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SYNTHESIS OF CATIONIC HYDRIDE AND RELATED COMPLEXES OF PALLADIUM AND NICKEL WITH TRICYCLOHEXYLPHOSPHINE OR TRIISOPROPYLPHOSPHINE

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Summary

The preparation and characterization of a series of cationic hydride complexes of palladium and nickel of the type $[MH(L)(PCy_3)_2]BPh_4$ (M = Pd, Ni; L = pyridines, pyrazole, imidazole; Cy = cyclohexyl; Ph = phenyl) from new hydride complexes, *trans*-$MH(NO)_3(PCy_3)_2$ are described. *Trans*-$PdH(NO_3)(PCy_3)_2$ is prepared conveniently by treatment of $Pd(NO_3)_2(PCy_3)_2$ (yellow form) with $NaBH_4$ (yield 93%). The relative stability of the nickel triad hydride complexes is discussed.

Preparation of $PdHCl(PR_3)_2$ (R = Cy or i-Pr = isopropyl) by a new method and their derivatives are also reported.

Introduction

The nickel triad hydride complexes stabilized by tricyclohexylphosphine or triisopropylphosphine are now well known [1], and the steric effect of the bulky phosphine ligands on the thermal stability and the reactivity of the complexes poses an interesting problem. The purpose of the present work was to synthesize cationic hydride complexes of palladium and nickel, $[MH(L)(PCy_3)_2]^+BPh_4^-$ (M = Pd, Ni; L = a neutral ligand, Cy = cyclohexyl; Ph = phenyl) and to compare them with the cationic hydride complexes of platinum of a similar type which have been extensively investigated by Clark and his co-workers [2]. For this study, a simple method of preparation of a neutral palladium hydride complex as the starting compound was needed.

We describe a convenient preparation of *trans*-$PdH(NO_3)(PCy_3)_2$ from which a new series of cationic hydrides $[PdH(L)(PCy_3)_2]BPh_4$ can be readily prepared, and the preparation of the nickel analogs. We have already reported the preliminary results elsewhere [3,4], and Clark and his co-workers recently reported analogous nickel and platinum cationic hydride complexes [2,5].

Prior to the discovery of the method of preparation of $PdH(NO_3)(PCy_3)_2$, we had found that $PdHCl(PR_3)_2$ (R = Cy or i—Pr) could be prepared by the reaction of $PdCl_2(PBu_3)_2$ (Bu = n-butyl) with $NaBH_4$, followed by the addition of tricyclohexylphosphine or triisopropylphosphine to the reaction solution. This procedure was simpler than the previous one which employed $NiH(BH_4)(PR_3)_2$ as the reducing agent, but the yields were not very satisfactory (ca. 50% based on Pd). We prepared some neutral hydrides, $MHX(PR_3)_2$ (M = Pd, Ni; R = Cy, i-Pr) starting from $MHCl(PR_3)_2$. The results are included in this paper.

Results and discussion

The elemental analysis, yields, melting points (decomp.) and IR and ^1H NMR data of the hydride complexes prepared in the present study are given in Tables 1 and 2.

The high-field ^1H NMR spectra of the cationic nickel hydride complexes show triplet (1 : 2 : 1) structures consistent with a square planar *trans* geometry, but the spectra of the palladium complexes show very small splittings (ca. 3 ~ 4 Hz) and the intensity ratios are not clear. Some of the palladium complexes do not show any splittings but the line-widths are about the same as those of the complexes which show splittings. We have noted that in square planar neutral hydride complexes of the nickel triad with tricyclohexylphosphine, the magnitude of $J(P—H_{cis})$ is generally in the order Pd < Pt < Ni [6]. Schunn also reported that $J(P—H_{cis})$ for a cationic square planar hydride complex, $[PdH(PEt_3)_3]BPh_4$, is nearly zero [7]. We consider that the nickel and palladium hydride complexes of the present study have similar square planar geometry.

