Preparation of a Five-co-ordinate Platinum–π-Ethylene Complex: (Biacetyl bismethylphenylhydrazone)dichloro-π-ethyleneplatinum(II)

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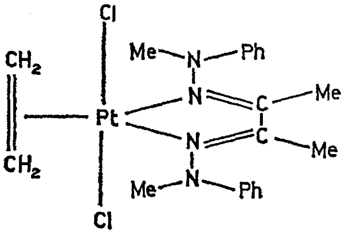
Summary Reaction of K[$PtCl_3(C_2H_4)$] with biacetyl bismethylphenylhydrazone leads to (biacetyl bismethylphenylhydrazone)dichloro-π-ethyleneplatinum(II), a trigonal bipyramidal complex with two chlorine atoms in the apical positions.

The reaction of Zeise's salt with chelating ligands (L–L) usually gives a *cis*-dichloro(L–L)platinum(II) complex,[1–4] probably *via* attack of the entering group on the position *trans* to the unsaturated ligand, followed by the substitution of a *cis*-chloride and subsequent replacement of the olefin by a halide ion.[3,5] In similar reactions with the analogous acetylene complex, the formation of a five-co-ordinate intermediate has been postulated.[6] The complex reported here is the first authenticated case of the isolation of a five-co-ordinate platinum(II) olefin intermediate, although five-co-ordinate ethylene complexes of rhodium(I)[7] and iridium(I)[8] have been reported.



(1)

The reaction between K[$PtCl_3(C_2H_4)$] and biacetyl bismethylphenylhydrazone in methanol at 0 °C, gives a quantitative yield of complex (**1**) as yellow-orange needles after a few minutes. Complex (**1**) is very stable in the crystalline state, is non-conducting in nitromethane, and dissolves in common organic solvents (including Et_2O) in which it slowly decomposes to (biacetyl bismethylphenylhydrazone)dichloroplatinum(II). The same transformation occurs at 100 °C in the solid state. Complex (**1**) gave satisfactory elemental analysis, and i.r. and n.m.r. spectra.

The n.m.r. spectrum in $CDCl_3$ shows phenyl resonances and signals at τ (downfield from Me_4Si) 6·10 (6H), 6·78 ($J_{Pt,H}$ 71 Hz, 4H), and 8·00 (6H). The signal at τ 6·78 had two satellites on either side due to coupling with ^{195}Pt (33·7% abundance) and was assigned to the ethylene protons (methyl resonances for the free ligand are at τ 6·87 and 7·81). The spectrum after about 1 h at room temperature in a sealed tube showed the same pattern, together with a new peak of very low intensity at τ 4·70 (free ethylene[9]). The n.m.r. spectrum in nitrobenzene shows resonances at τ 6·07 (6H), 6·79 ($J_{Pt,H}$ 70 Hz, 4H), and 7·94 (6H). The corresponding methyl protons in (biacetyl bismethylphenylhydrazone)-*cis*-dichloroplatinum(II) (**2**) give peaks at τ 6·19 and 7·74.

The i.r. spectrum below 400 cm^{-1} showed only one band, at 340 cm^{-1} (*trans*-Pt–Cl stretch) [the *cis*-dichloro-complex (**2**) gives two Pt–Cl stretching bands at 328 and 338 cm^{-1}].

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