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Hydrido Trifluoromethyl Platinum(II) Complexes

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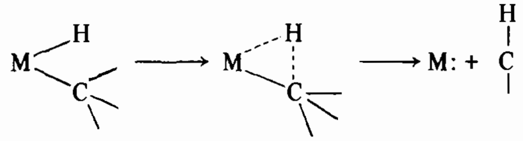
Hydrido σ-alkyl complexes of transition metals have been generally regarded as thermally unstable, and their intermediacy is suggested in catalytic hydrogenation of olefins with some metal complexes [1, 2]. The thermal instability of transition metal hydrido alkyls was interpreted on the basis of a three-centered interaction which is allowed when participation of *d* orbitals to the bonding occurs [3]:



This *cis* reductive elimination of $\geq$C–H provides the most prominent examples, but other pathways are possible [1,4].

Particularly interesting among hydrido σ-alkyl complexes are those of type [PtH(R)L_2] since they can be regarded as models of the intermediates being formed in catalytic processes involving activation of saturated hydrocarbons [3]. Even if hydrido σ-alkyl complexes of Pt(II) are postulated as labile intermediates in mechanisms of thermal decomposition of dialkyl complexes of Pt(II) [5, 6], hitherto only two complexes of this type, *trans*-[PtH(R)L_2] (R = CH_2SiMe_3, L = PEt_3 [7]; R = $C(CN)_3$, L = PPh_3 [8]), have been isolated. More recently, some of us have obtained derivatives of type [PtH(cyanoalkyl)LL′] and [PtH(cyanoalkyl)(L–L)] (cyanoalkyl = CH_2CN, CH_2CH_2CN, $CH_2CH_2CH_2CN$, L = L′ = PPh_3; L = PPH_3, L′ = isocyanide; L–L = diphosphine or diarsine) [9–11]*.

It appears that substitution with electronegative groups in the alkyl chain of R entails unusual stability in the Pt–C bond in both hydrido and halide derivatives [PtX(R)L_2] (X = H, halide). It is known that more stable M–C bonds are obtained on passing from alkyls to perfluoroalkyls [12, 13]. Thus, H. C. Clark *et al.* [14] have described a series of stable, both neutral and cationic, complexes of Pt(II), [PtX(CF_3)L_2] (L = PMe_2Ph; X = halide or pseudo-halide) and $[Pt(CF_3)L_2L']^+$ (L′ = CO, CNR, PR_3 or AsR_3).

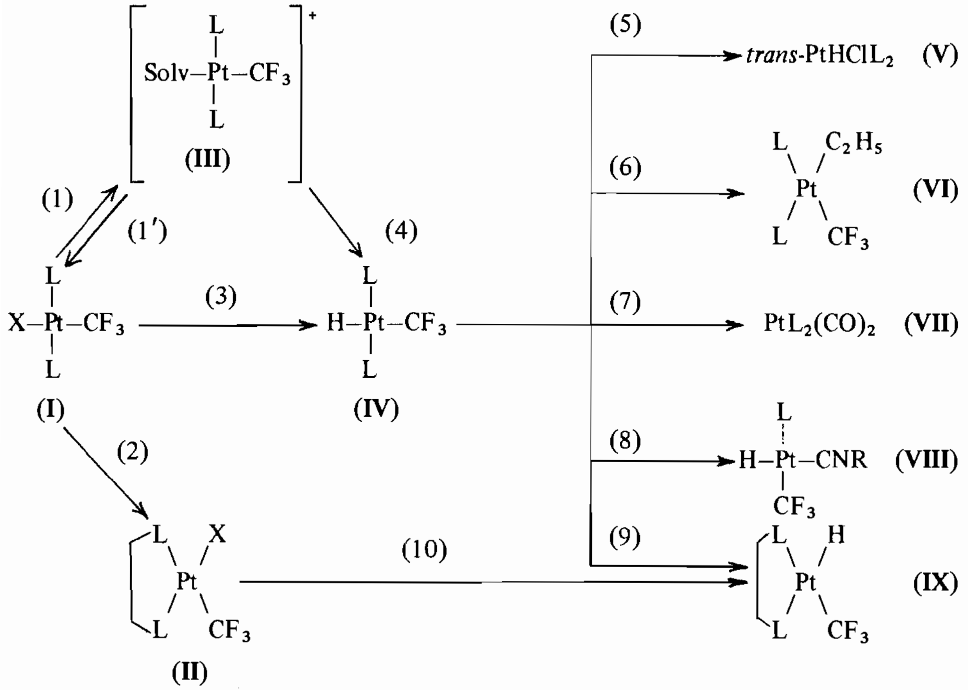
Along these lines we have succeeded in preparing novel hydrido complexes of type [PtH(CF_3)LL′] [Scheme 1: L = L′ = PPh_3, (IV); L = PPh_3, L′ = *p*-$CNC_6H_4OCH_3$, (VIII); L–L′ = *cis*-1,2-bis(diphenylphosphino)ethylene, (IX)] starting from *trans*-[PtBr(CF_3)$(PPh_3)_2$] (I) which was obtained by oxidative addition of CF_3Br on $Pt(PPh_3)_4$ in benzene in an analogous way to that reported by F. G. A. Stone *et al.* [15].

