

Preliminary communication

THIOCARBONYLRHODIUM COMPLEXES WITH PYRAZOLATE-TYPE LIGANDS

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Summary

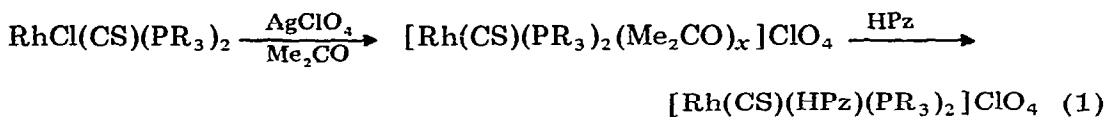
The first binuclear thiocarbonylrhodium complexes of formula $[\text{Rh}(\mu\text{-L})(\text{CS})(\text{PPh}_3)]_2$ (L = pyrazolate type ligand) have been prepared. The crystal structure of the complex with L = 3,5-dimethylpyrazolate has been determined by X-ray diffractometry. Other related mononuclear thiocarbonyl derivatives are also described.

Only few types of mononuclear thiocarbonylrhodium complexes have so far been reported [1—7], and to the best of our knowledge no binuclear thiocarbonylrhodium complex has hitherto been described. It was recently shown that the pyrazolate ligand (Pz in the following) is capable of bridging two rhodium atoms, thus forming very stable binuclear compounds [8] and we report below the preparation of novel mono- and bi-nuclear thiocarbonyl derivatives containing this ligand.

The reaction of complexes of the type *trans*- $\text{RhCl}(\text{CS})(\text{PR}_3)_2$ ($\text{PR}_3 = \text{PPh}_3$ [1] or PCy_3 [2,7]) with NaPz in methanol leads to the formation of complexes of the type $\text{Rh}(\text{Pz})(\text{CS})(\text{PR}_3)_2$. Whilst the PCy_3 derivative can be isolated as the stable end product ($\nu(\text{CS}): 1285 \text{ cm}^{-1}$), the PPh_3 derivative is unstable (isolated at -50°C) and very readily loses one mol of triphenylphosphine to give the red binuclear complex $[\text{Rh}(\mu\text{-Pz})(\text{CS})(\text{PPh}_3)]_2$ ($\nu(\text{CS}): 1305(\text{sh})$ and 1294 cm^{-1}). The proposed formula is confirmed by molecular weight measurements and analytical results. Whereas the preparation of binuclear pyrazolaterhodium complexes with different ancillary ligands has been

already described [8], no rhodium complex in which the pyrazolate group acts as a monodentate ligand has so far been reported*.

The addition of perchloric acid to $[\text{Rh}(\mu\text{-Pz})(\text{CS})(\text{PPh}_3)]_2$ in the presence of triphenylphosphine leads to the formation of $[\text{Rh}(\text{CS})(\text{HPz})(\text{PPh}_3)_2]\text{ClO}_4$, which, like the related complex $[\text{Rh}(\text{CS})(\text{HPz})(\text{PCy}_3)_2]\text{ClO}_4$ can also be prepared according to eq. 1.



($\text{PR}_3 = \text{PPh}_3$ and PCy_3)

The orange-coloured complexes obtained are 1/1 electrolytes in acetone and give correct analyses.

Whilst $[\text{Rh}(\text{CS})(\text{HPz})(\text{PCy}_3)_2]\text{ClO}_4$ reacts with potassium hydroxide to give $\text{Rh}(\text{Pz})(\text{CS})(\text{PCy}_3)_2$ the reaction of the related cations $[\text{Rh}(\text{CS})(\text{HPz})(\text{PPh}_3)_2]^+$ with potassium hydroxide or of $[\text{Rh}(\text{CS})(\text{PPh}_3)_2(\text{Me}_2\text{CO})_x]^+$ with sodium pyrazolate yields $[\text{Rh}(\mu\text{-Pz})(\text{CS})(\text{PPh}_3)]_2$ as the final product, though attempts to obtain suitable crystals for X-ray study proved unsuccessful. Good crystals of the analogously prepared complex $[\text{Rh}(\mu\text{-3,5-Me}_2\text{Pz})(\text{CS})(\text{PPh}_3)]_2$ were isolated from dichloromethane/methanol.

The crystals of $[\text{Rh}(\mu\text{-3,5-Me}_2\text{Pz})(\text{CS})(\text{PPh}_3)]_2$ are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions a 12.700(11), b 17.217(16), c 23.041(18) Å, β 116.55(8)°. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0.061$ for 1978 independent reflections.

The structure of the complex consists of discrete dimeric units in which each rhodium atom is in an approximately square planar arrangement, being bonded to a carbon atom of a thiocarbonyl group, to a phosphorus atom of a triphenylphosphine ligand and to two nitrogen atoms of two substituted pyrazolate ligands which doubly bridge the metal atoms. The thiocarbonyl and the triphenylphosphine ligands are in a *trans* disposition. The structure of this complex is very similar to that of the carbonyl rhodium complex $[\text{Rh}(\text{Pz})(\text{CO})\text{P}(\text{OPh})_3]_2$ [8].

Further work in this area is in progress.

We thank Professor F. Bonati for sending us a copy of ref. 9 prior to publication.

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*We have just been privately informed of the preparation of three novel rhodium complexes in which the anion 3,5-bis(trifluoromethyl)pyrazolate acts either as an exobidentate or a monodentate ligand or remains uncoordinated (CO, PPh₃ and diphos are the ancillary ligands) [9].

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