Cationic hydride complexes of palladium and nickel of the type $[MH(L)(PR_3)_2]^+X^-$ have not been much studied [1]. Well-characterized and thermally stable neutral palladium and nickel hydride complexes stabilized by tricyclohexylphosphine or triisopropylphosphine, $MHCl(PR_3)_2$ (M = Pd, Ni: R = cyclohexyl, isopropyl) [8,9], could be used as starting compounds for such cationic hydride complexes. However, the synthesis of the palladium hydrides was not simple [8] and more convenient methods were desirable. Previous attempts to prepare *trans*-$PdHCl(PCy_3)_2$ from *trans*-$PdCl_2(PCy_3)_2$ and $NaBH_4$ were not successful [8] because the reaction did not proceed under conditions similar to those which had been employed for the preparation of *trans*-$NiHCl(PCy_3)_2$ from *trans*-$NiCl_2(PCy_3)_2$ [9]. In order to facilitate the reduction by employing the better leaving ability of the NO_3^- ligand [10], in the present study we used $Pd(NO_3)_2(PCy_3)_2$ as a starting compound. We could prepare *trans*-$PdH(NO_3)(PCy_3)_2$ successfully, only from the yellow form of $Pd(NO_3)_2(PCy_3)_2$ which had been obtained almost quantitatively at —30°C in a reaction in ethanol (see Experimental). The green form of $Pd(NO_3)_2(PCy_3)_2$ which formed at higher temperatures (above room temperature) did not form the hydride complex on treatment with $NaBH_4$. The elemental analyses of these two forms of dinitrato complexes are consistent with the formulae given and the infrared spectra are almost identical, but we have not yet investigated the difference between them. After we had found the conditions necessary to obtain the yellow form of the dinitrato complex, we did not isolate it for the preparation of the hydride complex but treated it with $NaBH_4$ in situ.

