

CATIONIC HYDRIDE COMPLEXES OF NICKEL

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A series of cationic hydride complexes of nickel
 $[\text{NiH}(\text{L})(\text{PCy}_3)_2]^+\text{BPh}_4^-$ (PCy_3 = tricyclohexylphosphine, L = pyridines,
pyrazole and imidazole) have been synthesized and characterized.

During the course of our further study on nickel and palladium hydride complexes,¹⁾²⁾ we have recently isolated another stable nickel hydride complex $\text{NiH}(\text{NO}_3)(\text{PCy}_3)_2$ ($\text{Cy} = \text{C}_6\text{H}_{11}$).³⁾ The complex was now found to react readily with sodium tetraphenylborate in the presence of neutral ligands to give the cationic hydride complexes $[\text{NiH}(\text{L})(\text{PCy}_3)_2]^+\text{BPh}_4^-$ ($\text{Ph} = \text{C}_6\text{H}_5$), where L stands for pyridines, pyrazole and imidazole. The similar type of platinum complexes have been known for some years,^{4 - 6)} but no nickel analogue has been reported. Some cationic nickel hydride complexes of other types are known.^{7 - 9)}

Thus the treatment of $\text{NiH}(\text{NO}_3)(\text{PCy}_3)_2$ with sodium tetraphenylborate and a neutral ligand in benzene-methanol under N_2 at 20° precipitates the product as light yellow crystals which can be recrystallized from dichloromethane-hexane. The complexes tend to occlude the solvents of crystallization. These cationic hydride complexes are rather stable both thermally and towards air in the solid state. Conductivity measurements on 10^{-3} M-solutions in nitromethane confirmed that they are 1 : 1 electrolyte. The infrared spectra of the complexes showed $\nu_{\text{Ni-H}}$ in 1900 cm^{-1} region and the high-field ^1H n.m.r. spectra showed triplet signals (1 : 2 : 1) which are given in the table. The triplets indicate that tricyclohexylphosphine ligands are coordinated to nickel in mutually trans positions. The facile reaction of $\text{NiH}(\text{NO}_3)(\text{PCy}_3)_2$ with sodium tetraphenylborate seems to be another indication that NO_3 group is a good leaving group,⁶⁾ especially when assisted by strong trans effect of hydride H.

Compound	M.P.	Ir data ^a	¹ H n.m.r. data (Ni-H) ^b	
	(dec) °C	$\nu_{\text{Ni-H}}$ cm ⁻¹	Chem. Shift ppm (TMS)	J _{P-H} Hz
[NiH(pyridine)(PCy ₃) ₂]BPh ₄	190-192	1983	33.44	69.0
[NiH(α -picoline)(PCy ₃) ₂]BPh ₄	217-219	1970	33.38	71.0
[NiH(β -picoline)(PCy ₃) ₂]BPh ₄ ·CH ₂ Cl ₂	177-179	1984	33.48	69.5
[NiH(γ -picoline)(PCy ₃) ₂]BPh ₄ ·CH ₂ Cl ₂	174-175	1994	33.56	70.0
[NiH(4-Ph-pyridine)(PCy ₃) ₂]BPh ₄ ·C ₆ H ₆	173-175	1960	33.25	68.5
[NiH(pyrazole)(PCy ₃) ₂]BPh ₄	155-156	1938	33.66	70.0
[NiH(imidazole)(PCy ₃) ₂]BPh ₄ 1/2C ₆ H ₆	230-232	1984	33.67	72.0

a. KBr disc b. CH₂Cl₂ solution

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