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CATIONIC HYDRIDE COMPLEXES OF PALLADIUM

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A series of cationic hydride complexes of palladium $[PdH(L)(PCy_3)_2]^+BPh_4^-$ (PCy_3 = tricyclohexylphosphine, L = pyridines, pyrazole and imidazole) have been synthesized from a new palladium hydride complex $PdH(NO_3)(PCy_3)_2$ and characterized.

The number of well-characterized palladium hydride complexes is still limited$^{1)}$ and this is probably in part due to the lack of simple preparative methods. Tricyclohexylphosphine stabilizes palladium hydrides$^{1a)}$ but the direct reduction of $PdCl_2(PCy_3)_2$ with sodium tetrahydroborate does not proceed under the similar conditions which have been employed for the preparation of $NiHCl(PCy_3)_2$.$^{2)}$

We have found that $Pd(NO_3)_2(PCy_3)_2$ reacts readily with sodium tetrahydroborate to give $PdH(NO_3)(PCy_3)_2$ in a good yield. This new hydride complex is a good starting compound for a series of cationic hydride complexes $[PdH(L)(PCy_3)_2]^+BPh_4^-$ which are analogues of the cationic nickel hydrides.$^{3)}$

Thus treatment of solid palladium nitrate with a suspension of tricyclohexylphosphine in ethanol at -30° formed yellow $Pd(NO_3)_2(PCy_3)_2$ almost quantitatively. This compound was treated with an ethanolic solution of sodium tetrahydroborate in a mixed solvent of benzene and ethanol at 0° in an inert atmosphere. The brown solution was filtered, the solvents were removed in vacuo and the residue was washed with n-hexane to give white $PdH(NO_3)(PCy_3)_2$ (yield 90%). The complex could be recrystallized from benzene-hexane (yield 60%).

The cationic hydride complexes were prepared by treatment of a benzene solution of $PdH(NO_3)(PCy_3)_2$ with a methanolic solution of sodium tetraphenylborate in the presence of one of the neutral ligands listed in the Table. The precipitated solid was separated by filtration, washed with water and methanol and dried in vacuo.

The products were recrystallized from dichloromethane-ether. They are white crystals and stable thermally and toward air in the solid state. The ir spectra of the complexes indicate a sharp absorption at 2000 - 2100 cm^{-1} which can be assigned to Pd-H stretching vibration and ^1H nmr spectra of the dichloromethane solutions indicate a signal around τ25 which is due to Pd-H. Conductivity measurements in dichloromethane confirmed that they are 1 : 1 electrolytes.

Table

Compound	M.P. (dec) °C	Ir data* ν_{Pd-H} cm^{-1}	^1H nmr data** τ_{Pd-H} ppm
$PdH(NO_3)(PCy_3)_2$	128-130	2058	28.29
$[PdH(pyridine)(PCy_3)_2]BPh_4$	116-118	2076	25.67
$[PdH(\alpha\text{-picoline})(PCy_3)_2]BPh_4$	131-133	2051	25.51
$[PdH(\beta\text{-picoline})(PCy_3)_2]BPh_4$	124-125	2034	25.66
$[PdH(\gamma\text{-picoline})(PCy_3)_2]BPh_4\cdot CH_2Cl_2$	117-119	2065	25.67
$[PdH(4\text{-Ph-pyridine})(PCy_3)_2]BPh_4$	132-134	2047	25.58
$[PdH(4\text{-pyridine-methanol})(PCy_3)_2]BPh_4\cdot CH_2Cl_2$	114-115	2068	25.67
$[PdH(\gamma\text{-collidine})(PCy_3)_2]BPh_4$	110-111	2052	25.37
$[PdH(pyrazole)(PCy_3)_2]BPh_4\cdot CH_2Cl_2$	113-114	2080	25.56
$[PdH(imidazole)(PCy_3)_2]BPh_4$	129-131	2079	25.32

* KBr disk ** CH_2Cl_2 solution

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