

Hydrido Trifluoromethyl Platinum(II) Complexes

RINO A. MICHELIN, UMBERTO BELLUCO

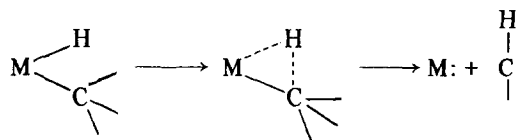
Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Istituto di Chimica Industriale, Via Marzolo 9, Padova, Italy

and RENZO ROS

Facoltà di Chimica Industriale, Università Ca' Foscari, Calle Larga S. Marta, 2137 Venezia, Italy

Received May 23, 1977

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 $\geq \text{C}-\text{H}$ provides the most prominent examples, but other pathways are possible [1, 4].

Particularly interesting among hydrido σ -alkyl complexes are those of type $[\text{PtH}(\text{R})\text{L}_2]$ 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*- $[\text{PtH}(\text{R})\text{L}_2]$ ($\text{R} = \text{CH}_2\text{-SiMe}_3$, $\text{L} = \text{PEt}_3$ [7]; $\text{R} = \text{C}(\text{CN})_3$, $\text{L} = \text{PPh}_3$ [8]), have been isolated. More recently, some of us have obtained derivatives of type $[\text{PtH}(\text{cyanoalkyl})\text{LL}']$ and $[\text{PtH}(\text{cyanoalkyl})(\text{L}-\text{L})]$ (cyanoalkyl = CH_2CN , $\text{CH}_2\text{CH}_2\text{CN}$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$, $\text{L} = \text{L}' = \text{PPh}_3$; $\text{L} = \text{PPh}_3$, $\text{L}' = \text{isocyanide}$; $\text{L}-\text{L} = \text{diphosphine}$ 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 $[\text{PtX}(\text{R})\text{L}_2]$ ($\text{X} = \text{H}$, 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), $[\text{PtX}(\text{CF}_3)_2\text{L}_2]$ ($\text{L} = \text{PMe}_2\text{Ph}$; $\text{X} = \text{halide}$ or pseudo-halide) and $[\text{Pt}(\text{CF}_3)_2\text{L}_2\text{L}']^+$ ($\text{L}' = \text{CO}$, CNR , PR_3 or AsR_3).

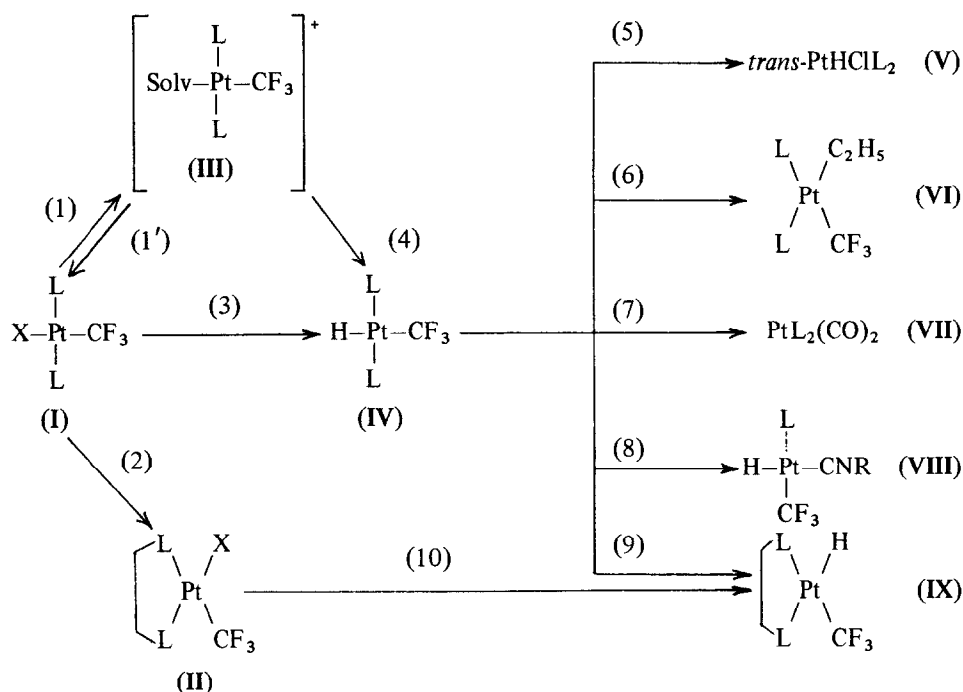
Along these lines we have succeeded in preparing novel hydrido complexes of type $[\text{PtH}(\text{CF}_3)\text{LL}']$ [Scheme 1: $\text{L} = \text{L}' = \text{PPh}_3$, (IV); $\text{L} = \text{PPh}_3$, $\text{L}' = p\text{-CNC}_6\text{H}_4\text{OCH}_3$, (VIII); $\text{L}-\text{L}' = \text{cis-1,2-bis(diphenylphosphino)ethylene}$, (IX)] starting from *trans*- $[\text{PtBr}(\text{CF}_3)(\text{PPh}_3)_2]$ (I) which was obtained by oxidative addition of CF_3Br on $\text{Pt}(\text{PPh}_3)_4$ 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*- $[\text{PtH}(\text{CF}_3)(\text{PPh}_3)_2]$ (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 $\{^1\text{H}\}$ FT NMR spectra:

