18 H, $CH_3CH_2P$) | 8.1 (s, $CH_3CH_2P$) | |
| | 0.48 (s, 6 H, $CH_3Pd$) | −6.3 (br, $CH_3Pd$) | |
| **6*** | 7.6 (m, 4 H, $C_6H_5$) | 129.0 (s, CH of $PhCH_2$) | 32.59 (s) |
| | 7.0 (m, 6 H, $C_6H_5$) | 128.2 (s, CH of $PhCH_2$) | |
| | 3.06 (br s, 4 H, $CH_2Pd$) | 124.2 (s, CH of $PhCH_2$) | |
| | 1.18 (m, 12 H, $CH_2P$) | 19.5 (d, $CH_2Pd$, $J_{CP}$ 3.8) | |
| | 0.68 (m, 18 H, $CH_3CH_2P$) | 14.7 (d, $CH_2P$, $J_{CP}$ 29.4) | |
| | | 7.6 (s, $CH_3CH_2P$) | |
| **7** | 1.75 (m, 24 H, $CH_2P$) | 14.6 (t, $CH_2P$, $J_{CP}$ 12.7) | 15.95 (s) |
| | 1.05 (m, 36 H, $CH_3CH_2P$) | 14.0 (t, $CH_2P$, $J_{CP}$ 12.5) | 14.87 (s) |
| | 0.22 (t, 3 H, $CH_3Pd$, $J_{PH}$ 5.8) | 8.3 (s, $CH_3CH_2P$) | |
| | 0.11 (t, 3 H, $CH_3Pd$, $J_{PH}$ 6.0) | 8.2 (s, $CH_3CH_2P$) | |
| | | −6.6 (t, $CH_3Pd$, $J_{CP}$ 4.0) | |
| | | −9.2 (t, $CH_3Pd$, $J_{CP}$ 4.7) | |
| **8** | 7.3 (m, 4 H, $C_6H_5$) | 17.9 (s, $CH_2Pd$) | 13.61 (s) |
| | 7.0 (m, 6 H, $C_6H_5$) | 15.6 (s, $CH_2Pd$) | 12.35 (s) |
| | 2.69 (t, 2 H, $CH_2Pd$, $J_{PH}$ 7.1) | 14.6 (t, $CH_2P$, $J_{CP}$ 12.6) | |
| | 2.59 (t, 2 H, $CH_2Pd$, $J_{PH}$ 7.1) | 13.9 (t, $CH_2P$, $J_{CP}$ 12.4) | |
| | 1.71 (m, 12 H, $CH_2P$) | 8.3 (s, $CH_3CH_2P$) | |
| | 1.00 (m, 18 H, $CH_3CH_2P$) | 8.2 (s, $CH_3CH_2P$) | |

* In $C_6D_6$.

$Me_2(\mu\text{-}OH)_2]$ a mixture of *syn* and *anti* isomers was also found in a ratio depending on the polarity of the solvent,[18] whereas the benzylnickel complex $[Ni_2(PMe_3)_2(CH_2Ph)_2(\mu\text{-}OH)_2]$ [19] and the perhalogenophenyl complexes $[Pd_2(PPh_3)_2R_2(\mu\text{-}OH)_2]$ (R = $C_6F_5$ or $C_6Cl_5$)[9] were exclusively *anti* isomers. The recently reported complex $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)_2]$ exists in solution as a 4 : 1 mixture of *anti* and *syn* isomers, although the *anti* geometry for this complex was found in the crystalline state.[8]

The reaction of the bis(hydroxo) complexes $[M_2R_4(\mu\text{-}OH)_2]^{2-}$ (M = Ni, Pd or Pt) with protic electrophiles (HL) has previously been used for the synthesis of complexes of the types $[M_2R_4(\mu\text{-}L)_2]^{2-}$.[4,17,20,21] Of these protic electrophiles, azoles have been most used because by deprotonation they produce the very versatile azolate anions which usually act as exobidentate ligands.[22] When complexes **1** and **2** were treated with 3,5-dimethylpyrazole (Hdmpz) in methanol, in a 1 : 2 molar ratio, they yielded the corresponding azolate-bridged complexes $[Pd_2(PEt_3)_2R_2(\mu\text{-}dmpz)_2]$ (R = Me **3** or $PhCH_2$ **4**).