TABLE 1

YIELDS, MELTING POINTS AND ANALYTICAL DATA OF THE HYDRIDE COMPLEXES

Compound [a]	Yield (%)	M.p. (decomp.) (°C)	Formula	Analysis found (calcd.) (%)			
				C	H	N	Ni
$[PdH(py)(PCy_3)_2]BPh_4$	92	168–169	$C_{65}H_{92}BNP_2Pd$	73.3(73.2)	9.0(8.7)	0.9(1.3)	
$[PdH(2\text{-methyl-py})(PCy_3)_2]BPh_4$	68	192–194	$C_{66}H_{94}BNP_2Pd$	73.4(73.4)	9.1(8.8)	1.0(1.3)	
$[PdH(3\text{-methyl-py})(PCy_3)_2]BPh_4$	54	177–179	$C_{66}H_{94}BNP_2Pd$	73.4(73.4)	8.9(8.8)	1.0(1.3)	
$[PdH(4\text{-methyl-py})(PCy_3)_2]BPh_4 \cdot CH_2Cl_2$	65	139–141 [c]	$C_{67}H_{96}BCl_2NP_2Pd$	69.4(69.1)	8.8(8.3)	1.4(1.2)	
$[PdH(4\text{-phenyl-py})(PCy_3)_2]BPh_4$	41	172–173	$C_{71}H_{96}BNP_2Pd$	74.2(74.6)	8.7(8.5)	0.9(1.2)	
$[PdH(4\text{-py-methanol})(PCy_3)_2]BPh_4 \cdot CH_2Cl_2$	80	123–125 [d]	$C_{67}H_{96}BCl_2NOP_2Pd$	68.8(68.2)	8.7(8.1)	1.3(1.2)	
$[PdH(2,4,6\text{-trimethyl-py})(PCy_3)_2]BPh_4$	64	170–172	$C_{68}H_{98}BNP_2Pd$	73.5(73.7)	9.3(8.9)	1.5(1.3)	
$[PdH(3,5\text{-dimethyl-py})(PCy_3)_2]BPh_4 \cdot 1/2CH_2Cl_2$	77	160–162 [d]	$C_{67.5}H_{97}BClNP_2Pd$	71.2(71.1)	9.0(8.6)	1.4(1.2) [b]	
$[PdH(pyrazole)(PCy_3)_2]BPh_4 \cdot CH_2Cl_2$	86	164–166	$C_{64}H_{93}BCl_2N_2P_2Pd$	66.9(67.4)	8.6(8.2)	2.6(2.5)	
$[PdH(imidazole)(PCy_3)_2]BPh_4$	83	165–167	$C_{63}H_{91}BN_2P_2Pd$	71.6(71.7)	8.8(8.7)	2.9(2.7)	
$[NiH(py)(PCy_3)_2]BPh_4$	70	190–192	$C_{65}H_{92}BNNiP_2$	76.9(76.6)	9.4(9.1)	1.1(1.4)	
$[NiH(2\text{-methyl-py})(PCy_3)_2]BPh_4$	66	217–219	$C_{66}H_{94}BNNiP_2$	76.5(76.7)	9.4(9.2)	1.3(1.4)	
$[NiH(3\text{-methyl-py})(PCy_3)_2]BPh_4 \cdot CH_2Cl_2$	73	177–179	$C_{67}H_{96}BCl_2NNiP_2$	72.4(72.1)	9.1(8.7)	1.3(1.3)	
$[NiH(4\text{-methyl-py})(PCy_3)_2BPh_4 \cdot CH_2Cl_2$	60	174–175	$C_{67}H_{96}BCl_2NNiP_2$	72.3(72.1)	8.3(8.7)	1.6(1.3) [c]	
$[NiH(4\text{-phenyl-py})(PCy_3)_2]BPh_4 \cdot C_6H_6$	82	173–175	$C_{77}H_{102}BNNiP_2$	79.8(78.8)	9.2(8.8)	1.2(1.2)	
$[NiH(pyrazole)(PCy_3)_2]BPh_4$	70	155–156	$C_{63}H_{91}BN_2NiP_2$	74.7(75.1)	9.5(9.1)	2.9(2.8)	
$[NiH(imidazole)(PCy_3)_2]BPh_4 \cdot 1/2C_6H_6$	71	230–232	$C_{66}H_{94}BN_2NiP_2$	75.9(75.7)	9.3(9.1)	2.8(2.7)	
$PdH(NO_3)(PCy_3)_2$	79	145–147 [d]	$C_{36}H_{67}NO_3P_2Pd$	59.2(59.2)	9.5(9.3)	2.0(1.9)	
$PdH(CN)(PCy_3)_2$	16	[e]	$C_{37}H_{67}NP_2Pd$	63.4(64.0)	9.8(9.7)	2.3(2.0)	
$PdH(NCS)(Pi\text{-}Pr_3)_2$	55	112–114	$C_{19}H_{43}NP_2PdS$	46.0(47.0)	8.7(8.9)	3.1(2.9)	
$PdH(Br)(Pi\text{-}Pr_3)_2$	36	97–98	$C_{18}H_{43}BrP_2Pd$	42.6(42.6)	8.6(8.5)		
$PdH(I)(Pi\text{-}Pr_3)_2$	63	139–140	$C_{18}H_{43}IP_2Pd$	39.3(39.0)	7.8(7.8)		
$PdH(CN)(Pi\text{-}Pr_3)_2$	34	107–108	$C_{19}H_{43}NP_2Pd$	50.8(50.3)	9.9(9.6)	3.4(3.1)	
$NiH(NO_3)(PCy_3)_2$	67	174–176	$C_{36}H_{67}NNiO_3P_2$	63.4(63.3)	10.1(9.9)	1.9(2.0)	
$NiH(NCO)(PCy_3)_2$	64	163–167	$C_{37}H_{67}NNiOP_2$	67.6(67.1)	10.3(10.1)	1.9(2.1)	8.8(8.9)
$NiH(NO_2)(PCy_3)_2$	83	117–124	$C_{36}H_{67}NNiO_2P_2$	64.9(64.9)	10.2(10.1)	2.2(2.1)	8.8(8.8)
$NiH(NCS)(Pi\text{-}Pr_3)_2$	60	[e]	$C_{19}H_{43}NNiP_2S$	51.4(52.1)	9.7(9.9)	3.5(3.2)	13.5(13.4)
$NiH(NCO)(Pi\text{-}Pr_3)_2$	39	43–49	$C_{19}H_{43}NNiOP_2$	54.1(54.1)	10.0(10.3)	3.5(3.3)	13.8(13.9)
$NiH(NO_2)(Pi\text{-}Pr_3)_2$	59	84–87	$C_{18}H_{43}NNiO_2P_2$	50.6(50.7)	10.7(10.2)	3.2(3.3)	13.9(13.8)
$NiH(CN)(Pi\text{-}Pr_3)_2$	47	ca. 70	$C_{19}H_{43}NNiP_2$	56.2(56.2)	10.8(10.7)	4.1(3.5)	14.3(14.5)

[a] Cy = cyclohexyl, Ph = phenyl, i-pr = isopropyl. [b] Cl 2.8(3.1). [c] Cl 6.5(6.4). [d] The complexes darkened without melting at this temperature. [e] Not measured.

