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Preliminary communication

Binuclear hydroxo-monopentahalophenyl complexes of palladium(II)

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Abstract

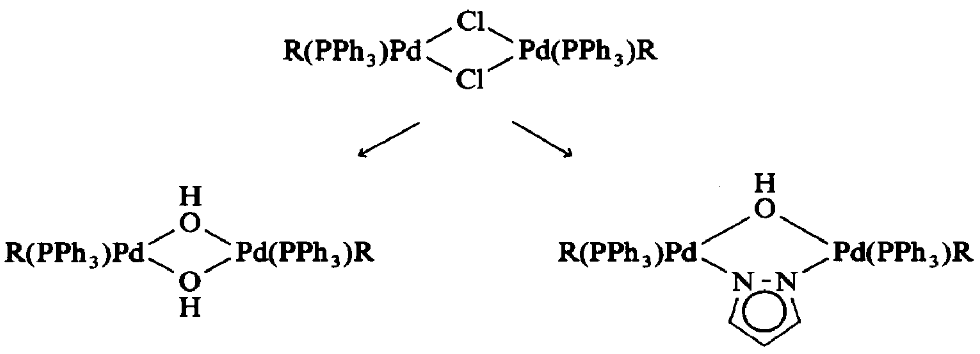
The novel binuclear hydroxo-bridged complexes *trans*-[R(PPh$_3$)Pd(μ-OH)$_2$-Pd(PPh$_3$)R] and *cis*-[R(PPh$_3$)Pd(μ-OH)(μ-pz)Pd(PPh$_3$)R] (R = C_6F_5 or C_6Cl_5; pz = pyrazolate) have been prepared, and their structures assigned on the basis of NMR data.

The late transition-metal hydroxides are attracting growing attention because of their relevance to some organic syntheses, in which they are believed to be important intermediates in various catalytic processes [1]. Such complexes had been neglected in earlier studies because the "hard and soft" acid and base concept had predicted weak metal–ligand bonding.

Monomeric [MR(OH)L$_2$]-type complexes (M = Pd, Pt; R = alkyl, aryl; L = phosphine) and their condensation reactions with active methyl groups have been described previously [2,3], and we recently reported the synthesis of the anionic complexes $[(C_6F_5)_2M(\mu\text{-}OH)_2M(C_6F_5)_2]^{2-}$ (M = Ni, Pd, Pt) [4]. Although some nickel complexes of the type [RLNi(μ-OH)$_2$NiLR] have recently been described [5], no binuclear uncharged hydroxo-palladium species is known. In this communication we show that such complexes can be prepared through metathetical reactions of the corresponding chloro-complex [RLPd(μ-Cl)$_2$PdLR].

The results are summarized in Scheme 1. In acetone, [PdR(PPh$_3$)(μ-Cl)]$_2$ (R = C_6F_5 or C_6Cl_5 [6]) reacts with [NBu$_4$]OH to give the di-μ-hydroxo complexes **1** and **2**. Similarly, the μ-hydroxo-μ-pyrazolato complexes **3** and **4** are obtained by treating the above chloro-complexes with [NBu$_4$]OH and pyrazolate (generated in situ from pyrazole and [NBu$_4$]OH).

The presence of a hydroxo ligand in compounds **1**–**4** is manifested by the observation of IR absorptions at 3610–3600 cm^{-1} and high-field proton resonances (ca −1.5 to −3.0 ppm). The IR spectra show the characteristic bands attributed to the C_6F_5 (**1** and **3**) [7] and C_6Cl_5 (**2** and **4**) [8] groups, and the proton resonance



R = C_6F_5 (**1**) or C_6Cl_5 (**2**)   R = C_6F_5 (**3**) or C_6Cl_5 (**4**)

Scheme 1. Compounds **1** and **2** were obtained by reaction of the chloro-complex with 20% [NBu_4]$OH_{(aq)}$ (1 : 2 molar ratio) in acetone, with constant stirring for 30 min. The solvent was evaporated under vacuum and methanol was added. The solids were filtered off and dried at 100 °C (70–80% yields). For the preparation of **3** and **4**, the chloro-complex was added to a mixture of pyrazole and 20% [NBu_4]$OH_{(aq)}$ (1 : 1 : 2 molar ratio) in acetone and the suspension was stirred for 30 min. The white solids were filtered off, washed with methanol, and dried at 100 °C (60–70% yields). Satisfactory C, H and N analyses were obtained for **1**–**4**.