Abstraction of Br^- by Ag^+ from (I) leads to the solvento-cationic species (III). Reduction by $NaBH_4$ in EtOH yields *trans*-[PtH(CF_3)$(PPh_3)_2$] (IV), as white microcrystals, soluble in benzene and dichloromethane, slightly soluble in alcohols. The *trans* geometry was deduced from ^1H, ^{19}F, and $^{31}P\{^1H\}$ FT NMR spectra:

trans-[PtH(CF_3)$(PPh_3)_2$]: δ(H) – 8.23ppm (quartet of triplets), ^1J(PtH) 544Hz, ^2J(PPtH) 18.5Hz, ^3J(FCPtH) 28Hz (in CD_2Cl_2 + TMS); δ(F) -16.8ppm (doublet of triplets), ^2J(PtCF) 448Hz, ^3J(HPtCF) 28Hz, ^3J(PPtCF) 10Hz (in CH_2Cl_2 + $CFCl_3$ as internal reference; negative values indicate a shift to high field); δ(P) 29.6ppm (quartet), ^1J(PtP) 3118Hz, ^3J(FCPtP) 10Hz (in toluene-d_8, external reference H_3PO_4 85%). I.R. in Nujol: ν(PtH) 2073 cm^{-1}. A strong *trans*-influence of the CF_3 group was suggested by H. C. Clark *et al.* [14] on the basis of indirect coupling constant ^3J(PtPCH) in methylphosphine cationic complexes $[PtRL_3]^+$ (R = Cl, CH_3, CF_3; L = PMe_2Ph); the *trans*-influence order was $CH_3 > CF_3 > PMe_2Ph >$ Cl. The *trans*-hydrido trufluoromethyl complex (IV) appears to be a good model for studying the *trans*-influence of the CF_3 group since it allows the determination of ^{195}Pt–^{1}H coupling constant between directly bound nuclei [16]. A comparison of ^1J(PtH) value of complex (IV) with those of analogous cyanoalkyl complexes *trans*-[PtH(R)$(PPh_3)_2$] [9] indicates the following *trans*-influence order: CF_3(544Hz) > $CH_2CH_2CH_2CN$ (636) > CH_2CN (746).

The strong *trans*-influence of the hydride ligand in (IV) is reflected in the ^2J(PtCF) which is much lower than those reported for complexes of type *trans*-[PtX(CF_3)$(PMe_2Ph)_2$] (X = halide or pseudo-halide) [14].

**Note added in proofs.* While this paper was being printed, Stone *et al.*, *J. Chem. Soc. Dalton*, 1006 (1977), have reported species of type *trans*-[PtH(Ar)L_2] [Ar = C_6F_5, $C_6F_3H_2$, L = $P(C_6H_{11})_3$].



Scheme 1. L = PPh_3, (L–L) = *cis*-1,2-bis(diphenylphosphino)ethylene. (1): $+Ag^+$/Solv., –AgX. (1′): + X^-. (2), (9): +(L–L), –2L. (3), (4), (10): $+NaBH_4$/EtOH, X = Cl. (5): +HCl/Et_2O. (6): $+CH_2{=}CH_2$ in 1,2-dichloroethane (40 atm, 20 °C). (7): +CO in 1,2-dichloroethane (30 atm, 20 °C). (8): + CNR, –L in n-heptane.

Complex **(IX)**, which bears the Pt–H and Pt–C bonds close to each other, is obtained by treatment of **(IV)** with diphosphine as white microcrystals sparingly soluble in CH_2Cl_2, C_6H_6, insoluble in alcohols (I.R. Nujol: ν(PtH) 2032 cm^{-1}).

The hydrides **(IV)** and **(IX)** can also be obtained by treatment of the parent chloride complexes **(I)** and **(II)** with $NaBH_4$ in EtOH, albeit with lower yields.

The known hydride *trans*-$[PtHCl(PPh_3)_2]$ **(V)** [17] arises from cleavage of the Pt–CF_3 bond by electrophilic attack of HCl in diethyl ether. The *cis*-dialkyl derivative **(VI)** is obtained by insertion of ethylene across the Pt–H bond. **(IV)** undergoes reductive elimination to the known $[Pt(PPh_3)_2(CO)_2]$ **(VII)** [18] on treatment with CO, whereas the reaction with *p*-methoxyphenylisocyanide leads to **(VII)** through displacement of one PPh_3 and *trans* →*cis* isomerization of Pt–H and Pt–C bonds. The geometry of **(VIII)** is deduced from ^1H and ^{19}F NMR spectra:

$[PtH(CF_3)(PPh_3)(CNC_6H_4OCH_3)]$: δ(Pt–H) – 5.77ppm (doublet of quartets), ^1J(PtH) 1118Hz, ^2J(PPtH) 20Hz, ^3J(FCPtH) 14.5Hz, $\delta(OCH_3)$ 3.71-ppm (singlet) (in CD_2Cl_2 + TMS); δ(F) –12.5ppm (doublet of doublets), ^2J(PtCF) 813Hz, ^3J(PPtCF) 58Hz, ^3J(HPtCF) 14.5Hz (in CH_2Cl_2 + $CFCl_3$ as internal reference).

We are at present carrying out an X-ray structure determination on **(IV)** and **(IX)** and reactivity studies with a variety of nucleophiles and electrophiles.

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