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Preliminary communication

SOME ADDUCTS OF $\text{RhCl}[\text{P}(\text{C}_6\text{H}_{11})_3]_2$, A RHODIUM COMPOUND SPONTANEOUSLY COORDINATING DINITROGEN

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Summary

Solutions of $\text{RhCl}(\text{PCy}_3)_2$ react with O_2 , N_2 , C_2H_4 , CO and H_2 to give *trans*- $\text{RhClA}(\text{PCy}_3)_2$ ($\text{A} = \text{O}_2$, N_2 , C_2H_4 and CO , $\text{Cy} = \text{cyclohexyl}$) and $\text{RhClH}_2(\text{PCy}_3)_2$; the spontaneous formation of the rather air-stable $\text{RhCl}(\text{PCy}_3)_2\text{N}_2$ is ascribed to a combination of the steric requirements and electronic properties of the phosphine ligand.

Tricyclohexylphosphine (PCy_3), like other bulky phosphines, is effective in stabilizing unusual coordination numbers and valence states [1, 2]. In the reaction of PCy_3 with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ no reduction to the Rh^{I} valence state occurs, but instead *inter alia* $\text{Rh}^{\text{III}}\text{Cl}_2(\text{PCy}_3)_2$ is formed [2]. Although the existence of $\text{Rh}^{\text{III}}\text{Cl}_3(\text{PCy}_3)_3$ has been reported [3], we did not succeed in its preparation and we have not found an indication for a PCy_3/Rh ratio exceeding 2 in any other complex. In this paper we report the preparation of Rh^{I} tricyclohexylphosphine compounds by cyclooctene displacement from $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ [4].

Addition of two moles of PCy_3 per mole of $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ resulted in the rapid formation of ochrous $[\text{RhCl}(\text{PCy}_3)(\text{C}_8\text{H}_{14})]_2$ (I). The solvated C_8H_{14} -free complex $\text{RhCl}(\text{PCy}_3)_2(\text{S})$ ($\text{S} = \text{solvent molecule}$) was rather slowly formed (20 min stirring) by reaction of either 4 moles or an excess (8 moles) of PCy_3 ($\text{Rh}/\text{PCy}_3 = 1/2$, resp. $1/4$) with $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ in C_6H_6 , and was isolated as a lilac precipitate of yet not fully identified nature. When $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ was used, yellow *trans*- $\text{RhCl}(\text{C}_2\text{H}_4)(\text{PCy}_3)_2$ (II) was obtained. The lilac product is unstable in the solid state, it decomposes within a few hours under vacuum and somewhat more slowly under nitrogen. It immediately turns brown upon exposure to air. In solution, however, $\text{RhCl}(\text{PCy}_3)_2(\text{S})$ reacts rapidly with oxygen to give the grayish-blue adduct *trans*- $\text{RhCl}(\text{O}_2)(\text{PCy}_3)_2$ (III), while the dinitrogen adduct *trans*- $\text{RhCl}(\text{N}_2)(\text{PCy}_3)_2$ (IV) is formed when a solution of

$\text{RhCl}(\text{PCy}_3)_2(\text{S})$ is exposed to 1 atm of N_2 for five days. CO equally adds to $\text{RhCl}(\text{PCy}_3)_2(\text{S})$ to yield the known *trans*- $\text{RhCl}(\text{CO})(\text{PCy}_3)_2$ (V) [2].

$\text{RhCl}(\text{PCy}_3)_2(\text{S})$, made in situ, catalyses the hydrogenation of cyclohexene in benzene at a rate which is about 40 times less than the rate of hydrogenation by $\text{RhCl}(\text{PPh}_3)_3$ under similar conditions [5]. The yellow dihydride $\text{RhClH}_2(\text{PCy}_3)_2$ (VI) and the corresponding $\text{RhClD}_2(\text{PCy}_3)_2$ (VII) can most conveniently be prepared by the reaction of $\text{RhCl}(\text{PCy}_3)_2(\text{C}_2\text{H}_4)$ with H_2 or D_2 .

Satisfactory analyses of the compounds have been obtained. Infrared spectroscopic data are given in Table 1. The large variation in Rh—Cl stretching vibration frequencies suggests that in the complexes $\text{RhClA}(\text{PCy}_3)_2$, Cl and A are in *trans* positions as are the two bulky PCy_3 ligands. The dihydride (VI) has a different structure and its Rh—Cl stretching vibration frequency may not be compared with those of the other adducts.

TABLE 1

INFRARED SPECTROSCOPIC DATA FOR COMPOUNDS $\text{RhCl}(\text{PCy}_3)_2\text{A}$

A	IR absorptions (cm^{-1})	
	$\nu(\text{Rh—Cl})$	others
C_2H_4	294m	3077w, 3040w, 3017w ($\nu(\text{CH})$); 1510w (br), 1208m, 1183w; 950m, 933w ($\delta(\text{CH})$)
CO	304m	1942vs ($\nu(\text{CO})$), 584s ($\delta(\text{CO})$)
N_2	317m	2103vs ($\nu(\text{NN})$), 470m ($\nu(\text{RhN})$)
O_2	328m	993m ^a
H_2	291m	2165(sh), 2120m ($\nu(\text{Rh—H})$), 622m(br) ($\delta(\text{Rh—H})$)
D_2	291m	1560(sh), 1528m ($\nu(\text{Rh—D})$)

^aNot assigned. PCy_3 absorbs in the 800-900 cm^{-1} region where MO_2 modes normally are found [7].

We assume the bulkiness of tricyclohexylphosphine to be one of the causes of the formation of the dinitrogen adduct (IV). For PCy_3 , neither formation of a tris-complex comparable to $\text{RhCl}(\text{PPh}_3)_3$ [5] nor of a dimer comparable to $[\text{RhCl}(\text{PPh}_3)_2]_2$ [5] seems possible. Also adducts with C_6H_6 or C_8H_{14} , the other molecules present, seem to be labilized by steric influences of the two PCy_3 ligands. We therefore postulate the transient existence of the 14 metal valence electron species $\text{RhCl}(\text{PCy}_3)_2$ as the N_2 -bonding species to account for this spontaneous dinitrogen coordination, which has not been reported before for rhodium(I) complexes. The comparable rhodium—dinitrogen compound $\text{RhCl}(\text{PPh}_3)_2(\text{N}_2)$ has been prepared by an indirect method [6]. The high basicity of PCy_3 may facilitate the addition of N_2 , and certainly improves the stability of $\text{RhCl}(\text{PCy}_3)_2(\text{N}_2)$, which is only partly decomposed by air upon standing overnight in C_6H_6 or CHCl_3 . At room temperature the N_2 -ligand can be replaced by CO, but not by C_2H_4 or H_2 . In similar reactions CO displaces C_2H_4 , H_2 , and O_2 from their adducts, to yield spectroscopically pure (V). Oxygen slowly replaces C_2H_4 and H_2 to give impure (III). In contrast to the behaviour of $\text{RhCl}(\text{PPh}_3)_2\text{A}$ (A = C_2H_4 or H_2) [5], $\text{RhCl}(\text{PCy}_3)_2\text{A}$ appears not to lose its coordinated molecule of C_2H_4 or H_2 on sweeping its solution with nitrogen.

A mixture of $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ [4] and PCy_3 in C_6H_6 does not coordinate dinitrogen. Reactions with this system and further reactions with the rhodium system are currently under investigation.

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