Journal of Organometallic Chemistry, 54 (1973) C3–C4

Preliminary communication

Chelated bis-silyl-platinum complexes

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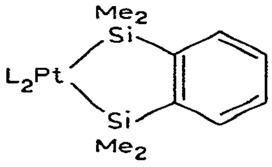
(Received April 18th, 1973)

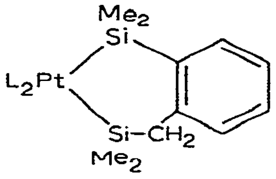
SUMMARY

The preparations are described of some bis-silyl-platinum complexes in which the Si–Pt–Si linkage forms part of a 4-, 5- or 6-membered ring.

The dihydrides *o*-$(HMe_2Si)_2C_6H_4$ and *o*-$(HMe_2Si)C_6H_4CH_2SiMe_2H$ have been found to react with $[PtL_2(C_2H_4)]$ ($L = PPh_3$) at room temperature to give the 5- and 6-membered cyclic bis-silyl complexes (I), m.p. 146–149° (dec.) and (II), m.p. 142–146°, respectively. The disiloxane $(HPh_2Si)_2O$ analogously gives a 4-membered cyclic species $[Pt(SiPh_2OSiPh_2)L_2]$, m.p. 166–170°, at 45°; $(HMe_2Si)_2O$, however, gives only the hydrido(silyl) complex, *cis*-$[PtH(SiMe_2OSiMe_2H)L_2]$, m.p. 100–104°, at 45°, but the latter cyclizes at 75° to give $[Pt(SiMe_2OSiMe_2)L_2]$, m.p. 172–174°. The dihydrides *o*-$(HMe_2SiCH_2)C_6H_4$ and $HMe_2Si(CH_2)_4SiMe_2H$, which could in principle give complexes involving 7-membered rings, in fact give only the hydrido(silyl) complexes, *cis*-$[PtH\{SiMe_2CH_2C_6H_4(CH_2SiMe_2H)\text{-}o\}L_2]$, m.p. 75–78°, and *cis*-$[Pt\{SiMe_2(CH_2)_4SiMe_2H\}L_2]$, m.p. 110–112°, which do not cyclize at 75°.



(I)

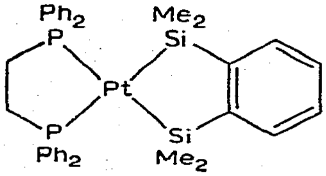


(II)

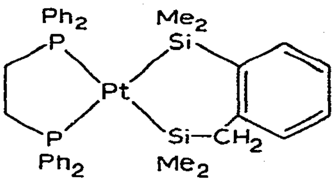
The compounds analogous to (I) and (II), but with $PMePh_2$ (L′) in place of PPh_3 ligands, are readily formed on treatment of either $[Pt(PMePh_2)_4]$ (neat) or $[Pt(PMePh_2)_2(CO_3)]$ (in benzene) with the appropriate dihydrides at room temperature.

The disiloxane $(HMe_2Si)_2O$ gives the cyclic $[Pt(SiMe_2OSiMe_2)L'_2]$ directly on reaction with $[Pt(PMePh_2)_4]$ in benzene under reflux or with $[Pt(PMePh_2)_2(CO_3)]$ in the same solvent at room temperature.

Compounds (I) and (II) react readily with 1,2-bis(diphenylphosphino)ethane to give the doubly-chelated species (III), m.p. 263–266°, and (IV), m.p. 246–248°, respectively. Compounds (I) and (II) also react readily with 2 molar proportions of bromine, methyl iodide, or phenylactylene with cleavage of both Si–Pt bonds; in the case of (I) [(II) was not examined in this respect], use of only 1 molar proportion of the reagents leads to the same products along with unchanged (I), indicating that once the first Si–Pt has been broken the second is cleaved markedly more rapidly.



(III)



(IV)

We thank the Science Research Council for the award of a Research Studentship (to T.N.M.), and Engelhard Industries Limited for a loan of platinum.