The single resonance observed in the $^{31}P$ NMR spectra of complexes **3** and **4** indicates that these are found exclusively as a single isomer in $CDCl_3$ solution. If the *syn* symmetry is assigned to **3** and **4** the CH group of the dmpz ring should give two $^1H$ and two $^{13}C$ resonances in the respective spectra. The experimental NMR data (Table 1) indicate that in $CDCl_3$ solution only the *anti* isomers are present because a single signal is observed for the CH group. Note that the two resonances observed in both the $^1H$ and the $^{13}C$ NMR spectra for the Me substituents of the dmpz ligand as well as the two different $^{13}C$ signals for $C^3$ and $C^4$ of the dmpz ring cannot be used to differentiate the *anti* and *syn* isomers. The $^1H$ NMR spectrum of compound **4** also shows that the $CH_2$ protons of the benzyl ligand are diastereotopic, a doublet and a doublet of doublets




**9** R = Me, L = $PEt_3$, R″ = $C_6H_5$
**10** $p$-$MeC_6H_4$
**11** $p$-$MeOC_6H_4$
**12** $p$-$ClC_6H_4$
**13** $p$-$O_2NC_6H_4$
**14** R = Ph, L = $PPh_3$, R″ = $C_6H_5$
**15** $p$-$MeC_6H_4$
**16** $p$-$MeOC_6H_4$
**17** $p$-$ClC_6H_4$
**18** $p$-$O_2NC_6H_4$

**Scheme 2** (*i*) $NH_2R''$

being observed; the last signal is seen as a pseudo-triplet due to the accidental coincidence of the coupling constants involved ($J_{HH} = J_{PH} = 8.9$ Hz). On irradiation of the doublet at δ 3.00 the original pseudo-triplet was transformed into a doublet ($J_{PH} = 8.9$ Hz) and on irradiation of the pseudo-triplet at δ 2.44 the original doublet was seen as a singlet. The absence of a symmetry plane in complex **4** may be a consequence of the folded basket structure which is characteristic of this type of complex.[23]

The reactions of the di-μ-hydroxo complexes **1** and **2** with oxalic acid ($H_2ox$) in 1 : 1 molar ratio lead to the formation of the corresponding oxalate complexes $[Pd_2(PEt_3)_2R_2(\mu\text{-ox})]$ (R = Me **5** or $PhCH_2$ **6**). Their IR spectra exhibit a strong absorption at 1600 $cm^{-1}$ arising from the asymmetric OCO stretching mode of doubly bridging tetradentate oxalate.[24] The NMR data show the presence of only one isomer. Accordingly, we suggest for them the structure shown in Scheme 1, which is similar to that found in $[Ni_2(PPh_3)_2Me_2(\mu\text{-ox})]$ or $[Pd_2(SBu_2)_2Ph_2(\mu\text{-ox})]$.[25,26]

Complexes **1** and **2** readily undergo bridge-cleavage reactions with $PEt_3$ to give the mononuclear hydroxo complexes $[Pd(PEt_3)_2R(OH)]$ (R = Me **7** or $PhCH_2$ **8**) shown in Scheme 1. Their NMR spectra (Table 1) indicate that both compounds exist in solution as 1 : 1 mixtures of *cis* and *trans* isomers. The virtual coupling gives rise to a triplet for the phosphine methylene group in the $^{13}C$ NMR spectrum of the *trans* isomers. Methyl(aryloxo)palladium complexes of the type $[Pd(PEt_3)_2R(OR'')]$ have been shown by $^1H$ NMR spectroscopy to exist in solution in the *trans* configuration with M–Me signals (δ 0.19) as triplets due to coupling with two magnetically equivalent phosphorus nuclei.[27]

The reactions of $[Pd_2L_2R_2(\mu\text{-OH})_2]$ with aniline and some *p*-substituted anilines ($p$-$XC_6H_4NH_2$; X = H, Me, MeO, Cl or $NO_2$) have also been studied. The reactions take place in dichloromethane, in 1 : 1 molar ratio, and the corresponding binuclear μ-hydroxo–μ-amido palladium complexes **10**–**18** (Scheme 2) are obtained in 67–80% yields. The analytical data for these air-stable compounds are consistent with the proposed formulae. Late transition-metal amides are still relatively uncommon[28–30] and the recent interest in their chemistry stems from their potential use to facilitate the formation of carbon–nitrogen bonds through the insertion of unsaturated organic molecules into the metal–nitrogen bond.† Monomeric arylamido and dimeric alkylamido complexes of palladium that produce arylamines through carbon–nitrogen bond-forming reductive elimination have been isolated.[32,33]

