SOME ADDUCTS OF RhCl[PCy₃]₂, A RHODIUM COMPOUND SPONTANEOUSLY COORDINATING DINITROGEN

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Summary

Solutions of RhCl(PCy₃)₂ react with O₂, N₂, C₂H₄, CO and H₂ to give trans-RhCl₂A(PCy₃)₂ (A = O₂, N₂, C₂H₄ and CO, Cy = cyclohexyl) and trans-RhClH₂(PCy₃)₂; the spontaneous formation of the rather air-stable RhCl(PCy₃)₂N₂ is ascribed to a combination of the steric requirements and electronic properties of the phosphine ligand.

Tricyclohexylphosphine (PCy₃), like other bulky phosphines, is effective in stabilizing unusual coordination numbers and valence states [1, 2]. In the reaction of PCy₃ with RhCl₃·3H₂O no reduction to the Rhᴵ valence state occurs, but instead inter alia Rh⁴Cl₂(PCy₃)₂ is formed [2]. Although the existence of Rh⁴Cl₃(PCy₃)₃ has been reported [3], we did not succeed in its preparation and we have not found an indication for a PCy₃/Rh ratio exceeding 2 in any other complex. In this paper we report the preparation of Rh¹ tricyclohexylphosphine compounds by cyclooctene displacement from [RhCl(C₈H₁₄)₂] [4].

Addition of two moles of PCy₃ per mole of [RhCl(C₆H₁₄)₂]₂ resulted in the rapid formation of ochrous [RhCl(PCy₃)(C₈H₁₄)]₂ (I). The solvated C₈H₁₄-free complex RhCl(PCy₃)₂(S) (S = solvent molecule) was rather slowly formed (20 min stirring) by reaction of either 4 moles or an excess (8 moles) of PCy₃ (Rh/PCy₃ = 1/2, resp. 1/4) with [RhCl(C₆H₁₄)₂]₂ in C₆H₆, and was isolated as a lilac precipitate of yet not fully identified nature. When [RhCl(C₂H₄)₂]₂ was used, yellow trans-RhCl(C₂H₄)(PCy₃)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(PCy₃)₂(S) reacts rapidly with oxygen to give the grayish-blue adduct trans-RhCl(O₂)(PCy₃)₂ (III), while the dinitrogen adduct trans-RhCl(N₂)(PCy₃)₂ (IV) is formed when a solution of
RhCl(PCy₃)₂(S) is exposed to 1 atm of N₂ for five days. CO equally adds to RhCl(PCy₃)₂(S) to yield the known trans-RhCl(CO)(PCy₃)₂ (V) [2].

RhCl(PCy₃)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(PPh₃)₃ under similar conditions [5]. The yellow dihydride RhClH₂(PCy₃)₂ (VI) and the corresponding RhClD₂(PCy₃)₂ (VII) can most conveniently be prepared by the reaction of RhCl(PCy₃)₂(C₂H₄) with H₂ or D₂.

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(PCy₃)₂, Cl and A are in trans positions as are the two bulky PCy₃ 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.

<p>| TABLE 1 |
| INFRARED SPECTROSCOPIC DATA FOR COMPOUNDS RhCl(PCy₃)₂A |</p>
<table>
<thead>
<tr>
<th>A</th>
<th>IR absorptions (cm⁻¹)</th>
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<tr>
<td>ν(Rh—Cl)</td>
<td>others</td>
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</table>
| C₆H₆ | 294m | 3077w, 3040w, 3017w (ν(CH));
1510w (br), 1208m, 1183w;
950m, 933w (δ(CH)) |
| CO | 304m | 1942vs (ν(CO)), 584s (δ(CO)) |
| N₂ | 317m | 2103vs (ν(NN)), 470m (ν(ReN)) |
| O₂ | 328m | 993m² |
| H₂ | 291m | 2165(sh), 2120m (ν(Rh—H)), 622m(br) (δ(Rh—H)) |
| D₂ | 291m | 1560(sh), 1528m (δ(Rh—D)) |

²Not assigned. PCy₃ absorbs in the 800-900 cm⁻¹ region where MO₂ 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 PCy₃, neither formation of a tris-complex comparable to RhCl(PPh₃)₃ [5] nor of a dimer comparable to [RhCl(PPh₃)₂]₂ [5] seems possible. Also adducts with C₆H₆ or C₆H₁₄, the other molecules present, seem to be labilized by steric influences of the two PCy₃ ligands. We therefore postulate the transient existence of the 14 metal valence electron species RhCl(PCy₃)₂ as the N₂-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(PPh₃)₂(N₂) has been prepared by an indirect method [6]. The high basicity of PCy₃ may facilitate the addition of N₂, and certainly improves the stability of RhCl(PCy₃)₂(N₂), which is only partly decomposed by air upon standing overnight in C₆H₆ or CHCl₃. At room temperature the N₂-ligand can be replaced by CO, but not by C₂H₄ or H₂. In similar reactions CO displaces C₂H₄, H₂, and O₂ from their adducts, to yield spectroscopically pure (V). Oxygen slowly replaces C₂H₄ and H₂ to give impure (III). In contrast to the behaviour of RhCl(PPh₃)₂A (A = C₂H₄ or H₂) [5], RhCl(PCy₃)₂A appears not to lose its coordinated molecule of C₂H₄ or H₂ on sweeping its solution with nitrogen.
A mixture of \([\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2\) \([4]\) and \(\text{PCy}_3\) in \(\text{C}_6\text{H}_6\) does not coordinate dinitrogen. Reactions with this system and further reactions with the rhodium system are currently under investigation.

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References