TABLE 2

INFRARED AND ^{1}H NMR DATA OF THE HYDRIDE COMPLEXES

Compound	IR data [a] ν(MH) (cm^{-1})	^{1}H NMR data	
		τ(MH)	J(PH) (Hz)
$[PdH(py)(PCy_3)_2]BPh_4$	2076	25.7 [b,e]	
$[PdH(2\text{-methyl-py})(PCy_3)_2]BPh_4$	2051	25.5 [b,e,f]	~4
$[PdH(3\text{-methyl-py})(PCy_3)_2]BPh_4$	2034	25.7 [b,e]	
$[PdH(4\text{-methyl-py})(PCy_3)_2]BPh_4 \cdot CH_2Cl_2$	2065	25.7 [b,e]	
$[PdH(4\text{-phenyl-py})(PCy_3)_2]BPh_4$	2047	25.6 [b,e]	
$[PdH(4\text{-py-methanol})(PCy_3)_2]BPh_4 \cdot CH_2Cl_2$	2068	25.6 [b,e]	
$[PdH(2,4,6\text{-trimethyl-py})(PCy_3)_2]BPh_4$	2052	25.4 [b,e,f]	~4
$[PdH(3,5\text{-dimethyl-py})(PCy_3)_2]BPh_4 \cdot 1/2CH_2Cl_2$	2049	25.5 [b,e]	
$[PdH(pyrazole)(PCy_3)_2]BPh_4 \cdot CH_2Cl_2$	2080	25.6 [b,e,f]	~4
$[PdH(imidazole)(PCy_3)_2]BPh_4$	2079	25.3 [b,e,f]	~4
$[NiH(py)(PCy_3)_2]BPh_4$	1983	33.4 [b,e,f]	69.0
$[NiH(2\text{-methyl-py})(PCy_3)_2]BPh_4$	1970	33.4 [b,e,f]	71.0
$[NiH(3\text{-methyl-py})(PCy_3)_2]BPh_4 \cdot CH_2Cl_2$	1984	33.5 [b,e,f]	69.5
$[NiH(4\text{-methyl-py})(PCy_3)_2]BPh_4 \cdot CH_2Cl_2$	1994	33.6 [b,e,f]	70.0
$[NiH(4\text{-phenyl-py})(PCy_3)_2]BPh_4 \cdot C_6H_6$	1960	33.3 [b,e,f]	68.5
$[NiH(pyrazole)(PCy_3)_2]BPh_4$	1938	33.7 [b,e,f]	70.0
$[NiH(imidazole)(PCy_3)_2]BPh_4 \cdot 1/2C_6H_6$	1984	33.7 [b,e,f]	72.0
$PdH(NO_3)(PCy_3)_2$	2058	28.3 [b,e,f]	~3
$PdH(CN)(PCy_3)_2$	1918	19.6 [b,d,f]	~2
$PdH(NCS)(Pi\text{-}Pr_3)_2$	2042	25.4 [c,d,g]	
$PdH(Br)(Pi\text{-}Pr_3)_2$	2004	23.2 [c,d,f]	6.5
$PdH(I)(Pi\text{-}Pr_3)_2$	2013	21.3 [c,d,f]	5
$PdH(CN)(Pi\text{-}Pr_3)_2$	1915	19.7 [c,d,h]	
$NiH(NO_3)(PCy_3)_2$	1953	38.6 [b,d,f]	76.5
$NiH(NCO)(PCy_3)_2$	1927	34.5 [b,e,f]	71.6
$NiH(NO_2)(PCy_3)_2$	1903	32.5 [b,d,f]	68
$NiH(NCS)(Pi\text{-}Pr_3)_2$	1953	33.3 [c,d,f]	67
$NiH(NCO)(Pi\text{-}Pr_3)_2$	1957	34.2 [c,d,f]	69
$NiH(NO_2)(Pi\text{-}Pr_3)_2$	1946	32.5 [c,d,f]	66
$NiH(CN)(Pi\text{-}Pr_3)_2$	1890	24.6 [b,d,f]	59

[a] KBr disk. [b] TMS as internal standard. [c] $MH(Cl)(PR_3)_2$ (M and R are the same as those of the sample) as an internal standard. [d] In benzene. [e] In dichloromethane. [f] Triplet. [g] Singlet with half width of 14 Hz. [h] Singlet with half width of 7 Hz.

