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Preliminary communication

FACILE INSERTION AND THE *cis*-GEOMETRY: REACTIVITY OF *cis*-π-OLEFINIC AND π-ACETYLENIC METHYLPLATINUM(II) COMPLEXES

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Summary

The reactivities of new *cis*-π-olefinic and π-acetylenic methylplatinum(II) complexes demonstrate that attainment of a *cis*-configuration by the olefin (or acetylene) and the Pt—C bond is not a sufficient condition for facile insertion.

Recent studies [1, 2], including kinetic investigations [3, 4], have demonstrated unambiguously that, in many cases, the insertion of olefins or acetylenes into Pt—H or Pt—C bonds occurs first by substitution of the ligand *trans* to hydride or alkyl, followed by rearrangement of the resulting four-coordinate species to give, ultimately, the inserted product. Formally at least, this would appear to involve a *trans*→*cis* isomerization in order to generate a *cis* intermediate which then undergoes the migratory rearrangement of insertion. Accordingly, we have now examined the reactivity towards insertion of some cationic and neutral methylplatinum(II) complexes each containing a π-bonded olefin or acetylene *cis* to the Pt—CH_3 group.

Reaction of $[(\text{diars})\text{PtMe}\{CH_3(C{=}O)CH_3\}]^+$ (prepared in situ from (diars)-PtMeCl and $AgPF_6$ in acetone) [diars = *o*-phenylenebis(dimethyl)arsine] with excess ethylene or propene afforded white crystalline π-complexes, $[(\text{diars})\text{PtMe(un)}]PF_6$, (where un = C_2H_4 or C_3H_6), which decompose slowly in the solid state and more rapidly in solution. The proton NMR spectrum for the ethylene complex in CD_2Cl_2 showed an averaged signal for free and complexed ethylene at τ 5.38, with no evidence of coupling to ^{195}Pt. The rapid intermolecular olefin exchange which must therefore be occurring, is stopped at −100° at which temperature a signal for complexed ethylene appears at τ 6.78 with $J(\text{PtH}) = 112$ Hz. In contrast, the complex *trans*-$[PtCH_3(PPh_2Me)_2(C_2H_4)]PF_6$, has a strongly bound ethylene since at +32°, the NMR spectrum shows distinct signals for free and complexed olefin, the latter showing Pt—H coupling. It seems apparent that *cis* olefin complexes $L_2PtCH_3(\text{un})^+$ are much more labile than their *trans* analogues. None of these complexes reacted further, at least at room temperature, to give inserted alkylplatinum compounds.

In contrast, the *cis*-complexes [LLPtMe{$CH_3C(=O)CH_3$}]PF_6 (LL = diars or diphos) and LLPtMeNO_3 (LL = diphos) reacted smoothly at 25° with the activated acetylenes $CF_3C{\equiv}CCF_3$ and MeOOCC≡CCOOMe to give the corresponding vinylic derivatives, LLPt(RC=CRCH$_3$)X. These reactions proceeded more slowly for X = NO_3 than for X = acetone, although in all cases the vinylic group had the *cis* geometry consistent with the collapse of the expected four-centred transition state. Clearly, the electron-withdrawing substituents on these acetylenes are important in inducing these facile insertions. This is further confirmed by our preparation of the complexes [$Et_2B(pz)_2$]PtMe(un) where pz = pyrazolyl, and un = PhC≡CH$_3$ or PhC≡CPh. These are stable monomeric, four coordinate complexes containing the π-bonded acetylene perpendicular to the plane of the complexes [5]. The electron-donating acetylenic substituents render these complexes somewhat inert towards insertion; thus for un = PhC≡CMe, the complex is unaffected by refluxing in benzene for 2 days. Attempts to prepare the analogous complex with $CF_3C{\equiv}CCF_3$ led immediately to the vinylic insertion product isolated as its triphenylphosphine adduct, (Et_2Bpz_2)Pt(RC=CRCH$_3$)PPh Such facile insertion which presumably occurs via a transient four coordinate *cis*-π-acetylenic complex contrasts with the great stability and inertness of the analogous five coordinate complex, ($HBpz_3$)PtMe($CF_3C{\equiv}CCF_3$), which also possesses a *cis* arrangement of acetylene and methyl ligands [6].

These results are consistent with the general statements that (a) in methylplatinum(II) compounds unsaturated ligands (olefins or acetylenes) are more labile when π-bound in the *cis* position than when similarly bound in the *trans* site; (b) an activated acetylene (e.g. C_4F_6) inserts into Pt—CH_3 more readily from a four coordinate than a five coordinate geometry, and (c) the ease of insertion is influenced at least as much by the electronic properties of the ligands about platinum and of the olefinic or acetylenic substituents, as it is by the attainment of a *cis* geometry.

Satisfactory analytical results were obtained for all of the new compounds described.

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References

1 H.C. Clark and H. Kurosawa, Inorg. Chem., 11 (1972) 1275.
2 M.H. Chisholm and H.C. Clark, Accounts Chem. Res., 6 (1973) 202.
3 H.C. Clark and C.R. Jablonski, Inorg. Chem., in press.
4 H.C. Clark and C.S. Wong, J. Amer. Chem. Soc., in press.
5 B.W. Davies and N.C. Payne, private communication.
6 H.C. Clark and L.E. Manzer, Inorg. Chem., 13 (1974) 1291.