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Preliminary communication

Five-coordinate hydrido/olefin platinum(II) complexes

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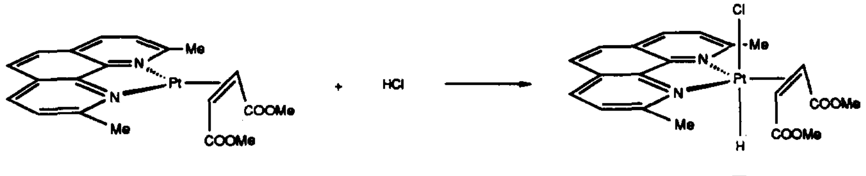
Abstract

Stable five-coordinate hydrido/olefin complexes of general formula [Pt(2,9-Me_2-1,10-phenanthroline)H(Cl)(olefin)] have been synthesized in high yield through oxidative addition of HCl to [Pt(2,9-Me_2-1,10-phenanthroline)(olefin)] precursors. Relevant spectroscopic features and some preliminary results concerning the reactivity of the new compounds are also reported.

Several catalytic processes [1] promoted by nickel, palladium and platinum involve hydrido-intermediates, often as coordinatively saturated species [2] and a variety of stable hydrido-complexes of these metals have been isolated [3,4]. However, there are few stable coordinatively saturated derivatives [5–10] of the M^{II} d^8 ions. As far as we are aware, all the stable five-coordinate mononuclear M^{II} hydrides contain stannyl and/or phosphine ligands, and only two are olefin complexes.

On the basis of earlier results [11] on complexes of the type [Pt(*N*,*N*-chelate)L(X)(olefin)] (I) we have tried to synthesize hydrido-complexes of the same general formula. This note reports preliminary results on the synthesis and reactions of stable [Pt(*N*,*N*-chelate)H(Cl)(olefin)] (II) complexes.

The oxidative addition of HCl to a suitable [12,13] three-coordinate species is a facile procedure for the syntheses of type II compounds, such as IIa.



III a

II a

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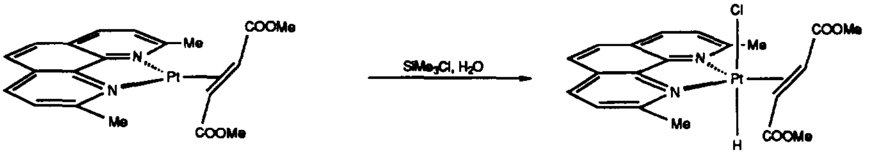
The reaction is immediate, upon addition of a 10% excess of gaseous HCl to a 0.05 *M* chloroform solution of IIIa at room temperature. The crystalline product [14*] can be isolated in high yield by addition of hexane to the reaction medium. Our preliminary results indicate that other synthetic procedures can be used for preparing type II complexes. Thus, the dimethylfumarate complex IIb [15*] was obtained directly after addition of trimethylchlorosilane to a suspension of the three-coordinate species IIIb in water-saturated toluene.



III b   II b

This process might involve the hydrolysis of a five-coordinate type I silicon derivative, or involve HCl formed by hydrolysis of the silane. In fact, the synthesis of IIb involving HCl addition to IIIb is easily obtained in 85% yield by the first procedure.

Stable type II hydrides with apical halide ligands other than Cl can also be obtained.

The most significant feature of the ^1H NMR spectra of the five-coordinate hydrides is the shift of the hydride resonance to higher fields when compared to the values normally observed for square planar derivatives [3]. We have also investigated the chemistry of these compounds. Treatment of an absolute ethanol suspension of IIa with an equimolar amount of KOH in the same solvent regenerates IIIa in a few minutes. Reductive elimination of HCl can be accomplished by other ways. Thus IIa reacts with fumarodinitrile in chloroform solution affording quantitatively the poorly soluble three-coordinate complex [Pt(2,9-Me_2-1,10-phen)(fumarodinitrile)] [16*]. Treatment of type III complexes containing other *N*–*N* ligands such as 1,10-phenanthroline and 2-methyl-1,10-phenanthroline in the above reported conditions affords tetra-coordinate functionalized alkyl derivatives. Thus, [Pt(1,10-phen)Cl(MeOOCCHCH_2COOMe)] [17*] is formed from [Pt(1,10-phen)(dimethylmaleate)].

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References and notes

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14gjFor IIa (only one of the two possible isomers is observed and the figure does not imply any configuration assignment): Anal. Found: C, 41.30; H, 3.69; N, 4.73. $C_{20}H_{21}ClN_2O_4Pt$ calc.: C, 41.14; H, 3.63; N, 4.80%. IR (Nujol): 2290 cm^{-1} (ν(Pt–H)). Selected ^1H NMR data ($CDCl_3$, $CHCl_3$ as internal standard): 4.08 [s, ^2J(Pt–H) = 83 Hz, 2H], 3.71 (s, OMe), 3.35 (s, NCMe), −25.70 [s, ^1J(Pt–H) = 1178 Hz, 1H]; non-electrolyte in chloroform.

15 For IIb: Anal. Found: C, 41.23; H, 3.59; N, 4.75. $C_{20}H_{21}ClN_2O_4Pt$ calc.: C, 41.14; H, 3.63; N, 4.80%. IR (Nujol): 2260 cm^{-1} (ν(Pt–H)). Selected ^1H NMR data ($CDCl_3$, $CHCl_3$ as internal standard): 4.70 [d, ^2J(Pt–H) = 71 Hz, 1H], 4.43 [d, ^2J(Pt–H) = 74 Hz, 1H], 3.76 (s, OMe), 3.67 (s, OMe), 3.47 (s, NCMe), 3.37 (s, NCMe), −25.90 [s, ^1J(Pt–H) = 1073 Hz, 1H]; non-electrolyte in chloroform.

16 Selected ^1H NMR data ($C_2D_2Cl_4$, $C_2H_2Cl_4$ as internal standard): 3.27 (s, NCMe), 2.90 [s, ^2J(Pt–H) = 88, 2H].

17 Selected ^1H NMR data ($CDCl_3$, $CHCl_3$ as internal standard): 4.25 [dd, ^2J(Pt–H) = 130 Hz, 1H], 3.16 (dd, 1H), 2.81 (dd, 1H).