The previously reported mixed amide–pentafluorophenyl palladium complexes $[Pd_2(PPh_3)_2(C_6F_5)_2(\mu\text{-OH})(\mu\text{-NHR}'')]$[15] are characterized by an *anti* structure, whereas the mixed acetate–amide cyclopalladated complexes $[\{Pd_2(L\text{–}L)_2(\mu\text{-}O_2CMe)(\mu\text{-NHR}'')]$ (L–L = 8-quinolylmethyl)[10] are characterized by a *syn* structure for the C,N chelate. The two resonances observed in the $^{31}P$ NMR spectra of the new palladium complexes **10**–**18** (Table 2), together with the observation of only one set of $^1H$ resonances for the arylamide ligand, are consistent with the *anti* structure proposed for them in Scheme 2. Two IR bands at 3610–3600 and 3320–3300 $cm^{-1}$ are assigned to the OH and NH stretching vibrations, respectively. The presence of the hydroxo ligand is also established by the observation of a high-field proton resonance at δ *ca.* −2.1 in the spectra of complexes **15**–**18**, which appears as a doublet due to coupling to the $^{31}P$ nucleus *trans* to it; this OH resonance could not be detected for **10**–**14**. Similarly, a broad $^1H$ resonance was observed for the amide NH group only in the spectra of **15**–**18**. On addition of deuteriated water to a solution of complex **18** in $CDCl_3$ the NH and OH resonances disappeared. Two 1 : 1 doublets for the methyl protons of **10**–**14** provide further evidence of their *anti* structures.

Attempts to prepare bis(μ-amido) complexes by treating the $[Pd_2L_2R_2(\mu\text{-OH})_2]$ complexes (R = Me, L = $PEt_3$; R = Ph, L = $PPh_3$) with 2 molar equivalents of the corresponding aromatic amine were unsuccessful, possibly due to kinetic factors.

The structure of complex **16** was determined by X-ray diffraction (Table 3, Fig. 1). The *anti* structure is further confirmed. Co-ordination at each of the palladium centres is approximately square planar, with predictable narrowing of the N–Pd–O angles (80.5, 80.9°) to accommodate the bridged structure. The angle between the co-ordination planes is 52.5°, indicating a substantially bent structure. Predictably the Pd–N distance when the N is *trans* to the aryl ligand is longer (2.147 Å) than when it is *trans* to phosphorus (2.099 Å). Similar differences in the Pd–O distances are also noted.

A number of complexes of the type $[Pd_2L_4(\mu\text{-X})(\mu\text{-Y})]$ and platinum analogues have been structurally characterized, and complexes with either a planar or a puckered $M_2XY$ ring are known. Thus $[Pd_2(N_3)_6]^{2-}$,[35] $[Pt_2(NH_3)_4(\mu\text{-OH})_2]CO_3\cdot 2H_2O$,[36] $[Pt_2(dmso)_4(\mu\text{-OH})_2][ClO_4]_2$ (dmso = dimethyl sulfoxide),[37] $[Pt_2(C_4H_8SO)(\mu\text{-OH})_2][NO_3]_2$,[38] $[NBu_4]_2[Pd_2(C_6F_5)_4(\mu\text{-OH})_2]$[4] and $[NBu_4]_2[Pt_2(dppf)(\mu\text{-OH})_2][BF_4]_2$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene][39] all have planar $M_2X_2$ cores. However, $[NBu_4]_2[Pd_2(dppe)(\mu\text{-OH})_2]X_2$ (dppe = $Ph_2PCH_2$-

