New Tertiary Phosphine Palladium Hydride Complexes

By H. MUNAKATA and M. L. H. GREEN*
(*Inorganic Chemistry Laboratory, South Parks Road, Oxford,* OX1 3QR)

Summary A new route to the palladium hydride complexes, *trans*-$(R^1{}_3P)_22PdHCl$, R^1 = cyclohexyl or isopropyl, is described involving use[1] of a hydridoborohydride complex, *trans*-$(R^1{}_3P)_2MH(BH_4)$, M = Ni or Pd, as a reducing agent and a tertiary phosphine ligands exchange reaction.

REDUCTION of *trans*-$(R^1{}_3P)_2PdCl_2$, R^1 = cyclohexyl or isopropyl, with borohydride reagents has failed to give hydride derivatives. However, ^1H n.m.r. studies show that treatment of *trans*-$(R^2{}_3P)_2PdCl_2$, R^2 = Et, Pr^n, or Bu^n, with *trans*-$[(Cy)_3P]_2NiH(BH_4)$ [(Cy) = cyclohexyl] gives an equilibrium mixture of hydrides, *e.g.*

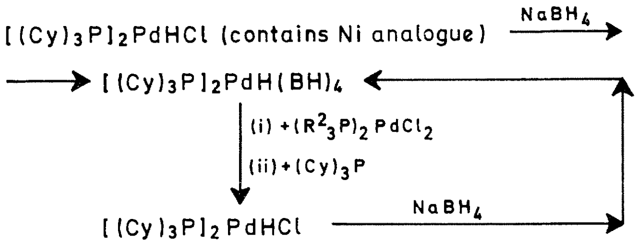
$$(R^2{}_3P)_2PdCl_2 + [(Cy)_3P]_2NiH(BH_4) \xrightarrow{B_2H_6\uparrow} (R^2{}_3P)_2MHCl + (R^2{}_3P)[(Cy)_3P]MHCl + [(Cy)_3P]_2MHCl$$

M = Ni and Pd. R^2 = Et, Pr^n, or Bu^n.
(Cy) = cyclohexyl.

Addition of $(Cy)_3P$ to this mixture allows isolation of *trans*-$[(Cy)_3P]_2PdHCl$ and *trans*-$[(Cy)_3P]_2NiHCl$ as a mixture. These hydrides may be partly separated by recrystallization.

The pure colourless stable palladium hydride, *trans*-$[(Cy)_3P]_2PdHCl$ is formed by the cyclic route shown in the Scheme.

Using this route, the palladium hydride complexes, $(R^1{}_3P)_2PdHCl$ and the palladium hydridoborohydride complexes $(R^1{}_3P)_2PdH(BH_4)$, R^1 = (Cy) or Pr^i, have been prepared and fully characterized. These complexes are stable at room temperature under argon, except $(Pr^i{}_3P)_2$-$PdH(BH_4)$ which decomposes within a few hours. The data are given in the Table.



SCHEME

In the ^1H n.m.r. spectra of the hydridoborohydride complexes the band at high field (τ 29·7) of complex (V) occurs as a triplet of quintets, which may be assigned to the terminal hydrogen bound to Ni. The terminal hydrogen bound to the metal couples with the two *cis*-^{31}P nuclei giving a triplet and it appears that this terminal hydrogen also couples equally with all four BH_4 hydrogens, thereby further splitting each component of the triplet into a quintet.

The apparent equivalence of all four BH_4 hydrogens suggests that a rapid intramolecular exchange occurs, as commonly observed in metal–BH_4 derivatives.[2]

The Pd–^1H band at high field (τ 23·2) of complex (IV) appears as five broad lines and these may be supposed to

I.r. and ^{1}H *n.m.r. data of hydride complexes*

Compounds		I.r. data[a]		^{1}H n.m.r. data		
(all *trans*-)		ν (M–H) cm^{-1}	δ (M–H) cm^{-1}	M–^{1}H τ[b]	*J* (H–P) Hz	*J* (H–BH$_4$) Hz
$[(Cy)_3P]_2PdHCl$	(I)	2002	726	24·4[c,f]	4·1	
$(Pr^i_3P)_2PdHCl$	(II)	2010	740	24·5[c,f]	4·6	
$[(Cy)_3P]_2PdH(BH_4)$	(III)	2002	730	[e]	[e]	[e]
$(Pr^i_3P)_2PdH(BH_4)$	(IV)	2013	740	23·2[d,h]	*ca.* 9	*ca.* 9
$(Pr^i_3P)_2NiH(BH_4)$	(V)	—	—	29·7[d,g]	70·5	6·0
$[(Cy)_3P]_2PdHBr$	(VI)	1991	720	23·3[c,f]	6·0	

[a] Nujol mull. [b] Me_4Si internal reference. [c] Solution in benzene. [d] Solution in toluene, −10°. [e] ^{1}H n.m.r. spectrum has not been obtained owing to the low solubility of the complex. [f] Triplet. [g] A triplet of quintets. [h] Seven lines.

be the most intense of the seven lines, if *J*(H–P) is approximately the same as *J*(H–BH$_4$) (*ca.* 9 Hz).

Bands due to the BH$_4$ hydrogens are not directly observed, probably due to line broadening by the ^{11}B quadrupole moment.

The complex (I) undergoes a typical metathetical replacement of Cl and gives, for example, the Br analogue (VI).

We thank Mitsubishi Chemical Industries Ltd. for a scholarship 1969—1971 (to H.M.).

(*Received, May* 11*th*, 1970; *Com.* 714.)

[1] M. L. H. Green, H. Munakata, and Taro Saito, *Chem. Comm.*, 1969, 1287.
[2] B. D. James, R. K. Nanda, and M. G. Wallbridge, *Inorg. Chem.*, 1967, 6, 1979, and references therein.