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Preliminary communication

SOME ADDUCTS OF $RhCl[P(C_6H_{11})_3]_2$, A RHODIUM COMPOUND SPONTANEOUSLY COORDINATING DINITROGEN

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Summary

Solutions of $RhCl(PCy_3)_2$ react with O_2, N_2, C_2H_4, CO and H_2 to give *trans*-$RhClA(PCy_3)_2$ ($A = O_2$, N_2, C_2H_4 and CO, Cy = cyclohexyl) and $RhClH_2(PCy_3)_2$; the spontaneous formation of the rather air-stable $RhCl(PCy_3)_2N_2$ 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 $RhCl_3 \cdot 3H_2O$ no reduction to the Rh^I valence state occurs, but instead inter alia $Rh^{II}Cl_2(PCy_3)_2$ is formed [2]. Although the existence of $Rh^{III}Cl_3(PCy_3)_3$ 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 $[RhCl(C_8H_{14})_2]_2$ [4].

Addition of two moles of PCy_3 per mole of $[RhCl(C_8H_{14})_2]_2$ resulted in the rapid formation of ochrous $[RhCl(PCy_3)(C_8H_{14})]_2$ (I). The solvated C_8H_{14}-free complex $RhCl(PCy_3)_2(S)$ (S = solvent molecule) was rather slowly formed (20 min stirring) by reaction of either 4 moles or an excess (8 moles) of PCy_3 ($Rh/PCy_3 = 1/2$, resp. 1/4) with $[RhCl(C_8H_{14})_2]_2$ in C_6H_6, and was isolated as a lilac precipitate of yet not fully identified nature. When $[RhCl(C_2H_4)_2]_2$ was used, yellow *trans*-$RhCl(C_2H_4)(PCy_3)_2$ (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, $RhCl(PCy_3)_2(S)$ reacts rapidly with oxygen to give the grayish-blue adduct *trans*-$RhCl(O_2)(PCy_3)_2$ (III), while the dinitrogen adduct *trans*-$RhCl(N_2)(PCy_3)_2$ (IV) is formed when a solution of

$RhCl(PCy_3)_2(S)$ is exposed to 1 atm of N_2 for five days. CO equally adds to $RhCl(PCy_3)_2(S)$ to yield the known *trans*-$RhCl(CO)(PCy_3)_2$ (V) [2].

$RhCl(PCy_3)_2(S)$, 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 $RhCl(PPh_3)_3$ under similar conditions [5]. The yellow dihydride $RhClH_2(PCy_3)_2$ (VI) and the corresponding $RhClD_2(PCy_3)_2$ (VII) can most conveniently be prepared by the reaction of $RhCl(PCy_3)_2(C_2H_4)$ 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 $RhClA(PCy_3)_2$, 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 $RhCl(PCy_3)_2A$

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

[a] Not 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 $RhCl(PPh_3)_3$ [5] nor of a dimer comparable to $[RhCl(PPh_3)_2]_2$ [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 $RhCl(PCy_3)_2$ 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 $RhCl(PPh_3)_2(N_2)$ 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 $RhCl(PCy_3)_2(N_2)$, 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 $RhCl(PPh_3)_2A$ ($A = C_2H_4$ or H_2) [5], $RhCl(PCy_3)_2A$ appears not to lose its coordinated molecule of C_2H_4 or H_2 on sweeping its solution with nitrogen.

A mixture of $[IrCl(C_8H_{14})_2]_2$ [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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