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Preliminary communication

A STABLE BINUCLEAR COMPLEX CONTAINING Pd—H—Pd BONDS

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Summary

The preparations of the binuclear hydrido-bridged cations [(terdentate ligand)Pd(μ-H)Pd(terdentate ligand)]$^+$ from [(terdentate ligand)Pd(acetone)]$^+$ and NaO_2CH and [(terdentate ligand)Pd(μ-H)Pt(terdentate ligand)]$^+$ from [(terdentate ligand)Pd(acetone)]$^+$ and [(terdentate ligand)PtH] (terdentate ligand = 2,6-$(Ph_2PCH_2)_2C_6H_3$) are reported. The preparation of the cation [(terdentate ligand)Pt(μ-H)Pt(terdentate ligand)]$^+$ is also reported.

Numerous complexes of the type $L_nM—H—ML_n$ are known and cations such as $[(PEt_3)_2(Ph)Pt(\mu\text{-}H)Pt(Ph)(PEt_3)_2]^+$ (1) have been recently described [1]. Palladium(II) complexes of this type, however, do not appear to have been reported, although a mixed palladium-platinum species $[(2)Pd(\mu\text{-}H)_2Pt(PPh_3)_2]^+$ (2 = 2,6-bis-[(dimethylamino)methyl]-phenyl) has been recently described [2].

In the course of our study of the reactions of platinum complexes such as 3b [3] we observed the easy formation of the stable binuclear species 5b, which is fully analogous to 1. Thus, we tried the analogous reaction sequence with 3a as shown in Scheme 1.

As can be seen, the binuclear species 5a is easily obtained in practically quantitative yield. It is noteworthy that while [5a][CF_3SO_3] is stable both in solution and in the solid state, [5a][BPh_4], prepared by adding Na[BPh_4] to a methanolic solution of [5a][CF_3SO_3], decomposes gradually in solution, with deposition of metallic palladium.

The ^1H NMR spectrum, in the hydride region, appears as a quintet centered at —8.59 ppm (CD_3COCD_3) with a $^2J(^{31}P, ^1H)$ value of 14.2 Hz; the signals arising from the CH_2 protons appear as a pseudo-triplet centered at 3.64 ppm ($|^2J(^{31}P,^1H) + {}^4J(^{31}P,^1H)|$ 4.9 Hz) because of "virtual coupling" [4].

The $^{31}P\{^1H\}$ NMR spectrum shows one signal at 43.0 ppm (CD_3COCD_3) indicating the near-equivalence of the four phosphorus atoms. Thus, apart from

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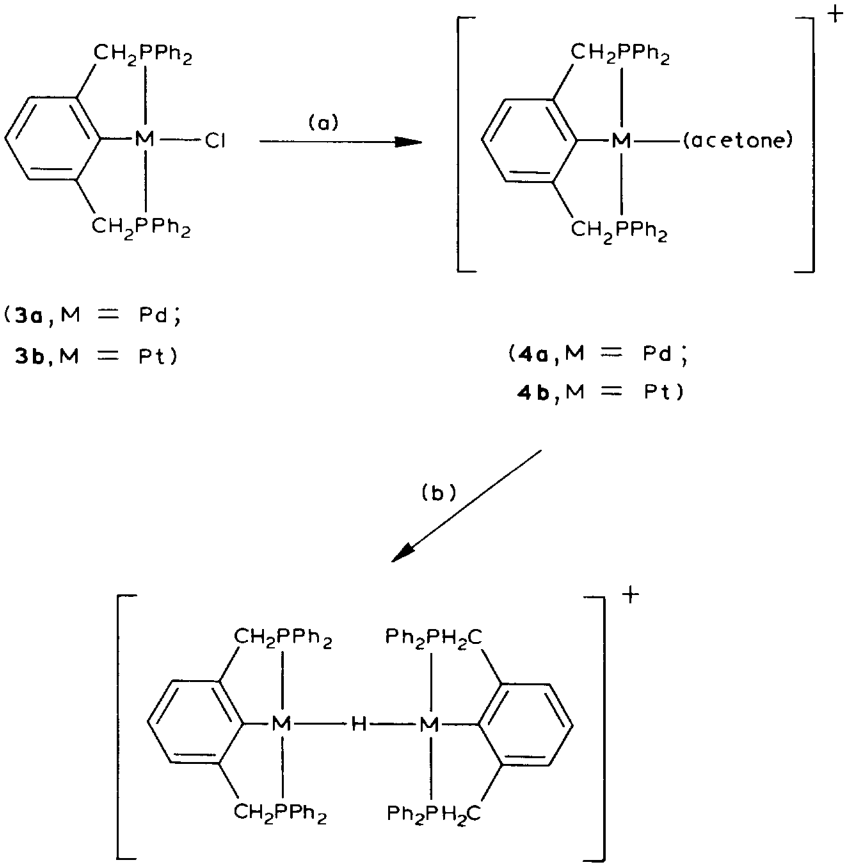

(3a, M = Pd;
3b, M = Pt)

(4a, M = Pd;
4b, M = Pt)

(5a, M = Pd;
5b, M = Pt)

SCHEME 1.
(a) $Ag^+ CF_3SO_3^-$ in acetone, 30 min; (b) NaO_2CH (exc.) in CH_3OH, 30 min. ~ 100%.
All the above complexes give satisfactory microanalyses.

the absence of signals arising from ^{195}Pt couplings, the NMR spectra of 5a and 5b are fully analogous and establish the structure of 5a.

The stability of the binuclear species 5a contrasts that of the mononuclear species [PdH(6)] (6 = 2,6-bis-[(diphenylphosphino)methyl]phenyl) which, unlike the corresponding complex [PtH(6)] [3], decomposes in solution. This is indicated by the reaction of 5a with KBr in acetone which gives metallic palladium and [PdBr(6)]. However, the analogous compound [PdH(7)] (7 = 2,6-bis-[(di-t-butylphosphino)methyl]-phenyl) is stable and its stability has been attributed to the presence of the bulky t-butyl groups which screen the hydride ligand from incoming reagents [5]. Finally the cation $[Pd(6)(ac)]^+$ and [PtH(6)] give the heterobimetallic cation $[(6)Pd(\mu\text{-}H)Pt(6)]^+$ which is analogous to 5a and 5b.

The above observations provide another example of the higher stability of hydrido-bridged species relative to the corresponding mononuclear complexes [1].

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