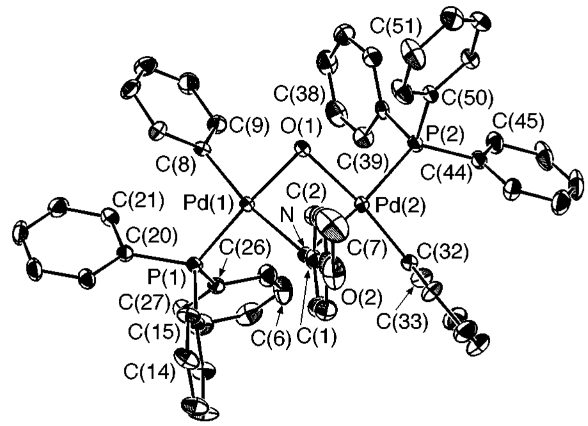



**Fig. 1** An ORTEP[34] drawing of complex **16** showing the non-H atoms as 20% thermal vibration ellipsoids. The phenyl groups are numbered sequentially around the rings and only the first two atoms of each ring are labelled

† For example, the reported reaction of amines with hydroxo-bridged palladium(II) and platinum(II) complexes in the presence of $CS_2$ to give dialkyldithiocarbamate complexes, $>M(\mu\text{-OH})_2M< + 2\ RNH_2 + 2\ CS_2 \longrightarrow 2{>}MS_2CNHR_2 + 2\ H_2O$, might be the insertion of $CS_2$ into the M–N bond of an intermediate amido complex.[31]

**Table 2** The NMR data ($J$ in Hz) for the amide complexes (in $CDCl_3$)

| Complex | $^1H$ δ($SiMe_4$) | $^{31}P$ δ($H_3PO_4$) |
|---|---|---|
| **9** | 7.21 [d, 1 H, $H_o$, $J(H_oH_m)$ 8.1] | 25.3 (s) |
| | 7.17 [d, 1 H, $H_o$, $J(H_oH_m)$ 8.1] | 24.5 (s) |
| | 7.00 (m, 2 H, $H_m$) | |
| | 6.63 (dd, 2 H, $H_p$, $J$ 7.7) | |
| | 1.54 (m, 12 H, $CH_2P$) | |
| | 1.06 (m, 18 H, $CH_3CH_2P$) | |
| | 0.18 (d, 3 H, $CH_3Pd$, $J_{PH}$ 3.4) | |
| | 0.11 (d, 3 H, $CH_3Pd$, $J_{PH}$ 3.4) | |
| **10** | 7.13 [d, 1 H, $H_o$, $J(H_oH_m)$ 8.0] | 24.9 (s) |
| | 7.09 [d, 1 H, $H_o$, $J(H_oH_m)$ 8.0] | 24.1 (s) |
| | 6.81 [d, 2 H, $H_m$, $J(H_oH_m)$ 8.0] | |
| | 2.15 (s, 3 H, $CH_3$ of $p$-$MeC_6H_4$) | |
| | 1.55 (m, 12 H, $CH_2P$) | |
| | 1.08 (m, 18 H, $CH_3CH_2P$) | |
| | 0.18 (d, 3 H, $CH_3Pd$, $J_{PH}$ 3.3) | |
| | 0.11 (d, 3 H, $CH_3Pd$, $J_{PH}$ 3.3) | |
| **11** | 7.20 [d, 2 H, $H_o$, $J(H_oH_m)$ 8.3] | 24.7 (s) |
| | 6.63 [d, 2 H, $H_m$, $J(H_oH_m)$ 8.3] | 23.9 (s) |
| | 3.67 (s, 3 H, $CH_3$ of $p$-$MeOC_6H_4$) | |
| | 1.55 (m, 12 H, $CH_2P$) | |
| | 1.05 (m, 18 H, $CH_3CH_2P$) | |
| | 0.18 (d, 3 H, $CH_3Pd$, $J_{PH}$ 3.0) | |
| | 0.11 (d, 3 H, $CH_3Pd$, $J_{PH}$ 3.0) | |