An analogous nickel hydride, *trans*-$NiH(NO_3)(PCy_3)_2$, was prepared from $Ni(NO_3)_2(PCy_3)_2$, from nickel dinitrate hexahydrate and tricyclohexylphosphine in solution at room temperature. The dinitrato complex was not isolated in this case either and was treated with $NaBH_4$ in situ for the preparation of *trans*-$NiH(NO_3)(PCy_3)_2$.

Addition of an acetone or methanol solution of $NaBPh_4$ to a benzene solution of *trans*-$PdH(NO_3)(PCy_3)_2$ precipitated $NaNO_3$ even in the absence of an incoming neutral ligand (eg. pyridine), but similar treatment of *trans*-$NiH(NO_3)(PCy_3)_2$ did not precipitate $NaNO_3$. The results suggest that a solvated cation, $[PdH(solvent)(PCy_3)_2]^+$ (solvent = acetone or methanol) forms, as with the similar platinum complexes [2]. However, in the case of the nickel complex, NO_3^- may not be eliminated unless one of the N-ligands (eg. pyridine) coordinates to nickel [5]. Because of the lability of the NO_3^- group, the formation of cationic hydride complexes with a ligand listed in Table 1 is rapid under mild conditions and no decomposition was observed in the case of either the palladium or the nickel complexes.

We could not obtain cationic hydride complexes with tertiary phosphines, carbon monoxide, triethylamine or ammonia as the neutral ligand. Only pyridines, pyrazole or imidazole, which are not very bulky and possess some π-acceptor property, appear to be suitable for the formation of the cationic hydride complexes of palladium and nickel having two bulky tricyclohexylphosphine ligands.

It was generally believed that the order of the thermal stability of the hydride complexes of the nickel triad was Ni < Pd < Pt [11]. Attig and Clark suggested that the high thermal stability of the platinum hydride complexes with tricyclohexylphosphine was exemplified by the high melting points of the complexes [2]. We have measured the melting points of the cationic hydride complexes of palladium and nickel in vacuum-sealed capillary tubes. The melting points were not very sharp and the values in Table 1 indicate the temperatures at which the complexes darkened and melted completely. As we have not checked the actual decomposition points of the cationic hydride complexes at which the M—H bond ruptures, any conclusion about the relative thermal stability of the palladium and nickel hydride complexes seems to be meaningless.

Experimental

All experimental procedures for the preparation and purification of the complexes were performed in an inert atmosphere of nitrogen or argon. Infrared spectra were recorded on a Hitachi EPI G2 spectrometer. ^{1}H NMR spectra were recorded on a JEOL PS-100 spectrometer. Elemental analyses were performed in the Organic Analysis Laboratory of our Department.

Preparation of $PdH(NO_3)(PCy_3)_2$

To a suspension of tricyclohexylphosphine (4.86 g, 0.0174 mol) in ethanol (75 ml), solid palladium dinitrate (2.00 g, 0.0868 mol) was added at −30°C. The mixture was stirred for 1.5 h, the temperature was raised to 0°C and benzene (150 ml) was added to the mixture. A solution of $NaBH_4$ (0.33 g, 0.0877 mol) in ethanol (20 ml) was added dropwise with stirring. After the addition was completed, the temperature was gradually raised to ca. 20°C and the stirring was continued for 24 h. The orange solution was filtered, the solvents were removed in vacuo from the filtrate to give the product (5.90 g, yield 93%). The product was washed with three 50 ml portions of n-hexane to give greyish white solid (5.00 g, yield 79%). The complex was sufficiently pure for the subsequent preparation of the cationic hydride complexes but it could be recrystallized from benzene-n-hexane to yield a purer compound which was almost white (recrystallization yield 66%). The hydride complex is stable thermally and towards air in the solid state but decomposes gradually in solutions which have not been degassed. It is soluble in benzene, tetrahydrofuran, dichloromethane, and slightly soluble in diethyl ether.

