A New Class of Hydride-bridged Platinum Complex with Application as Hydrosilylation Catalysts; Molecular and *X*-Ray Crystal Structure of *trans*-Di-μ-hydrido-bis(tricyclohexylphosphine)bis(triethylsilyl)diplatinum(*Pt–Pt*)

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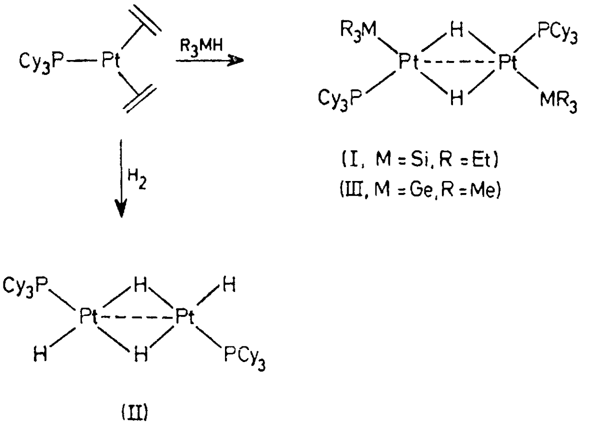
Summary The reaction of $[Pt(C_2H_4)_2(PCy_3)]$ (Cy = cyclohexyl) with H_2 or R_3MH (M = Si, Ge; R = alkyl, aryl, alkoxy, Cl) affords, respectively, the hydride bridged dinuclear species $[PtH(\mu\text{-}H)(PCy_3)]_2$ and $[PtMR_3(\mu\text{-}H)(PCy_3)]_2$; the triethylsilyl complex, which along with the other group 4a species catalyses the addition of R_3MH to olefins and acetylenes, was identified structurally by single crystal *X*-ray crystallography.

DURING a study of the chemistry of zero-valent complexes $[Pt(C_2H_4)_2(PR_3)]$[1] we have observed the formation of novel hydride bridged dinuclear complexes, which are very effective catalysts for hydrosilylation of olefins and acetylenes. The reaction (light petroleum; 20 °C) of R_3MH (M = Si; R = alkyl, aryl, alkoxy, Cl) with $[Pt(C_2H_4)_2(PCy_3)]$ affords a series of yellow to white crystalline complexes formulated on the basis of spectroscopy and elemental analysis as $[PtMR_3(H)(PCy_3)]_n$ (Scheme). The ^{31}P n.m.r. spectrum of the triethylsilyl complex (I, M = Si, R = Et) showed a singlet at −63·2 p.p.m. [(rel. ext. H_3PO_4) with two sets of ^{195}Pt satellites, *J*(PPt) 3228 and 60 Hz], and a second-order spectrum (AA′XX′) arising from molecules with two active platinum nuclei. This implied that (I) was a dinuclear complex. Confirmation was therefore sought by a single crystal *X*-ray diffraction study. *Crystal data:* monoclinic, space group $P2_1/c$, $Z = 4$, $a = 20{\cdot}72(2)$, $b = 13{\cdot}88(1)$, $c = 18{\cdot}97(1)$ Å; $\beta = 101{\cdot}15(7)°$. *R* is currently 0·075 for 3150 independent reflections [$I > 2{\cdot}0\,\sigma(I)$] collected on a Syntex $P2_1$ four-circle diffractometer at 200 K ($2{\cdot}9 \leqslant 2\theta \leqslant 40°$).



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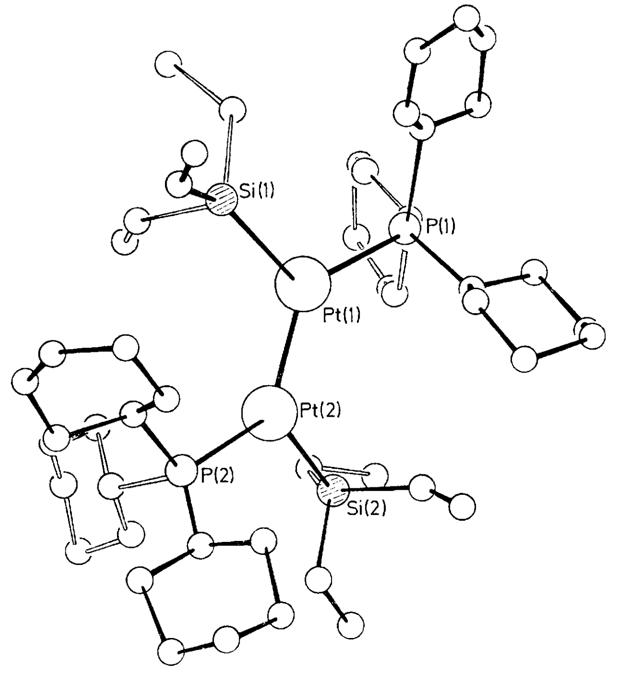

FIGURE. Molecular structure of $[PtSiEt_3(\mu\text{-}H)(PCy_3)]_2$. Pt(1)–P(1), 2·282(9); Pt(2)–P(2), 2·271(9); Pt(1)–Si(1), 2·33(1); Pt(2)–Si(2), 2·34(1) Å; ∠Si(1)–Pt(1)–Pt(2), 124·9(3); Si(2)–Pt(2)–Pt(1), 123·5(3); P(1)–Pt(1)–Pt(2), 131·4(3); P(2)–Pt(2)–Pt(1), 133·9(3)°.

