Journal of Organometallic Chemistry C59
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

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trans/cis-Isomerism and isomerisation of Pd^{II} and Pt^{II} carbene complexes; the crystal and molecular structures of *cis*- and *trans*-$PtCl_2[C(NPhCH_2)_2]$-PEt_3

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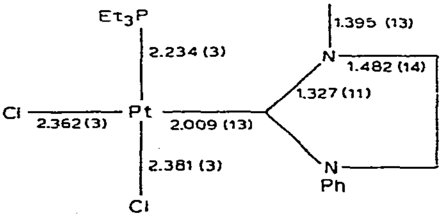
(Received September 11th, 1972)

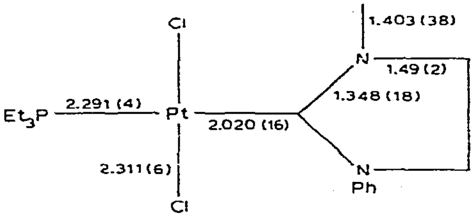
SUMMARY

trans-Pt^{II} or *trans*-Pd^{II} carbene complexes are isomerised to the thermodynamically more stable *cis* compounds; *cis*- and *trans*-isomeric pairs are compared with respect to reactivity and physical properties, including spectroscopic and X-ray data.

Since the preparation of the first transition-metal carbene compound[1] in 1964 more than two hundred complexes have been characterised[2]; however, no case of *cis/trans*-isomerism, other than that due to restricted rotation about a C—N or C—O bond, has been observed. We now report on (*i*) the thermal isomerisation of *trans*-Pt^{II} and *trans*-Pd^{II} complexes to give the thermodynamically more stable *cis* compounds; (*ii*) the characterisation of a series of *cis*- and *trans*-carbene complexes such as (I) and (II); and (*iii*) the crystal and molecular structure of *cis*-$PtCl_2[C(NPhCH_2)_2]PEt_3$ (I); and further refinement[3] of (II). This work follows the discovery[3] that the electron-rich olefin (III; R = Ph) reacts with the bridged compound $Pt_2Cl_4(PEt_3)_2$ in boiling xylene to give *trans*-$PtCl_2[C(NPhCH_2)_2]PEt_3$. Items (*ii*) and (*iii*) permit generalisations about *cis*- and *trans*-isomeric pairs to be made. Additionally, the *trans* influence of the nucleophilic carbene ligand is reliably assessed.



(I)



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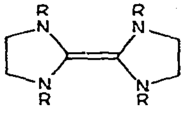

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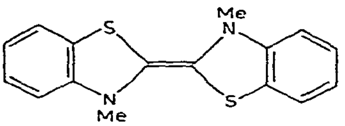

(IV)

Three electron-rich (for photoelectron data, see ref. 4) olefins have been examined, (III) (R = Ph or Me) and (IV)[5]. Reaction of the olefin (III) or (IV) with the halide (Cl or Br) bridged complexes (Pd or Pt) generally gave the *trans*-isomer, and is evidently kinetically controlled. However, in some cases a mixture of isomers, or only the *cis* compound was isolated. Thus the following compounds were prepared by (i) reaction of the appropriate bridged metal complex and olefin, or (ii) by thermal isomerisation of the corresponding *trans*-isomer. Data given are respectively, method (and conditions), yield, and m.p.: *trans*-$PtCl_2[C(NPhCH_2)_2]PEt_3$, (i), (xylene, 140°, 1 h), 50%, 201° (partially melting); *cis*-isomer, (ii), (~205°, 1 h), 100%, 308–315°; *trans*-$PtCl_2[C(NMeCH_2)_2]PEt_3$, (i), (benzene, 20°, 3 h), 82%, 183–185°; *cis*-isomer, (i); (benzene, 20°, 3 h), 4%, 280–290°; *trans*-$PdCl_2[C(NPhCH_2)_2]PEt_3$, (i), (xylene, 140°, 1 h), 17%, 197–200°; *cis*-isomer, (ii), (methanol, 56°, 1 h), 81%, 275–290°; *trans*-$PtCl_2(\overline{CNMe\cdot C_6H_4\text{-}o\cdot S})PEt_3$, (i), (xylene, 140°, 10 min), 25%, 156–158°; *cis*-isomer, (i), (xylene, 140°, 10 min), 46%, 250–275°; *trans*-$PtCl_2[C(NMeCH_2)_2]PBu_3$, (i), (benzene, 80°, ½ h), 28%, 95–96°; *cis*-isomer, (ii), (160–180°, 1½ h), 100%, 186–188°.

