Preliminary communication

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

H.L.M. VAN GAAL, F.G. MOERS and J.J. STEGGERDA
Department of Inorganic Chemistry, Catholic University, Toernooiveld, Nijmegen (The Netherlands)
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Summary

Solutions of RhCl(PCy₃)₂ react with O₂, N₂, C₂H₄, CO and H₂ to give trans-RhClA(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 Rh¹ valence state occurs, but instead inter alia RhIIICl₂(PCy₃)₂ is formed [2]. Although the existence of RhIIIICl₃(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(C₈H₁₄)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(C₈H₁₄)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(PCy\textsubscript{3})\textsubscript{2} (S) is exposed to 1 atm of N\textsubscript{2} for five days. CO equally adds to RhCl(PCy\textsubscript{3})\textsubscript{2} (S) to yield the known trans-RhCl(CO)(PCy\textsubscript{3})\textsubscript{2} (V) [2].

RhCl(PCy\textsubscript{3})\textsubscript{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\textsubscript{3})\textsubscript{3} under similar conditions [5]. The yellow dihydride RhClH\textsubscript{2}(PCy\textsubscript{3})\textsubscript{2} (VI) and the corresponding RhClD\textsubscript{2}(PCy\textsubscript{3})\textsubscript{2} (VII) can most conveniently be prepared by the reaction of RhCl(PCy\textsubscript{3})\textsubscript{2}(C\textsubscript{2}H\textsubscript{4}) with H\textsubscript{2} or D\textsubscript{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 RhCl\textsubscript{A}(PCy\textsubscript{3})\textsubscript{2}, Cl and \textsubscript{A} are in trans positions as are the two bulky PCy\textsubscript{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\textsubscript{3})\textsubscript{2} A**

<table>
<thead>
<tr>
<th>( \nu(\text{Rh—Cl}) )</th>
<th>( \nu(\text{Rh—Cl}) )</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{2}H\textsubscript{4}</td>
<td>294m</td>
<td>3077w, 3040w, 3017w (( \nu(\text{CH}) )); 1510w (br), 1208m, 1183w; 950m, 933w (( \delta(\text{CH}) ))</td>
</tr>
<tr>
<td>CO</td>
<td>304m</td>
<td>1942vs (( \nu(\text{CO}) )), 584s (( \delta(\text{CO}) ))</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>317m</td>
<td>2103vs (( \nu(\text{NN}) )), 470m (( \nu(\text{RhN}) ))</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>328m</td>
<td>993m \textsuperscript{a}</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>291m</td>
<td>2165(sh), 2120m (( \nu(\text{Rh—H}) )), 622m(br) (( \delta(\text{Rh—H}) ))</td>
</tr>
<tr>
<td>D\textsubscript{2}</td>
<td>291m</td>
<td>1560(sh), 1528m (( \nu(\text{Rh—D}) ))</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Not assigned. PCy\textsubscript{3} absorbs in the 800-900 cm\textsuperscript{-1} region where MO\textsubscript{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\textsubscript{3}, neither formation of a tris-complex comparable to RhCl(PPh\textsubscript{3})\textsubscript{3} [5] nor of a dimer comparable to [RhCl(PPh\textsubscript{3})\textsubscript{2}]\textsubscript{2} [5] seems possible. Also adducts with C\textsubscript{6}H\textsubscript{6} or C\textsubscript{8}H\textsubscript{14}, the other molecules present, seem to be labilized by steric influences of the two PCy\textsubscript{3} ligands. We therefore postulate the transient existence of the 14 metal valence electron species RhCl(PCy\textsubscript{3})\textsubscript{2} as the N\textsubscript{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\textsubscript{3})\textsubscript{2}(N\textsubscript{2}) has been prepared by an indirect method [6]. The high basicity of PCy\textsubscript{3} may facilitate the addition of N\textsubscript{2}, and certainly improves the stability of RhCl(PCy\textsubscript{3})\textsubscript{2}(N\textsubscript{2}), which is only partly decomposed by air upon standing overnight in C\textsubscript{6}H\textsubscript{6} or CHCl\textsubscript{3}. At room temperature the N\textsubscript{2}-ligand can be replaced by CO, but not by C\textsubscript{2}H\textsubscript{4} or H\textsubscript{2}. In similar reactions CO displaces C\textsubscript{2}H\textsubscript{4}, H\textsubscript{2}, and O\textsubscript{2} from their adducts, to yield spectroscopically pure (V). Oxygen slowly replaces C\textsubscript{2}H\textsubscript{4} and H\textsubscript{2} to give impure (III). In contrast to the behaviour of RhCl(PPh\textsubscript{3})\textsubscript{2} A (A = C\textsubscript{2}H\textsubscript{4} or H\textsubscript{2}) [5], RhCl(PCy\textsubscript{3})\textsubscript{2} A appears not to lose its coordinated molecule of C\textsubscript{2}H\textsubscript{4} or H\textsubscript{2} on sweeping its solution with nitrogen.
A mixture of \([\text{IrCl(C}_8\text{H}_{14})_2]\) \([4]\) 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
