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Preliminary communication

PREPARATION AND REACTIVITY OF CYANOALKYL COMPLEXES OF PLATINUM(II)

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Summary

Neutral and cationic cyanoalkyls of platinum(II) have been prepared; in some cases the coordination of the CN group promotes *cis—trans* isomerization, as well as addition reaction of alcohols to give imino ether complexes, while the longer chain cyanoalkyls undergo CO insertion.

There are several features of potential interest with cyanoalkyl complexes of transition metals in low oxidation states. In particular, insertion reactions should give organic moieties with two functional groups, coordination of the cyano group could lead to isomerizations, and π-bonded-CN should be prone to addition reactions. Cyanomethyl complexes of d^8 metals are known in the case of Ir^{III} [1], Pd^{II} [2], Rh^{III} [3] and recently Bennett et al. [4] obtained unsymmetrical *cis*-dialkyls of Pt^{II} from hydroxo-complexes.

We now report the preparation and some properties of complexes of the type $PtX(RCN)L_2$ (I) ($L = PPh_2CH_3, PPh_3$; $R = (CH_2)_n$, $n = 1, 2, 3$, o-$CH_2C_6H_4$; $X = Cl, Br$) and their cationic derivatives $[Pt(RCN)L_2L']BF_4$ ($L' = CO, CH_3CN$, ArNC) and $[Pt(RCN)L_2]BF_4$ in which the cyano group is also coordinated*.

The oxidative addition of $ClCH_2CN$ to $Pt(PPh_2CH_3)_4$ in benzene at room temperature gives a *cis—trans* mixture of I (30/70), from which the *trans* isomer is separated by fractional crystallization. The *trans* isomer [^1H NMR of CH_2: δ 0.9 ppm (t, J(PtH) 107 Hz, J(PH) 8 Hz); of $P—CH_3$: δ 2.3 ppm (J(PtH) 28 Hz, J(PH) 7 Hz, separation of the two outer peaks of the 1/2/1 triplet [5])] is isomerized to the original *cis—trans* mixture in boiling benzene in the presence of free phosphine [*cis* isomer: 2 doublets $\delta(PCH_3)$ 2.07 ppm (10 Hz), 1.78 ppm (10 Hz)].

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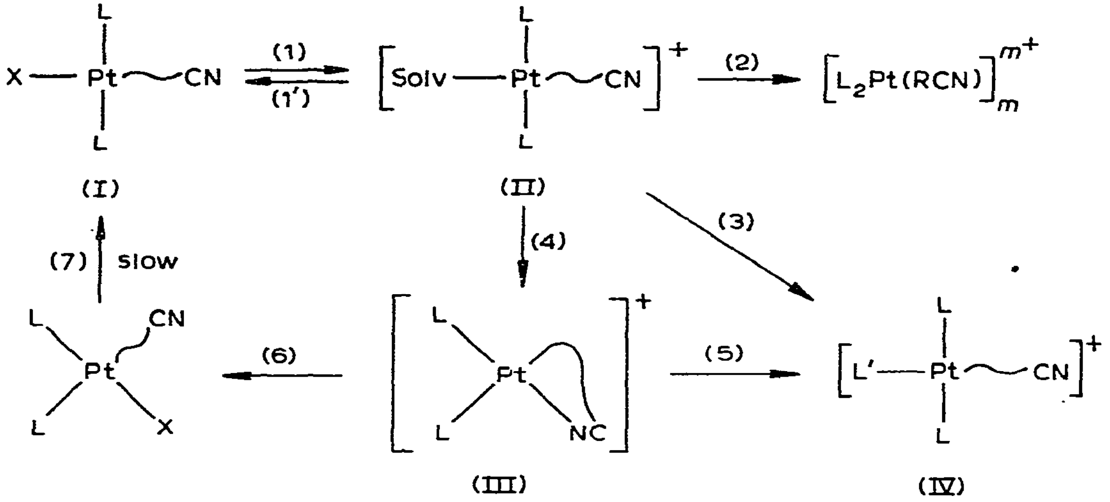
*Good elemental analyses were obtained for all complexes.

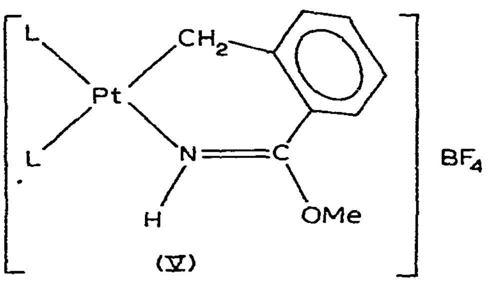
The reaction of XRCN with $Pt(PPh_3)_4$ at room temperature gives only the monomeric *trans*-$PtX(RCN)L_2$ (I) in 70—90% yield (Refluxing or longer times of reaction reduce the yield by formation of PtX_2L_2.) Abstraction of X^- by Ag^+ is rapid, and leads to various cationic species, as shown in Scheme 1.



Scheme 1

(1): + Ag^+/Solv., —AgX. (2): Solv. = Me_2CO, CH_2Cl_2 ; R = CH_2, CH_2CH_2. (3) (5): L' = CO, ArNC, Me_2S. (4): R = *o*-$CH_2C_6H_4$. (1') (6) (7): + LiX.

Complexes of type II have been isolated for small chain cyanoalkyls with Solv. = CH_3CN. As shown by ^{31}P NMR, isomerization occurs for *o*-cyanobenzyl (III). The CN group seems to be σ-bonded (ν(CN) 2260 cm^{-1} compared to 2220 cm^{-1} for I), even though Dreiding molecular models show that considerably more strain is involved in the σ- than in the π-arrangement. Coordination of CN in this cationic species facilitates the addition of weak protic solvents. For example, dissolution of the tetrafluoroborate salt of III in methanol and precipitation by ether gives the imino ether complex V.



Except for the cyanomethyl complex the compounds of type I undergo CO insertion into the σ-Pt—C bond (90% yield, 3 days at 50 atm), and the intermediate complexes IV have been isolated. The pyrolysis and the Pt—C bond scission of these complexes and their Pd^{II} analogs is under investigation.

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