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Preliminary communication

HYDRIDO CYANOALKYLS OF PLATINUM(II)

RENZO ROS
Facoltà di Chimica Industriale, University of Venice (Italy)
RAYMOND BATAILLARD and RAYMOND ROULET*
Institute of Inorganic and Analytical Chemistry, Place du Château 3, University of Lausanne (Switzerland)

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Summary

The preparation and reactions are described of some novel platinum(II) complexes with a hydride ligand group *trans* to an sp^3 carbon, viz. [$PtH(YCN)(PPh_3)_2$] with Y = $(CH_2)_n$ (n = 1—3) or *o*-$CH_2C_6H_4$.

We previously reported the preparation, spectroscopic properties and reactivity of various cyanoalkyl complexes of platinum(II) of the type $PtX(YCN)L_2$ (L = tertiary phosphine; Y = $(CH_2)_n$, n = 1,2,3,*o*-$CH_2C_6H_4$; X = Cl, Br) and their cationic derivatives $[Pt(YCN)L_2]_m(BF_4)_m$ [1]. We have now shown that while heating the cationic complexes in methanol leads to nucleophilic attack at the CN group, yielding iminoether complexes, methanolic NaOH gives good yields of the novel hydride complexes *trans*-$PtH(YCN)L_2$. The *trans* geometry is deduced from ^1H and $^{31}P\{^1H\}$ FT NMR spectra:

trans-$PtH(CH_2CN)(PPh_3)_2$: δ(H) −7.32 ppm (triplet of triplets), ^1J(PtH) 746 Hz, ^2J(PPtH) 16 Hz, ^3J(HCPtH) 3 Hz; $\delta(CH_2)$ 0.63 ppm (triplet of doublets), ^2J(PtCH) 69.6 Hz, ^3J(PPtCH) 6.2 Hz (in CH_2Cl_2/CD_2Cl_2 + TMS). δ(P) 32.2 ppm (s), ^1J(PtP) 3034 Hz (external reference: H_3PO_4 85%). IR in Nujol: ν(CN) 2183, ν(PtH) 2027, δ(PtH) 808 cm^{-1}. *trans*-$PtH(C_3H_6CN)(PPh_3)_2$: δ(H) −4.51 ppm (t), ^1J(PtH) 636 Hz, ^2J(PPtH) 18 Hz; $\delta(C_3H_6)$ 0.4 — 1.1 ppm (multiplet, broad); δ(P) +35.1 ppm (s), ^1J(PtP) 3160 Hz. IR in Nujol: ν(CN) 2245, ν(PtH) 1950, δ(PtH) 827 cm^{-1}.

Both the ^{195}Pt—^1H coupling constants and ν(PtH) show that the cyanopropyl group has a stronger *trans* influence than cyanomethyl.

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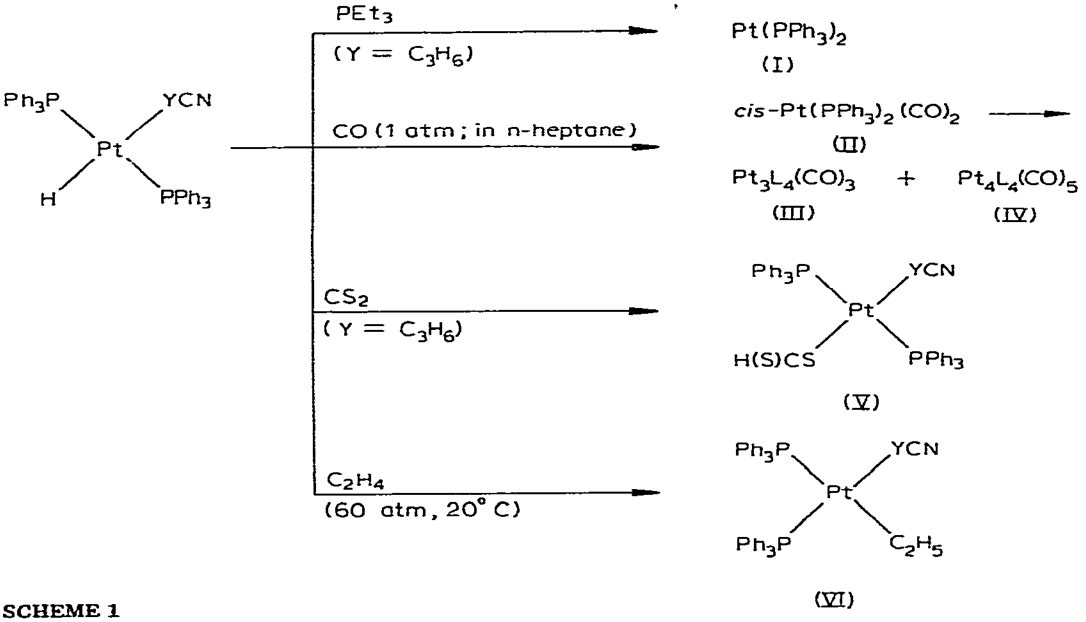
*To whom correspondence should be addressed.

The same complexes are obtained by treating *cis*- or *trans*-$PtCl(YCN)L_2$ or *trans*-$[Pt(YCN)L_2]_m(BF_4)_m$ with $NaBH_4$ in ethanol. The hydride complexes are stable white microcrystalline powders, soluble in benzene and dichloromethane, and slightly soluble in alcohols. They react with $CHCl_3$ giving *trans*-$PtCl(YCN)L_2$ and CH_2Cl_2. In reactions with small molecules, they undergo reductive elimination to platinum(0) complexes or insertion into the platinum—hydride bond (Scheme 1).



SCHEME 1

Compounds I—IV have already been obtained by other methods [2,3]. V has a *trans* geometry (δ(P) + 26.1 ppm, ^1J(PtP) 3170 Hz), whereas only *cis*-dialkyls were obtained: *cis*-$Pt(C_3H_6CN)(C_2H_5)(PPh_3)_2$: δ(P) 26.6 ppm (d), $^1J(PtP^1)$ 1872 Hz and 26.2 ppm (d), $^1J(PtP^2)$ 1684 Hz with P^1 *trans* to the ethyl group. Treating the cationic complexes of *cis* geometry, for example *cis*-$[Pt(CH_2CN)(PPh_3)_2]_2(BF_4)_2$, with NaOH in methanol/water does not yield hydride complexes but instead *cis*-$PtOH(CH_2CN)(PPh_3)_2$. The reactivity of these hydroxo complexes is under investigation.

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