| **12** | 7.12 [d, 1 H, $H_o$, $J(H_oH_m)$ 7.9] | 25.8 (s) |
| | 7.10 [d, 1 H, $H_o$, $J(H_oH_m)$ 7.9] | 25.0 (s) |
| | 6.92 [d, 2 H, $H_m$, $J(H_oH_m)$ 7.9] | |
| | 1.52 (m, 12 H, $CH_2P$) | |
| | 1.07 (m, 18 H, $CH_3CH_2P$) | |
| | 0.15 (d, 3 H, $CH_3Pd$, $J_{PH}$ 3.0) | |
| | 0.08 (d, 3 H, $CH_3Pd$, $J_{PH}$ 3.0) | |
| **13** | 7.94 [d, 2 H, $H_o$, $J(H_oH_m)$ 9.0] | 26.0 (s) |
| | 7.17 [d, 2 H, $H_m$, $J(H_oH_m)$ 9.0] | 25.4 (s) |
| | 1.60 (m, 12 H, $CH_2P$) | |
| | 1.11 (m, 18 H, $CH_3CH_2P$) | |
| | 0.39 (d, 3 H, $CH_3Pd$, $J_{PH}$ 3.0) | |
| **14** | 7.4–6.4 (aromatics) | 33.2 (s) |
| | 1.61 (br, NH) | 30.2 (s) |
| | −2.10 (d, 1 H, OH) | |
| **15** | 7.4–7.1 (m, 30 H, $C_6H_5Pd$) | 33.1 (s) |
| | 6.96 (m, 4 H, $H_o$ of $C_6H_5Pd$) | 30.0 (s) |
| | 6.81 (d, 2 H, $H_o$ of $p$-$MeC_6H_4N$, $J$ 7.5) | |
| | 6.7–6.5 (m, 8 H, $H_m$ + $H_p$ of $C_6H_5Pd$ and $H_m$ of $p$-$MeC_6H_4N$) | |
| | 2.19 (s, 3 H, $CH_3$) | |
| | 1.60 (br, NH) | |
| | −2.12 (d, 1 H, OH, $J_{PH}$ 3.3) | |
| **16** | 7.5–7.1 (m, 30 H, $C_6H_5P$) | 34.1 (s) |
| | 7.02 (m, 4 H, $H_o$ of $C_6H_5Pd$) | 30.7 (s) |
| | 6.86 (d, 2 H, $H_o$ of $p$-$MeOC_6H_4N$, $J$ 7.8) | |
| | 6.7–6.5 (m, 8 H, $H_m$ + $H_p$ of $C_6H_5Pd$ and $H_m$ of $p$-$MeOC_6H_4N$) | |
| | 3.78 (s, 3 H, MeO) | |
| | 1.62 (br, NH) | |
| | −2.09 (d, 1 H, OH, $J_{PH}$ 3.6) | |
| **17** | 7.4–7.1 (m, 30 H, $C_6H_5P$) | 33.2 (s) |
| | 6.94 (m, 4 H, $H_o$, $C_6H_5Pd$) | 30.4 (s) |
| | 6.8–6.5 (m, 8 H, $H_m$ + $H_p$ of $C_6H_5Pd$ and $H_m$ of $p$-$ClC_6H_4N$) | |
| | 1.55 (br, NH) | |
| | −2.11 (d, 1 H, OH, $J_{PH}$ 3.3) | 32.8 (s) |
| **18** | 7.75 (d, 2 H, $J$ 9.3) | 31.3 (s) |
| | 7.4–7.0 (m, 34 H, $C_6H_5P$ + $H_o$ of $C_6H_5Pd$) | |
| | 6.8–6.4 (m, 8 H, $H_m$ + $H_p$ of $C_6H_5Pd$ and $H_m$ of $p$-$O_2NC_6H_4N$) | |
| | 1.70 (br, 1 H, NH) | |
| | −1.90 (d, 1 H, OH, $J_{PH}$ 3.4) | |

