

Preliminary Communication

Cis-(hydrido)hydrocarbylplatinum(IV) complexes as intermediates
in the Pt^{II}–C bond breaking [☆]

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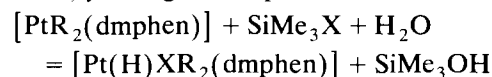
Abstract

Platinum(IV) complexes containing a *cis*-hydridohydrocarbyl arrangement have been obtained selectively on reaction of halotrimethylsilanes with bis(hydrocarbyl)(*N,N*-chelate)platinum(II) complexes. Hydrocarbon reductive elimination can be observed subsequently in solution.

Keywords: Platinum; Hydride; Oxidative addition; Reductive elimination

It is generally accepted [1] that the cleavage of the Pt^{II}–C bond by protic acids occurs by a mechanism involving the oxidative addition of the electrophile to the metal, followed by the reductive elimination of hydrocarbon. A kinetic study, consistent with this mechanism has been also reported [2]. To the best of our knowledge a six-coordinate Pt^{IV}-hydridohydrocarbyl intermediate has never been isolated, although some examples of Pt^{IV} hydrido complexes have been described [3].

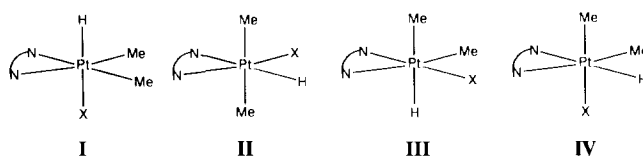
By reaction of SiMe₃X (X = Cl or Br) with [PtR₂(dmphen)] (dmphen = 2,9-dimethyl-1,10-phenanthroline; R = Me, or 4-MeOC₆H₄) in wet acetone/diethyl ether, fairly stable Pt^{IV} complexes, formally deriving by HX oxidative addition [4], were isolated in good yield as white precipitates. Generally, the water content in the reagent-grade commercial solvents was sufficient to ensure complete hydrolysis of the halosilanes, yielding electrophilic HX.



[☆] Dedicated to Prof. Fausto Calderazzo in recognition of his prominent contribution to the advancement of organometallic chemistry.

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The presence of a Pt–H bond in the products is indicated by a medium absorption band in the IR spectrum at ca. 2300 cm⁻¹, and a singlet in the ¹H NMR spectrum at ca. –22 δ (*J*_{PtH} ca. 1400 Hz). In principle, four different stereochemical arrangements are possible, as indicated below for [Pt(H)XMe₂(dmphen)] (X = Cl or Br; **1**, **2**).

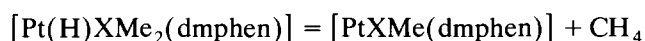


The type **I** structure is commonly observed [5] as the result of a *trans* addition in the reaction of electrophiles to *cis*-[PtR₂L₂]. In our case, however, the non-equivalence of the two halves of the symmetric dmphen and of the two Pt-bound methyl groups in the ¹H NMR spectrum rules out this geometry, as well as **II**. The large value of the Pt–H coupling constant for the hydride is considered diagnostic [3b] for a hydride *trans* to a Pt^{IV}-bound nitrogen, favours structure **IV** over structure **III**.

This stereochemical arrangement could be a consequence of the steric demands of the dmphen [6]. The ¹H NMR spectrum of the mother liquor when the solvent was acetone-d₆ showed no evidence for plat-

inum hydride species other than the precipitated product.

Complexes **1** and **2** are stable in the solid state, but a reductive elimination process complete after 2 h, takes place in chloroform solution.



The arylhydrido complex $[\text{Pt}(\text{H})\text{Cl}(4\text{-MeO-C}_6\text{H}_4)_2(\text{dmphen})]$ (**3**) was isolated only in the solid state. Its decomposition in solution, to $[\text{PtCl}(4\text{-MeOC}_6\text{H}_4)(\text{dmphen})]$ and anisole, was faster than that of the methyl derivatives, thus preventing complete characterization by ^1H NMR spectroscopy.

Further studies on the reactivity of these hydrido species are currently in progress.

1. Experimental details

1.1. General synthetic procedure

To a suspension of red $[\text{PtR}_2(\text{dmphen})]$ [**7**] (0.1 mmol) in 2 ml of 1:1 diethylether/acetone, Me_3SiX was added in a slight excess (1.1:1 ratio) at room temperature. After 0.5 h stirring, a white solid was separated by filtration, washed twice with diethyl ether, and dried. Yields were 50–60% [**8**].

