Cationic Tertiary Phosphine Palladium Hydride Complexes

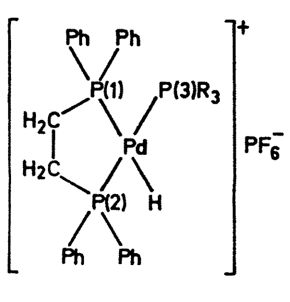
By M. L. H. GREEN and H. MUNAKATA

(*Inorganic Chemistry Laboratory, South Parks Road, Oxford* OX1 3QR)

Summary Cationic square-planar palladium hydride complexes are described which act as efficient catalysts for butadiene oligomerization.

STABLE, neutral palladium hydride complexes have been described recently.[1,2] We now report the first example of cationic palladium hydride complexes. They have been prepared by treatment of the neutral palladium hydride complexes, *trans*-$(R_3P)_2PdHCl$ [R = Pr^i or Cy (Cy = cyclohexyl)], in benzene–methanol with 1,2-bisdiphenylphosphinoethane and ammonium hexafluorophosphate [equation (1)].

$$trans\text{-}(R_3P)_2PdHCl + Ph_2PCH_2CH_2PPh_2 + NH_4PF_6 \longrightarrow$$



(1)

(I) R = (Cy)

(II) R = Pr^i

Cationic hydride complexes

Compounds	Colour	M.p.	I.r. data (cm^{-1})[a]	^{1}H N.m.r. data		
			M-H	(MτH)[b]	J[H-*trans*-P(1)] Hz	J[H-*cis*-P(2 or 3)] Hz
$[(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)(Cy_3P)PdH]^+$-$PF_6^-$[i] (I)	Colourless	190—192° dec.	1895	15·52[c,e,g]	196	14·8, 5·6
$[(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)(Pr_3P)PdH]^+$-$PF_6^-$ (II)	V. pale yellow	173—175° dec.	1959	15·31[c,f,h]	196	19·8
$[(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2NiH]^+PF_6^-$	Orange		1930	23·0[d,f]	[quintet, J(H–P) 5·0]	

[a] Nujol mulls. [b] Me_4Si internal reference. [c] Perkin-Elmer R14 at 100 MHz. [d] JEOL-C-60H at 60 MHz. [e] In $CH_2{\cdot}Cl_2$. [f] In $(CD_3)_2CO$. [g] A doublet of double-doublets. [h] A doublet of doublets. [i] Equivalent conductivity in CH_2Cl_2 assuming monomeric formulae 60Ω cm^2.

The corresponding reaction using *trans*-$(R_3P)_2NiHCl$ gives a *five*-co-ordinated cationic nickel hydride complex, $[(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2NiH]^+PF_6^-$. Similar types of nickel hydrides have been described.[3]

The ^{1}H n.m.r. data are given in the Table. The Pd–H resonance of complex (I) appears as a doublet of double-doublets, and for complex (II) as a doublet of doublets. These couplings may be assigned as shown in the Table on the basis of J(H-*trans*-P) ≫ J(H-*cis*-P) observed in related platinum complexes.[4]

Preliminary studies on butadiene oligomerization showed that these cationic palladium hydride complexes act as efficient catalysts, [*e.g.* in equation (2)]. These hydrides,

$$\text{1,3-Butadiene} \xrightarrow[\text{MeOH}]{\text{(I),60 °C 6h.}} \text{n-Octa-1,3,7-triene} + \text{3-Methoxyocta-1,7-diene} + \text{1-Methoxyocta-2,7-diene} \quad (2)$$

therefore, catalyse the same class of reactions as do palladium neutral derivatives such as $(Ph_3P)_4Pd$ and $(Ph_3P)_2Pd$ (maleic acid anhydride).[5]

We thank Mitzubishi Chemical Industries Ltd. for a scholarship (to H.M.).

(*Received, April 5th,* 1971; *Com.* 502.)

---

[1] H. Munakata and M. L. H. Green, *Chem. Comm.*, 1970, 881.

[2] M. L. H. Green, H. Munakata, and T. Saito, *J. Chem. Soc.* (*A*), 1971, 469.

[3] R. A. Schunn, *Inorg. Chem.*, 1970, 9, 394.

[4] F. Glockling and K. A. Hooton, *J. Chem. Soc.* (*A*), 1968, 826.

[5] S. Takahashi, T. Shibano, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1968, **41**, 454.