$CH_2PPh_2$) has an angle between the $PdO_2$ planes of 33.8(8)°[40] and the angle between the $PtN_2$ planes in $[Pt_2(PMe_2Ph)_4(\mu\text{-}NH_2)_2][BF_4]_2$ is 32°.[41] With few exceptions, phosphine ligands seem to predispose complexes to adopt a puckered form. Examples include $[Pt_2(PEt_3)_4(\mu\text{-}OH)_2][BF_4]_2$ (36.4°),[42] $[Pt_2(PPh_3)_2Cl_2(\mu\text{-}NH_2)_2]$ (45°),[43] $[Pt_2(PPh_3)_2Me_2(\mu\text{-}NH_2)_2]$ (45°)[30] and *anti*-$[\{Pd(Bu^tNC)(C_6F_5)(\mu\text{-}NHPh)\}_2]$ (32.7°).[15] The present structure shows one of the most puckered rings observed to date; looking at the data available for comparison it is tempting to attribute this to steric interference between the bulky phosphine and the bridging group, but this cannot be conclusive.

**Table 3** Selected bond lengths (Å) and angles (°) for complex **16**

| | | | |
|---|---|---|---|
| Pd(1)–O(1) | 2.093(4) | Pd(1)–P(1) | 2.213(2) |
| Pd(1)–C(8) | 1.994(7) | Pd(1)–N | 2.147(6) |
| Pd(2)–O(1) | 2.159(5) | Pd(2)–P(2) | 2.242(2) |
| Pd(2)–C(32) | 1.979(8) | Pd(2)–N | 2.099(5) |
| O(1)–Pd(1)–N | 80.9(2) | Pd(1)–O(1)–Pd(2) | 87.9(2) |
| O(1)–Pd(2)–N | 80.5(2) | Pd(1)–N–Pd(2) | 87.9(2) |

## Experimental

The analyses (C, H, N) were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5 °C $min^{-1}$ and the solid samples under a nitrogen flow (100 $cm^3$ $min^{-1}$). The NMR spectra were recorded on a Bruker AC 200E or a Varian Unity 300 spectrometer, infrared spectra on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. Solvents were dried by the usual methods. The precursor $[Pd_2(PEt_3)_2Me_2(\mu\text{-}Cl)_2]$ was prepared by the procedure described elsewhere[19] and $[Pd_2(PEt_3)_2(CH_2Ph)_2(\mu\text{-}Cl)_2]$ by the following method. A commercially available diethyl ether solution (1 M) of $Mg(CH_2Ph)Cl$ (1 $cm^3$, 1 mmol) was added to an orange suspension of $[Pd_2(PEt_3)_2Cl_2(\mu\text{-}Cl)_2]$ (0.2 g, 0.338 mmol) in diethyl ether–tetrahydrofuran (1 : 1 v/v, 14 $cm^3$). The mixture was stirred for 1.5 h to give a yellow solution. Methanol was then added to solvolyse the magnesium by-product and the solvent was completely evaporated. The residue was extracted with diethyl ether–dichloromethane (1 : 1 v/v, 14 $cm^3$), and then the extract was concentrated to dryness. Addition of hexane followed by vigorous stirring rendered a yellow suspension, from which a yellow solid was filtered off and air-dried. Yield 0.146 g, 62%.

### Preparations

**Complex 1.** To a solution of $[\{Pd(PEt_3)Me(\mu\text{-}Cl)\}_2]$ (0.2 g, 0.364 mmol) in acetone (10 $cm^3$) was added 20% $[NBu_4]OH$ (aq) (0.95 $cm^3$, 0.728 mmol), with constant stirring for 15 min. After partial evaporation of the solvent under reduced pressure, addition of water followed by vigorous stirring and filtration afforded a white solid which was air-dried. Yield 90% (Found: C, 32.2; H, 7.2. Calc. for $C_{14}H_{38}O_2P_2Pd_2$: C, 32.8; H, 7.5%). M.p. 112 °C (decomp.). IR (Nujol, $cm^{-1}$): 3520 (OH str) and 525 (PdC str).

**Complex 2.** To a solution of $[\{Pd(PEt_3)(PhCH_2)(\mu\text{-}Cl)\}_2]$ (0.2 g, 0.285 mmol) in acetone–methanol (1 : 1, 10 $cm^3$) was added 20% $[NBu_4]OH$ (aq) (0.74 $cm^3$, 0.57 mmol). After 5 min of stirring solvent was partially evaporated under reduced pressure. Addition of water gave a yellow precipitate which was filtered off and air-dried. Yield 89% (Found: C, 46.6; H, 6.8. Calc. for $C_{26}H_{46}O_2P_2Pd_2$: C, 46.9; H, 7.0%). M.p. 112 °C (decomp.). IR (Nujol, $cm^{-1}$): 3500 (OH str) and 525 (PdC str).