1.2. Reductive elimination

A 5 mg sample of the hydrido complex was dissolved in 0.5 ml of CDCl_3 . The reductive elimination of the hydrocarbon was monitored by ^1H NMR spectroscopy. Addition of diethyl ether after the reaction was completed caused crystallization of yellow $[\text{PtXR}(\text{dmphen})]$ [**9**] in quantitative yield.

Acknowledgments

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References and notes

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- [3] (a) J.E. Bentham, S. Cradock and E.A.V. Ebsworth, *J. Chem. Soc.*, (A) (1971) 587; (b) I.C.M. Wehman-Ooyevaar, D.M. Grove, P. de Vaal, A. Dedieu and G. Van Koten, *Inorg. Chem.*, **31** (1992) 5484.
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- [6] V.G. Albano, G. Natile and A. Panunzi, *Coord. Chem. Rev.*, **133** (1994) 67.
- [7] $[\text{PtR}_2(\text{dmphen})]$ were prepared by adapting described procedures. P.K. Monaghan and R.J. Puddephatt, *Organometallics*, **3** (1984), 444; M.E. Cucciolito, V. De Felice, A. Panunzi and A. Vitagliano, *Organometallics*, **8** (1989) 1180. ^1H NMR data for $[\text{PtMe}_2(\text{dmphen})]$ ($(\text{CD}_3)_2\text{CO}$) δ ppm: 8.52 (d, 2H), 7.87 (s, 2H), 7.70 (d, 2H), 2.96 (s, 6H, 2 Me), 1.06 (s, $^2J_{\text{PtH}} = 80$ Hz, 6H, Pt–Me); $[\text{Pt}(4\text{-MeOC}_6\text{H}_4)_2(\text{dmphen})]$ (CDCl_3) δ ppm: 8.28 (d, 2H), 7.80 (s, 2H), 7.47 (d, 2H), 7.29 (d, $^3J_{\text{PtH}} = 74$ Hz, 4H, 4 Ar–H), 6.55 (d, 4H, 4 Ar–H), 3.69 (s, 6H, 2 OMe), 2.20 (s, 6H, 2 Me).
- [8] Selected physical and spectroscopic data. **1**: IR (Nujol): 2300 cm^{-1} (ν Pt–H). ^1H NMR data (CDCl_3) δ ppm: 8.32 (d, 1H), 8.30 (d, 1H), 7.84 (s, 2H), 7.80 (d, 1H), 7.64 (d, 1H), 3.19 (s, 2 Me), 1.64 (s, Pt–Me_{eq}, $^2J_{\text{PtH}} = 71$ Hz, 3H), 0.52 (s, Pt–Me_{ax}, $^2J_{\text{PtH}} = 71$ Hz, 3H), –22.10 (s, Pt–H, $^1J_{\text{PtH}} = 1404$ Hz, 1H). Elemental Anal. Found: C, 40.95; H, 4.00; N, 5.85. $\text{C}_{16}\text{H}_{19}\text{ClN}_2\text{Pt}$, Calc.: C, 40.90; H, 4.07; N, 5.96%.
2: IR (Nujol): 2300 cm^{-1} (ν Pt–H). ^1H NMR data (CDCl_3) δ ppm: 8.32 (d, 1H), 8.30 (d, 1H), 7.84 (s, 2H), 7.78 (d, 1H), 7.66 (d, 1H), 3.20 (s, 6H, 2 Me), 1.69 (s, Pt–Me_{eq}, $^2J_{\text{PtH}} = 70$ Hz, 3H), 0.57 (s, Pt–Me_{ax}, $^2J_{\text{PtH}} = 71$ Hz, 3H), –21.88 (s, Pt–H, $^1J_{\text{PtH}} = 1350$ Hz, 1H). Elemental Anal. Found: C, 37.50; H, 3.85; N, 5.35. $\text{C}_{16}\text{H}_{19}\text{BrN}_2\text{Pt}$, Calc.: C, 37.36; H, 3.72; N, 5.45%.
3: IR (Nujol): 2290 cm^{-1} (ν Pt–H). Elemental Anal. Found: C, 47.30; H, 4.20; N, 4.80. $\text{C}_{22}\text{H}_{23}\text{ClN}_2\text{O}_2\text{Pt}$, Calc.: C, 47.02; H, 4.12; N, 4.98%.
- [9] The compounds were identified by comparison with independently synthesized samples V. De Felice, A. De Renzi, D. Tesauero and A. Vitagliano, *Organometallics*, **11** (1992) 3669.