Preparation of $[PdH(pyridine)(PCy_3)_3]BPh_4$

A solution of pyridine (0.054 g, 0.68 mmol) and $NaBH_4$ (0.205 g, 0.60 mmol) in methanol (5 ml) was added dropwise to a solution of $PdH(NO_3)(PCy_3)_2$ (0.416 g, 0.57 mmol) in benzene (20 ml) at 20°C. The cationic hydride precipitated together with sodium nitrate. The mixture was kept overnight at 5°C and filtered. The crude product containing sodium nitrate was dissolved in dichloromethane (15 ml). After filtration, diethyl ether (60 ml) was added slowly to the solution. Shiny white crystals precipitated (0.56 g, yield 92%). The product is stable thermally and towards air in the solid state and is soluble in dichloromethane. The conductivity in dichloromethane was $\Lambda = 34\ \Omega^{-1}\ cm^2\ mol^{-1}$ for a solution of $6.14 \times 10^{-3}\ M$ at 25°C.

Preparation of $[PdH(L)(PCy_3)_2]BPh_4$ *(L = 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 4-phenylpyridine, 4-pyridinemethanol, 2,4,6-trimethylpyridine, 3,5-dimethylpyridine, pyrazole or imidazole)*

The preparation of the above complexes were similar to that of the pyridine complex and the yields are listed in Table 1. 4-Methylpyridine, 4-pyridinemethanol, 3,5-dimethylpyridine, and pyrazole complexes contain dichloromethane as a solvent of crystallization which could not be removed by heating the samples at 60°C in vacuo for 24 h. The content of the solvent was determined from ^1H NMR spectra. The complexes are white crystals and are soluble in dichloromethane. They are stable thermally and towards air in the solid state for several months.

Preparation of $NiH(NO_3)(PCy_3)_2$

To a solution of tricyclohexylphosphine (10.0 g, 0.0357 mol) in benzene (200 ml), a solution of nickel dinitrate hexahydrate (5.0 g, 0.0172 mol) in ethanol (50 ml) was added, and a solution of $NaBH_4$ (0.67 g, 0.0181 mol) in ethanol (35 ml) was added dropwise in 20 min at 20°C. After it had been stirred for 1 h, the solution was filtered and methanol (500 ml) was added to the filtrate and it was cooled at 0°C for 24 h. The precipitated solid was filtered, washed with methanol (50 ml) and dried in vacuo to give a yellow crystalline complex (8.0 g, yield 72%). The solid complex is stable towards air for short periods but should be stored under an inert atmosphere. Its solutions are less stable and decompose in a short time in contact with air. The complex is soluble in benzene, tetrahydrofuran, dichloromethane, and slightly soluble in diethyl ether.

Preparation of $[NiH(2\text{-}methylpyridine)(PCy_3)_2]BPh_4$

A solution of $NaBH_4$ (0.50 g, 1.46 mmol) in ethanol (20 ml) was added dropwise to a solution of $NiH(NO_3)(PCy_3)_2$ (1.00 g, 1.46 mmol) and 2-methylpyridine (0.20 g, 2.15 mmol) in benzene (100 ml). After stirring for 1 h, the precipitate was filtered and the crude product was dissolved in dichloromethane (30 ml). The solution was filtered to remove $NaNO_3$ and a mixture of dichloromethane (20 ml) and petroleum ether (80 ml) was added slowly to the filtrate. The resulting solution was kept in a refrigerator (ca. 5°C) for 48 h. Light yellow crystals precipitated (0.60 g, yield 40%). The product is stable thermally and towards air in the solid state. It is soluble in dichloromethane and nitromethane.

The conductivity in nitromethane was $\Lambda = 74\ \Omega^{-1}\ cm^2\ mol^{-1}$ for a $1.2 \times 10^{-3}\ M$ solution at 30°C indicating that it is probably a 1 : 1 electrolyte.

Preparations of [$NiH(L)(PCy_3)_2$]BPh_4 (L = pyridine, 3-methylpyridine, 4-methylpyridine, 4-phenylpyridine, pyrazole or imidazole

The preparations of the above complexes were similar to that of the 2-methylpyridine complex and the yields are listed in Table 1. The 3-methylpyridine and 4-methylpyridine complexes contain dichloromethane as solvent of crystallization and the 4-phenylpyridine and imidazole complexes contain benzene as solvent of crystallization. These could not be removed by heating at 60°C in vacuo for 24 h. The content of the solvents was determined from the ^1H NMR spectra. The complexes are pale yellow crystals and soluble in dichloromethane. They are stable thermally and towards air in the solid state.