**Complexes 3–6.** To a solution of the corresponding hydroxo complex (**1** or **2**) (0.156 mmol) in methanol was added 3,5-dimethylpyrazole (0.312 mmol) or oxalic acid (0.156 mmol) with constant stirring for 1 h to afford a suspension from which solvent was partially evaporated under reduced pressure. The precipitate was filtered off and air-dried. Complex **3**: yield 69% (Found: C, 42.8; H, 7.5; N, 8.1. Calc. for $C_{24}H_{50}N_4P_2Pd_2$: C, 43.1; H, 7.5; N, 8.4%); m.p. 266 °C (decomp.); IR (Nujol, $cm^{-1}$) 525 (PdC str). Complex **4**: yield 68% (Found: C, 52.2; H, 6.8; N, 7.0. Calc. for $C_{36}H_{58}N_4P_2Pd_2$: C, 52.6; H, 7.1; N, 6.8%); m.p. 210 °C (decomp.). Complex **5**: yield 65% (Found: C, 33.6; H, 6.2. Calc. for $C_{16}H_{36}NO_4P_2Pd_2$: C, 33.9; H, 6.4%); m.p.: 186 °C (decomp.); IR (Nujol, $cm^{-1}$) 1600 ($CO_2$ asym str) and 545 (PdC str). Complex **6**: yield 70% (Found: C, 46.6; H, 5.2. Calc. for $C_{28}H_{44}O_4P_2Pd_2$: C, 46.8; H, 6.2%); m.p. 206 °C (decomp.); IR (Nujol, $cm^{-1}$) 1600 ($CO_2$ asym str).

**Complexes 7 and 8.** Triethylphosphine (0.312 mmol) was added to a solution of complex **1** or **2** (0.156 mmol) in acetone (6 $cm^3$). The solution was stirred for 15 min and concentrated under reduced pressure. On addition of water **7** or **8** precipitated as a solid which was filtered off and air-dried. Complex **7**: yield 63% (Found: C, 41.0; H, 8.8. Calc. for $C_{13}H_{34}OP_2Pd$: C, 41.7; H, 9.1%); m.p. 216 °C (decomp.); IR (Nujol, $cm^{-1}$) 515 (PdC str). Complex **8**: yield 65% (Found: C, 49.9; H, 8.1. Calc. for $C_{19}H_{38}OP_2Pd$: C, 50.6; H, 8.5%); m.p. 191 °C (decomp.).

**Complexes 9–13.** The appropriate amine $R''NH_2$ (0.1169 mmol) was added to a solution of $[Pd_2(PEt_3)_2Me_2(\mu\text{-}OH)_2]$ (60 mg, 0.1169 mmol) in dichloromethane (4 $cm^3$) and the solution stirred at room temperature for 30 min and concentrated to dryness under vacuum. The residue was treated with $Pr^iOH$ and the pale yellow (orange for **5**) solid was filtered off and air-dried. Complexes **9**–**13** were recrystallized from dichloromethane–hexane. Complex **9**: yield 76% (Found: C, 40.5; H, 7.2; Calc. for $C_{20}H_{34}NOP_2Pd_2$: C, 40.8; H, 7.4; N, 2.4%); m.p. 167 °C (decomp.); IR (Nujol, $cm^{-1}$) 3605 (OH str) and 3305 (NH str). Complex **10**: yield 71% (Found: C, 41.5; H, 7.3; N, 2.1. Calc. for $C_{21}H_{45}NOP_2Pd_2$: C, 41.9; H, 7.5; N, 2.3%); m.p. 169 °C (decomp.); IR (Nujol, $cm^{-1}$) 3600 (OH str) and 3300 (NH str). Complex **11**: yield 75% (Found: C, 40.4; H, 7.1; N, 2.4. Calc. for $C_{21}H_{45}NO_2P_2Pd_2$: C, 40.8; H, 7.3; N, 2.3%); m.p. 169 °C (decomp.); IR (Nujol, $cm^{-1}$) 3600 (OH str) and 3300 (NH str). Complex **12**: yield 67% (Found: C, 38.2; H, 6.5; N, 2.2. Calc. for $C_{20}H_{42}ClNOP_2Pd_2$: C, 38.6; H, 6.8; N, 2.3%); m.p. 165 °C (decomp.); IR (Nujol, $cm^{-1}$) 3605 (OH str) and 3305 (NH str). Complex **13**: yield 71% (Found: C, 37.6; H, 6.5; N, 4.5. Calc. for $C_{20}H_{42}N_2O_3P_2Pd_2$: C, 37.9; H, 6.7; N, 4.4%); m.p. 187 °C (decomp.); IR (Nujol, $cm^{-1}$) 3600 (OH str) and 3300 (NH str).