trans- $[\text{PtH}(\text{CF}_3)(\text{PPh}_3)_2]$: $\delta(\text{H}) - 8.23\text{ppm}$ (quartet of triplets), $^1\text{J}(\text{PtH}) 544\text{Hz}$, $^2\text{J}(\text{PtH}) 18.5\text{Hz}$, $^3\text{J}(\text{FCPtH}) 28\text{Hz}$ (in $\text{CD}_2\text{Cl}_2 + \text{TMS}$); $\delta(\text{F}) - 16.8\text{ppm}$ (doublet of triplets), $^2\text{J}(\text{PtCF}) 448\text{Hz}$, $^3\text{J}(\text{HPtCF}) 28\text{Hz}$, $^3\text{J}(\text{PPtCF}) 10\text{Hz}$ (in $\text{CH}_2\text{Cl}_2 + \text{CFCl}_3$ as internal reference; negative values indicate a shift to high field); $\delta(\text{P}) 29.6\text{ppm}$ (quartet), $^1\text{J}(\text{PtP}) 3118\text{Hz}$, $^3\text{J}(\text{FCPtP}) 10\text{Hz}$ (in toluene- d_8 , external reference H_3PO_4 85%). I.R. in Nujol: $\nu(\text{PtH}) 2073\text{cm}^{-1}$. 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 $^3\text{J}(\text{PtPCH})$ in methylphosphine cationic complexes $[\text{PtRL}_3]^+$ ($\text{R} = \text{Cl}$, CH_3 , CF_3 ; $\text{L} = \text{PMe}_2\text{Ph}$); the *trans*-influence order was $\text{CH}_3 > \text{CF}_3 > \text{PMe}_2\text{Ph} > \text{Cl}$. The *trans*-hydrido trifluoromethyl complex (IV) appears to be a good model for studying the *trans*-influence of the CF_3 group since it allows the determination of $^{195}\text{Pt}-^1\text{H}$ coupling constant between directly bound nuclei [16]. A comparison of $^1\text{J}(\text{PtH})$ value of complex (IV) with those of analogous cyanoalkyl complexes *trans*- $[\text{PtH}(\text{R})(\text{PPh}_3)_2]$ [9] indicates the following *trans*-influence order: $\text{CF}_3(544\text{Hz}) > \text{CH}_2\text{CH}_2\text{CH}_2\text{CN}(636) > \text{CH}_2\text{CN}(746)$.

The strong *trans*-influence of the hydride ligand in (IV) is reflected in the $^2\text{J}(\text{PtCF})$ which is much lower than those reported for complexes of type *trans*- $[\text{PtX}(\text{CF}_3)(\text{PMe}_2\text{Ph})_2]$ ($\text{X} = \text{halide}$ 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*- $[\text{PtH}(\text{Ar})\text{L}_2]$ [$\text{Ar} = \text{C}_6\text{F}_5$, $\text{C}_6\text{F}_3\text{H}_3$, $\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$].



