An Electron-rich Olefin as a Source of Co-ordinated Carbene; Synthesis of *trans*-$PtCl_2[C(NPhCH_2)_2]PEt_3$

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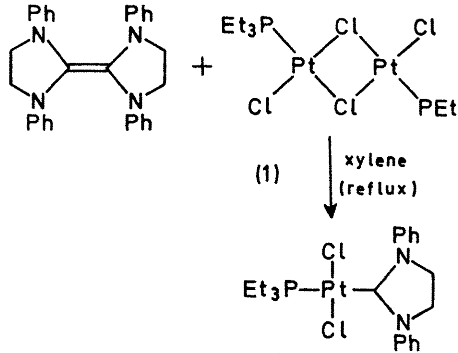
Summary Interaction of the appropriate electron-rich olefin and chloride bridged Pt^{II} dimer has yielded the unreactive *trans*-Pt^{II} carbene complex (I) which is believed to isomerise thermally to the *cis*-isomer; the structure of the *trans*-complex is established *inter alia* by a single crystal *X*-ray analysis.

WE have examined the possibility of preparing transition-metal carbene complexes using neutral precursors as sources of the organic ligand. (For previous synthesis see ref. 1 and 2, and possible trapping experiments, ref. 3 and 4.)

Di-μ-chlorodichlorobis(triethylphosphine)diplatinum(II) is known to react readily with ligands, forming mononuclear complexes;[5] co-ordinated carbenes so far reported have nucleophilic character (but see ref. 3 and 4).[6] Reaction (1) provides the first example of the synthesis of a transition-metal carbene complex derived from an electron-rich olefin. Bridged binuclear complexes are generally susceptible to nucleophilic attack, and thus may prove useful traps also for other transient intermediates, *e.g.*, benzynes.



(I)

The product (I), after recrystallisation from methanol forms lemon yellow needles, having satisfactory elemental analysis (C, H, N, P, Cl). It melts partially at 201°, but resolidifies at 205°, not melting finally until 308—315° (decomp.) in a sealed tube. A sample was heated to about 210°, and kept at this temperature for 1 h. The product, which is essentially insoluble in common organic solvents, forms white crystals from a large volume of methanol. It shows two i.r. bands at 308 and 277 cm^{-1}, attributed to ν(Pt–Cl); and has an identical elemental analysis to the carbene complex (I). We suggest that this is the *cis*-isomer of (I). The mass spectrum of this sample in addition to an ion at *m/e* 607, the same mass number as the molecular ion of (I), shows two peaks at higher *m/e* presumably originating from the products of reactions occurring within the spectrometer (at *m/e* 643, probably arising from chloride ion capture, and *ca.* 680).

Compound (I) is diamagnetic, and its 100 MHz ^1H n.m.r. spectrum in $CDCl_3$ shows a singlet for the imidazolidine ring protons (τ 5·82), and the expected Me, CH_2 (centred at τ 9·08 and 8·41) (from Et_3P) and Ph peaks (two multiplets centred at τ 2·05 and 2·74) with satisfactory integration, and no other absorptions. ^{31}P n.m.r. shows a single peak, with platinum satellites, $J(^{195}Pt–^{31}P)$ 2·44 kHz, suggesting that phosphorus is *trans* to a ligand other than chlorine. The *trans*-configuration is in accord with its solubility, colour, and *X*-ray crystal structure. The i.r. spectrum shows ν(Pt–Cl) as a band at 340 cm^{-1} having a shoulder at 425 cm^{-1}, suggesting further that the two chlorine atoms are *trans* to one another.

Compound (I) has also been obtained from 1,3-diphenyl-2-trichloromethylimidazolidine[7] and the platinum dimer in xylene under reflux.

A single-crystal *X*-ray structure analysis has been carried out, based on 2356 independent diffraction data. The stereochemistry of (I) has been definitely established, and the bond lengths at the current stage of refinement (R = 0·057) are shown in the Figure.

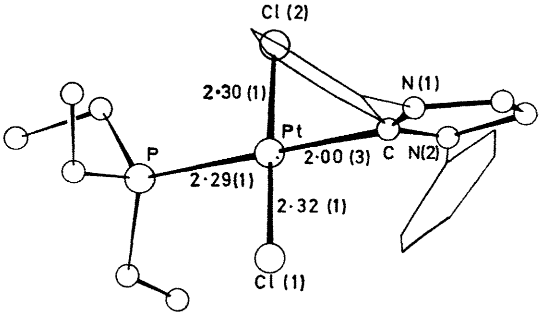


FIGURE. *Bond lengths (Å) in* (I).

Complex (I) is thus the first example of a platinum(II) carbene complex with the *trans*-configuration. The carbene–carbon is approximately trigonal, and the N–C–(Pt)–N plane lies at 70° to the co-ordination plane of the platinum ($PtCCl_2P$). The Pt–C bond length is [2·00(3) Å] longer than that in carbonyl-platinum complexes [*cf.*[8] 1·74 in *trans*-$PtCl_2(CO)(ONC_6H_5OMe)$]; and longer than that in *cis*-$PtCl_2(COEtNHPh)PEt_3$. The Pt–P distance enables us to estimate the *trans*-influence of the carbene ligand, which is about equal to that of a tertiary phosphine; as has been found (based on Pt–Cl bond lengths) for the carbene ligand C(OEt)NHPh in *cis*-$PtCl_2(COEtNHPh)PEt_3$.[9]

We have also examined the reactions of precursors of electrophilic carbenes,[10] but have not isolated carbene complexes [see for example equations (2) and (3).]

$$(CF_3)_2CN_2 + trans\text{-}(Et_3P)_2Pt_2Cl_4 \rightarrow trans\text{-}(Et_3P)_2[(CF_3)_2CCl]_2Pt_2Cl_2 \qquad (2)$$

$$(CF_3)_2CN_2 + (Ph_3P)_3Pt \rightarrow (Ph_3P_2)_2Pt(CF_3)_4C_2N_2 \qquad (3)$$

The product in equation (3) has been independently obtained by Dr. M. Green, Professor F. G. A. Stone, and their co-workers.

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