**Complexes 14–18.** The appropriate amine $R''NH_2$ (0.0866 mmol) was added to a solution of $[Pd_2(PPh_3)_2(\mu\text{-}OH)_2]$ (80 mg, 0.0866 mmol) in dichloromethane (6 $cm^3$) and the solution was stirred at room temperature for 30 min and concentrated to dryness under vacuum. The residue was treated with ether–hexane and the white or pale yellow solid was filtered off and air-dried. Complexes **14**–**18** were recrystallized from dichloromethane–hexane. Complex **14**: yield 79% (Found: C, 64.5; H, 4.6; N, 1.5. Calc. for $C_{54}H_{47}NOP_2Pd_2$: C, 64.8; H, 4.7; N, 1.4%); m.p. 178 °C (decomp.); IR (Nujol, $cm^{-1}$) 3600 (OH str) and 3320 (NH str). Complex **15**: yield 78% (Found: C, 65.1; H, 4.9; N, 1.5. Calc. for $C_{55}H_{49}NOP_2Pd_2$: C, 65.1; H, 4.9; N, 1.4%); m.p. 176 °C (decomp.); IR (Nujol, $cm^{-1}$) 3610 (OH str) and 3320 (NH str). Complex **16**: yield 77% (Found: C, 63.9; H, 4.9; N, 1.4. Calc. for $C_{55}H_{49}NO_2P_2Pd_2$: C, 64.1; H, 4.8; N, 1.4%); m.p. 178 °C (decomp.); IR (Nujol, $cm^{-1}$) 3605 (OH str) and 3305 (NH str). Complex **17**: yield 76% (Found: C, 62.6; H, 4.5; N, 1.4. Calc. for $C_{54}H_{46}ClNOP_2Pd_2$: C, 62.7; H, 4.5; N, 1.4%); m.p. 184 °C (decomp.); IR (Nujol, $cm^{-1}$) 3605 (OH str) and 3315 (NH str). Complex **18**: yield 80% (Found: C, 62.2; H, 4.6; N, 2.6. Calc. for $C_{54}H_{46}N_2O_3P_2Pd_2$: C, 62.0; H, 4.4; N, 2.7%); m.p. 182 °C (decomp.); IR (Nujol, $cm^{-1}$) 3605 (OH str) and 3315 (NH str).

### Crystallography

Suitable crystals (dichloromethane solvated) of complex **16** were obtained from dichloromethane–hexane.

**Crystal data.** $C_{56}H_{51}Cl_2NO_2P_2Pd_2$, $M = 1115.7$, crystal size 0.2 × 0.2 × 0.1 mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.834(4)$, $b = 12.388(3)$, $c = 21.345(10)$ Å, $\alpha = 94.18(3)$, $\beta = 93.40(4)$, $\gamma = 94.04(3)°$, $U = 2581.5(2)$ Å$^3$ (by least-squares refinement on 25 reflections $7 < \theta < 9°$, $\lambda = 0.710\ 73$ Å), $Z = 2$, $D_c = 1.44$ g $cm^{-3}$, $\mu$(Mo-K$\alpha$) = 8.9 $cm^{-1}$, $F(000) = 1132$.

**Data collection and processing.** Enraf-Nonius CAD 4 diffractometer, $\theta$–$2\theta$ mode, graphite-monochromated Mo-K$\alpha$ radiation, $h$ 0–11, $k$ −14 to 14, $l$ −25 to 25, $2 < \theta < 25°$. 9075 Total unique reflections measured, 6519 significant reflections $[|F^2| > 2\sigma(F^2)]$. Maximum change in standard reflections −0.4%, no decay correction. Empirical absorption, $T_{max} = 1.00$, $T_{min} = 0.80$ from $\psi$ scans, $T = 293$ K.

**Structure analysis and refinement.** Non-H atoms located by heavy-atom methods (SHELXS 86).[44] Full-matrix least squares refinement with non-H atoms anisotropic (MOLEN).[45] Hydrogen atoms on O(1) and C(7) were omitted; the rest were calculated positions, $U_{iso} = 1.3\ U_{eq}$ for parent atom. $R = 0.058$, $R' = 0.065$, $S = 1.7$. Number of variables 586, number of observed reflections 6519. $(\Delta/\sigma)_{max} = 0.5$, $(\Delta/\rho)_{max,min}$ + 1.37, −0.15 e Å$^{-3}$. $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}L_\rho$, $w = \sigma^{-2}(F)$, $\Sigma w(|F_o| - |F_c|)^2$ minimised.

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