The molecular structure is shown in the Figure. The geometry of the phosphine and silyl groups is unexceptional; however, the six atoms comprising the main skeleton of the molecule are significantly non-coplanar with a dihedral angle of 21° between the planes defined by Pt(1)P(1)Si(1) and Pt(2)P(2)Si(2). The Pt–Pt separation of 2·692(3) Å is not unusual and there are examples of both bridged and unbridged Pt–Pt bonds longer and shorter than this distance.[2] This complex may be contrasted with the well known halide-bridged dimers of platinum where the Pt–Pt separation of 3·48 Å represents a non-bonding interaction.[3] The presence of bridging hydrogens was indicated by the unexpectedly small P–Pt–Si bond angles of 102 and 103°. Support for this structural feature† was provided by the i.r. spectrum of (I), which showed no evidence for a ν(PtH) stretching frequency in the region 2300—1900 cm^{-1} but had a broad absorption at *ca.* 1600 cm^{-1}; this is assigned to a

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† Bridged hydride ligands have been postulated (R. A. Schunn, *Inorg. Chem.*, 1976, **15**, 208) for (Pd–H–Pd) and confirmed for (Ni–H–Ni) (P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Vol. I, Academic Press, London, 1974, p. 145; and references cited therein.)

bridged hydride. So far, attempts to confirm the presence of a bridged hydride by ^{1}H n.m.r. spectroscopy have been unsuccessful, this difficulty arising probably from dynamic behaviour.

TABLE. Representative hydrosilylation and hydrogermylation reactions

Substrate	R_3MH	Catalyst[a] (room temp.)	Product (yield)
Hex-1-ene	Me_2EtSiH	A	n-$Me_2EtSiC_6H_{13}$ (90%)
Hex-1-ene	Me_3GeH	B	n-$Me_3GeC_6H_{13}$ (80%)
Hexa-1,5-diene	Me_2PhSiH	A	1,6-$(Me_2PhSi)_2C_6H_{12}$ (100%)
Styrene	Me_2EtSiH	A	$PhCH_2CH_2SiMe_2Et$ (92%)
4-Vinylcyclohex-1-ene	Me_2PhSiH	A	$PhMe_2SiCH_2CH_2C_6H_9$ (75%)
Norbornene	$MeCl_2SiH$	C	*exo*-$MeCl_2SiC_7H_{11}$ (85%)
Allyl chloride	Cl_3SiH	D	$Cl_3SiCH_2CH_2CH_2Cl$ (70%)
$PhC{\equiv}CH$	Me_2ClSiH	C	*trans*-$PhCH{=}CH$-$SiMe_2Cl$ (92%)

[a] A = $[PtSiMe_2Et(\mu\text{-}H)(PCy_3)]_2$; B = $[PtGeMe_3(\mu\text{-}H)(PCy_3)]_2$; C = $[PtSiMe_2Bz(\mu\text{-}H)(PCy_3)]_2$; D = $[PtSiCl_3(\mu\text{-}H)(PCy_3)]_2$.

The related reaction of hydrogen (bubbled) with $[Pt(C_2H_4)_2(PCy_3)]$ in light petroleum at room temperature gives the yellow crystalline complex (II) [^{31}P n.m.r. (^{1}H decoupled) resonance at 50·2 p.p.m. (s with two sets of ^{195}Pt satellites, $^{1}J_{PPt}$ 3468 and $^{2}J_{PPt}$ 150 Hz)]. An i.r. band at 2090 cm^{-1} is ascribed to a terminal Pt–H stretch and a broad band at 1550 cm^{-1} to a bridging hydride (Pt–H–Pt). As with the silyl complexes, there was no evidence in the ^{1}H n.m.r. spectrum for either Pt-H or Pt–H–Pt. The deuterium analogue (IIa) showed a terminal Pt–D stretch at 1490 cm^{-1}, but the region in which the bridging deuteride vibration was expected (*ca.* 1100 cm^{-1}) was obscured by other ligand vibrations.

The silyl complexes, for example (I), are excellent hydrosilylation catalysts. Under mild conditions (20 °C) and relatively low catalyst concentrations (10^{-4}—10^{-6} mol. catalyst/mol. silane) they promote the ready addition of silanes to acetylenes and terminal or strained olefins (Table). Internal olefins are not hydrosilylated under the same conditions and do not isomerise.

A brief study has also been made of the corresponding reactions with germanes. Trimethylgermane reacts with $[Pt(C_2H_4)_2(PCy_3)]$ to give (III) $[PtGeMe_3(\mu\text{-}H)(PCy_3)]_2$, which is a catalyst for the hydrogermylation of terminal olefins.

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[3] S. F. Watkins, *J. Chem. Soc.* (*A*), 1970, 168.