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SOME ADDUCTS OF RhCl[P(C₆H₃)₃]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-RhCl₂(PCy₃)₂ (A = O₂, N₂, C₂H₄ and CO, Cy = cyclohexyl) and 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 Rh²⁺ valence state occurs, but instead inter alia RhIIICl₂(PCy₃)₂ is formed [2]. Although the existence of RhIIICl₃(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]² [4].

Addition of two moles of PCy₃ per mole of [RhCl(C₆H₁₄)₂]₂ resulted in the rapid formation of ochrous [RhCl(PCy₃)(C₆H₁₄)]₂ (I). The solvated C₆H₁₄⁻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-RhCl₂(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-RhCl₂(O₂)(PCy₃)₂ (III), while the dinitrogen adduct trans-RhCl₂(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.

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>INFRARED SPECTROSCOPIC DATA FOR COMPOUNDS RhCl(PCy3)2A</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>IR absorptions (cm⁻¹)</td>
</tr>
<tr>
<td></td>
<td>ν(Rh—Cl)</td>
</tr>
<tr>
<td>C2H4</td>
<td>294m</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>304m</td>
</tr>
<tr>
<td>N2</td>
<td>317m</td>
</tr>
<tr>
<td>O2</td>
<td>328m</td>
</tr>
<tr>
<td>H2</td>
<td>291m</td>
</tr>
<tr>
<td>D2</td>
<td>291m</td>
</tr>
</tbody>
</table>

aNot 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 C₈H₁₄, 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 \([\text{IrCl(C}_8\text{H}_{14})_2]_2\) [4] and PCy\(_3\) in C\(_6\)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