Scheme 1. L = PPh₃, (L-L) = *cis*-1,2-bis(diphenylphosphino)ethylene. (1): +Ag⁺/Solv., -AgX. (1'): +X⁻. (2), (9): +(L-L), -2L. (3), (4), (10): +NaBH₄/EtOH, X = Cl. (5): +HCl/Et₂O. (6): +CH₂=CH₂ 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 CH₂Cl₂, C₆H₆, insoluble in alcohols (I.R. Nujol: $\nu(\text{PtH})$ 2032 cm⁻¹).

The hydrides (IV) and (IX) can also be obtained by treatment of the parent chloride complexes (I) and (II) with NaBH₄ in EtOH, albeit with lower yields.

The known hydride *trans*-[PtHCl(PPh₃)₂] (V) [17] arises from cleavage of the Pt-CF₃ 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(PPh₃)₂(CO)₂] (VII) [18] on treatment with CO, whereas the reaction with *p*-methoxyphenylisocyanide leads to (VIII) through displacement of one PPh₃ and *trans* → *cis* isomerization of Pt-H and Pt-C bonds. The geometry of (VIII) is deduced from ¹H and ¹⁹F NMR spectra:

[PtH(CF₃)(PPh₃)(CNC₆H₄OCH₃)]: $\delta(\text{Pt-H})$ - 5.77ppm (doublet of quartets), ¹J(PtH) 1118Hz, ²J(PtH) 20Hz, ³J(FCPtH) 14.5Hz, $\delta(\text{OCH}_3)$ 3.71ppm (singlet) (in CD₂Cl₂ + TMS); $\delta(\text{F})$ -12.5ppm (doublet of doublets), ²J(PtCF) 813Hz, ³J(PtCF) 58Hz, ³J(HPtCF) 14.5Hz (in CH₂Cl₂ + CFCl₃ 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.

References

- 1 R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1973.
- 2 D.M. Roundhill, *Adv. Organometal. Chem.*, **13**, 273 (1975).
- 3 A. Nakamura and S. Otsuka, *J. Am. Chem. Soc.*, **95**, 7262 (1973).
- 4 P. J. Davidson, M. F. Lappert and R. Pearce, *Chem. Rev.*, **76**, 219 (1976) and references therein.
- 5 G. M. Whitesides, J. F. Gaasch and E. R. Stedronsky, *J. Am. Chem. Soc.*, **94**, 5258 (1972).
- 6 J. X. Dermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, **95**, 4451 (1973).
- 7 B. Worniak, J. D. Ruddick and G. Wilkinson, *J. Chem. Soc., A*, 3116 (1971).
- 8 W. Beck, K. Schorpp, C. Oetker, R. Schlodder and H. S. Smedal, *Chem. Ber.*, **106**, 2144 (1973).
- 9 R. Ros, R. Bataillard and R. Roulet, *J. Organometal. Chem.*, **118**, C53 (1976).
- 10 R. Ros, R. A. Michelin, G. Carturan and U. Belluco, *J. Organometal. Chem.*, in press.
- 11 R. Ros, R. A. Michelin, R. Bataillard and R. Roulet, *J. Organometal. Chem.*, in press.
- 12 M. L. H. Green, "Organometallic Compounds", Vol. II, 3rd ed., G. E. Coates, M. L. H. Green and K. Wade Ed., Methuen, London, 1968.
- 13 T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
- 14 T. G. Appleton, M. H. Chisholm, H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **11**, 1786 (1972).
- 15 D. T. Rosevear and F. G. Stone, *J. Chem. Soc., A*, 164 (1968).
- 16 F. R. Hartley, *Chem. Soc. Rev.*, **2**, 163 (1973) and references quoted.
- 17 L. Collamati, A. Furlani and G. Attioli, *J. Chem. Soc. A*, 1964 (1970).
- 18 P. Chini and G. Longoni, *J. Chem. Soc. A*, 1542 (1970).