Preparation of $PdHCl(PCy_3)_2$

A solution of $PdCl_2(PBu_3)_2$ (2.0 g) in 95% ethanol (50 ml) was treated with $NaBH_4$ (0.14 g) at room temperature for 1 h and tricyclohexylphosphine (3.5 g) was added. The solution was stirred for 1 h and the solvent was removed in vacuo. The residue was washed with n-hexane (20 ml), two 20 ml portions of methanol/water (1 : 1) and methanol (15 ml) and dried in vacuo to give the product (1.2 g). The product could be recrystallized from toluene/methanol, but for further syntheses this crude compound was used.

Preparation of $PdHCl(P\text{-}i\text{-}Pr_3)_2$

A solution of $PdCl_2(PBu_3)_2$ (2.0 g) in benzene (10 ml) was treated with a solution of $NaBH_4$ (0.15 g) in ethanol (90 ml) at room temperature for 12 h and the solution was filtered. Triisopropylphosphine (2.4 g) was added, and the solution was stirred for 30 min. Then the solvent was removed in vacuo to give a brown oil. n-Hexane (50 ml) and water (10 ml) were added, and the hexane layer was separated, concentrated to ca. 20 ml and cooled to —78°C. The crystals were filtered off, and recrystallized from n-hexane to give the product (0.72 g). The compound obtained by this method was slightly colored by impurities.

Preparation of $MHX(PR_3)_2$ (M = Pd, R = Cy, X = CN; R = i-Pr, X = Br, I, NCS, CN: M = Ni, R = Cy, X = NCO, NO_2; R = i-Pr, X = NCS, NCO, NO_2)

These complexes were prepared by the metathetical reactions of $PdHCl(PR_3)_2$ or $NiHCl(PR_3)_2$ with a corresponding alkali metal salt and the yields are listed in Table 1.

Preparation of $NiH(CN)(P\text{-}i\text{-}Pr_3)_2$

As the starting compound, $Ni(CN)_2(P\text{-}i\text{-}Pr_3)_2$ was prepared by metathetical reaction of $NiCl_2(P\text{-}i\text{-}Pr_3)_2$ with stoichiometric amount of potassium cyanide in benzene followed by recrystallization from dichloromethane. The suspension of $Ni(CN)_2(P\text{-}i\text{-}Pr_3)_2$ (5.0 g) in hexane (200 ml) was treated with a solution of $NaBH_4$ (0.46 g) in ethanol (60 ml) at —10 ~ —5°C with stirring. After 15 min, water (70 ml) was added and the mixture was stirred for 1 min. Then the hexane layer was filtered, concentrated to ca. 100 ml at 0°C and cooled to —78°C. The crystals were filtered off, and dried in vacuo to give the product (2.2 g). The compound prepared by this method was slightly contaminated with $Ni(CN)_2(P\text{-}i\text{-}Pr_3)_2$, but we did not recrystallize it because the compound tended to decompose slowly in hexane or in diethyl ether above 0°C.

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References

1 D.M. Roundhill, Adv. Organometal. Chem., 13 (1975) 273.
2 T.G. Attig and H.C. Clark, Can. J. Chem., 53 (1975) 3466, and refs. cited therein.
3 T. Saito, Chem. Lett., (1974) 1545.
4 H. Moriyama, T. Saito and Y. Sasaki, Chem. Lett., (1976) 175.
5 H.C. Clark and A. Shaver, Can. J. Chem., 53 (1975) 3462.
6 H. Imoto, T. Saito and Y. Sasaki, unpublished.
7 R. Schunn, Inorg. Chem., 15 (1976) 208.
8 M.L.H. Green, H. Munakata and T. Saito, J. Chem. Soc. A, (1971) 469.
9 M.L.H. Green, T. Saito and P.J. Tanfield, J. Chem. Soc. A, (1971) 152.
10 A.J. Deeming, B.F.G. Johnson and J. Lewis, Chem. Commun., (1970) 598.
11 M.L.H. Green and D.J. Jones, Adv. Inorg. Chem. Radiochem., 7 (1965) 115.