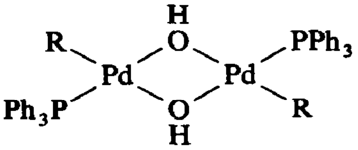
signals arising from the bridging pyrazolate in compounds **3** and **4** are similar to those observed for related compounds [9].

The NMR data listed in Table 1 show unambiguously that compounds **1** and **2** exist in chloroform solution exclusively as the *trans* isomers (I), since the ^{1}H spectra exhibit a unique high-field resonance for the OH groups consisting of a doublet arising from coupling to ^{31}P of the phosphine *trans* to OH. No coupling to ^{31}P of the phosphine *cis* to OH is observed.

Table 1

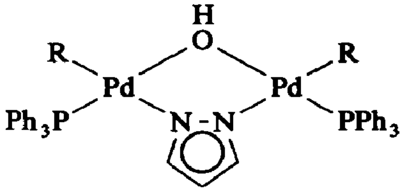
NMR data (J in Hz) for the palladium complexes (solvent $CDCl_3$)

	^{1}H δ (ppm) ($SiMe_4$)	^{31}P δ (ppm) (H_3PO_4)	^{19}F δ (ppm) ($CFCl_3$)
1	7.6 (m, 12H, Ph) 7.4 (m, 18H, Ph) −1.6 (d, 2H, OH, J(PH) 3.4)	30.5 (t, $J(PF_o)$ 9.9)	−117.2 (dd, $4F_o$, J_{om} 22.0, $J(PF_o)$ 9.9) −161.2 (t, $2F_p$, J_{mp} 19.8) −163.9 (m, $4F_m$)
2	7.7 (m, 12H, Ph) 7.3 (m, 18H, Ph) −1.7 (d, 2H, OH, J(PH) 2.2)	28.4 (s)	
3	7.7–7.0 (m, 30H, Ph) 6.6 (dd, 2H, 3- and 5-H of pz, J(HH) ≈ J(PH) 2.0) 5.9 (tt, 1H, 4-H of pz, J(HH) 2.0; J(PH) 1.8) −2.6 (t, 1H, OH, J(PH) 2.0)	28.5 (t, $J(PF_o)$ 8.6)	−117.3 (dd, $4F_o$, J_{om} 28.2, $J(PF_o)$ 8.6) −161.5 (t, $2F_p$, J_{mp} 19.2) −163.4 (m, $4F_m$)
4	7.5–7.0 (m, 30H, Ph) 6.6 (dd, 2H, 3- and 5-H of pz, J(HH) ≈ J(PH) 2.0) 5.9 (tt, 1H, 4-H of pz, J(HH) 2.0; J(PH) 1.8) −3.0 (t, 1H, OH, J(PH) 1.7)	26.6 (s)	



(I)

In contrast, compounds **3** and **4** exist in solution as the *cis* isomers (**II**), with two equivalent phosphines (only a single resonance is observed in the $^{31}P\{^1H\}$ spectrum) *trans* to the bridging OH group, as suggested by the high-field triplets observed in their respective ^1H spectra.



(II)

The ^{19}F spectra of compounds **1** and **3** show the expected NMR pattern for two equivalent C_6F_5 groups; the values of the coupling constants $J(FP)$ are quite similar to those for complexes *cis*-[Pd(2,4,6-$C_6F_3H_2)_2$(phosphine)$_2$] [10].

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