Reactivity orders, with respect to both carbene complex formation from olefin and isomerisation, are: (a) Pd > Pt, (b) Cl ≈ Br, (c) (III, R = Me) > (IV) > (III, R = Ph), and (d) for isomerisation only $PEt_3 > PBu_3$. Triethylphosphine is not a catalyst for the isomerisation under these conditions, of either *cis*- or *trans*-complexes. *Cis* → *trans* isomerisations are well-known in Pt^{II} chemistry[6]; the reverse process is uncommon[7].

The *cis*- and *trans*-carbene complexes are distinguishable (all compounds afforded satisfactory analyses and parent ions in mass spectra) by (a) colour (*cis* are white, *trans* are yellow), (b) solubility in non-polar solvents (*trans* > *cis*); (c) m.p. (*cis* > *trans*); (d) $\nu(MX_2)$ far IR characteristics {both in number of strong bands [*cis* (2), *trans* (1)] and energy (*trans* > *cis*)}; (e) $J(^{195}Pt–^{31}P)$ (*cis* > *trans*); (f) l(Pt–Cl) (*cis* > *trans*); (g) l(Pt–P) (*trans* > *cis*); and (h) thermodynamic stability (*cis* > *trans*). Many of these features are attributed to the greater ionic character of the *cis* compared with the *trans* complexes, which in turn relates to the *trans* influence order P ≈ carbene > Cl^-.

It is remarkable that accurate structural data are available for very few *cis*–*trans* pairs of platinum(II) complexes. A single crystal X-ray structure analysis (see Fig. 1) has been carried out on the *cis* complex (I) (M = Pt, X = Cl, R = Ph and P = PEt_3). An orthorhombic unit cell of dimensions a = 15.991(2), b = 8.601(2), and c = 16.703(2) Å, contains four molecules; the space group is *Pnam* (No. 62 D_{2h}^{16}). The structure has been refined by least-squares methods to R 0.048 for 1808 diffractometric data. The coordination plane of the platinum atom coincides with a crystallographic mirror plane to which the five-membered ring containing the carbene carbon atom is perpendicular. Bond length data for the *cis*-

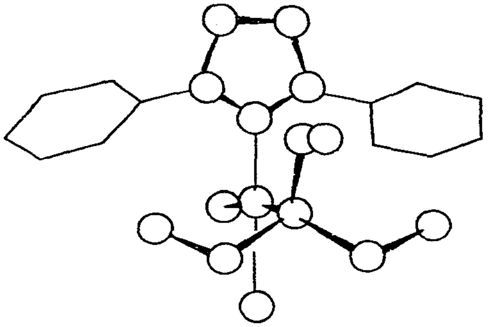

Fig. 1. *cis*-$PtCl_2[CNPhCH_2]_2PEt_3$.

isomer are compared with averaged values for the *trans*-isomer (now with R 0.048 and formerly[3] with R 0.057) in (I) and (II). The geometries of the carbene ligands are very similar in the two isomers; in particular, the N—$C_{carbene}$ distances of 1.33 and 1.35 Å suggest that in both compounds there is a significant interaction between the vacant *p*-orbital of the carbene carbon atom and the nitrogen lone pairs. The Pt—$C_{carbene}$ distances are significantly shorter than the Pt^{II}—C_{alkyl} distances, for example 2.079(14) Å in *trans*-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$[9]; however, about half this difference can be accounted for by the different covalent radii of sp^3 and sp^2 carbon atoms. It would therefore seem that in these compounds stabilisation of the Pt—$C_{carbene}$ bond by $d\pi$—$p\pi$ bonding is not of major importance. In this connection it is worth noting that, judged by the length of *trans*-Pt—Cl bonds, the *trans* influence of carbene is greater than that of π-acids, such as carbonyl and isonitrile, but less than that of σ-vinyl (in *trans*-$[PtCl(CH{=}CH_2)(PEt_2Ph)_2]$ the Pt—Cl distance is 2.401(4) Å)[10]. Finally, our results indicate that the upper limit of the difference between Pt—$C_{carbene}$ (*trans* to P) and Pt—$C_{carbene}$ (*trans* to Cl) distances is 0.06 Å.

We thank the S.R.C. for support, and Dr. C.G. Smith, Engelhard Ltd., for a loan of platinum metals.

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