Cationic Methyl Platinum(II) Nitrile and Imino-ether Complexes

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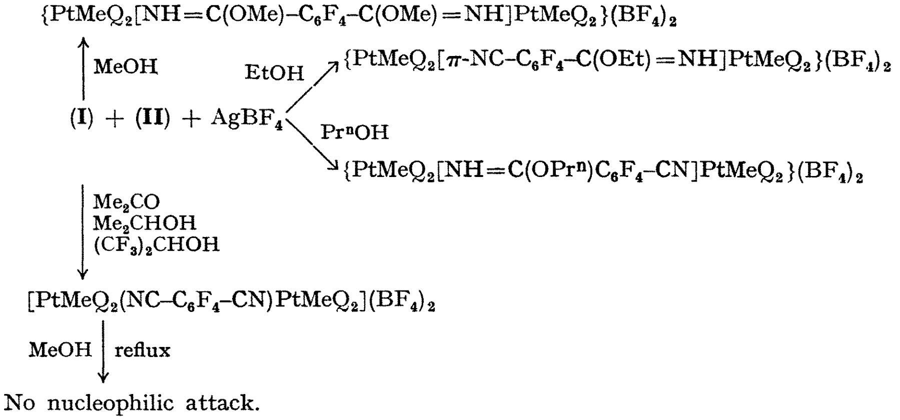
Summary Cationic methylplatinum(II) imino-ether and nitrile complexes have been isolated from reactions of *trans*-$MeClPt(PMe_2Ph)_2$ with perfluoronitriles and AgX, where X = PF_6^- and BF_4^-, in the presence of alcohols.

Alcohols have recently been shown to react with co-ordinated unsaturated systems such as isocyanides[1–3] and acetylenes[4] to yield various carbene complexes. We now report the first examples of nucleophilic attack by alcohols at co-ordinated nitriles to give imino-ether complexes. *trans*-$MeClPtQ_2$ (Q = $PhMe_2P$) (I) with pentafluorobenzonitrile and silver hexafluorophosphate in methanol at 25° gives *trans*-$[MePt(NCC_6F_5)Q_2]^+PF_6^-$, in which the nitrile is a σ-donor as shown by the increase[5] of ν(C≡N) to 2274 cm^{-1}. However, with silver tetrafluoroborate, the imino-ether complex *trans*-$[MePt(NH{=}C(OMe)C_6F_5)Q_2]BF_4$ was obtained, which showed no ν(C≡N) but ν(C=N) at 1653 cm^{-1}.



Scheme 1

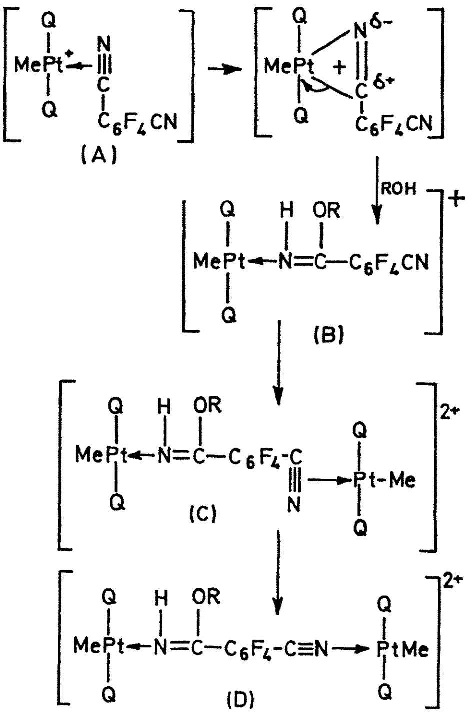
2,3,5,6-Tetrafluoroterephthalonitrile (II) and silver tetrafluoroborate gave various products (Scheme 1) depending on the alcohol.

All the imino-ether complexes show strong, sharp ν(C=N) Raman and i.r. absorptions in the 1630—1660 cm^{-1} region. I.r. absorption due to ν(N–H) appears as a weak peak at 3300—3400 cm^{-1}. The ^{1}H n.m.r. spectra of the co-ordinated imino-ether complexes show N–H resonances as broadened singlets at δ (NH) *ca.* −9·10 p.p.m. Platinum–methyl resonances, where δ (Me) is in the region −0·60 to −0·20 p.p.m. show *J* (Pt–C–H) *ca.* 80 Hz, when methyl is *trans* to σ-bonded nitrile and about 75 Hz when methyl is *trans* to imino-ether, indicating a stronger *trans* influence[6] for the co-ordinated imino-ether.

In the reaction with ethanol, just described in Scheme 1, the product contains an imino-ether group, shown by ν(C=N) at 1648 cm^{-1}, as well as a π-bonded nitrile group. This is revealed spectroscopically by the shift to lower frequency of the ν(C≡N) i.r. absorption by 119 to 2141 cm^{-1}. In contrast, the product with n-propanol contains one σ-bonded nitrile, in which ν(C≡N) is shifted slightly to higher frequency.

A plausible mechanism for imino-ether formation is based on a transition-metal-stabilised carbonium ion.[7]

Initial π-bond formation (A) is apparently essential for nucleophilic attack, since refluxing of the σ-bonded co-ordinated dinitrile in methanol did not lead to imino-ether formation. It is also consistent with characterisation of the π-bonded function in the ethanol product just described.



Scheme 2

The apparent decrease in the reactivity of the second nitrile group of the ligand, for different alcohols in the order MeOH $>$ EtOH $>$ Pr^nOH $>$ Pr^iOH, $(CF_3)_2CHOH$, may be due to the large steric requirements of the –OR and C_6F_4 groups. However, these reactions are also anion dependent; the reactions with pentafluorobenzonitrile described above illustrate this. Also, silver hexafluorophosphate and *trans*-$MeClPtQ_2$ (Q = $PhMe_2P$ or Me_3As) with (II) in methanol give attack at only one nitrile, the second being σ-bonded to platinum. Reactions in ethanol and higher alcohols, again using the hexafluorophosphate, gave the σ-bonded dinitriles. We studied various aromatic nitriles, including terephthalonitrile, but observed nucleophilic attack by alcohols only with the perfluoronitriles.

With perfluoroalkylnitriles, such as CF_3CN, dealkylation of the nitrile occurs,[8] to give methylplatinum complexes which are currently being studied, but which contain no perfluoroalkyl groups.

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