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A novel and easy way to prepare the $Rh_2(\mu\text{-}SR)_2(CO)_4$ and $Rh_2(\mu\text{-}SR)_2(CO)_2(PR'_3)_2$ complexes on a large scale

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Abstract

Large amounts of the tetracarbonyl starting material $Rh_2(\mu\text{-}SR)_2(CO)_4$ can be easily and quantitatively produced by addition of the thiol HSR onto the anion $[RhCl_2(CO)_2]^-$, which is generated by reduction of hydrated rhodium trichloride in refluxing methanol under an atmosphere of CO. The μ-thiolato complexes can be isolated (R = Me, Ph, CH_2Ph, C_6F_5, t-Bu) and quantitatively transformed into the disubstituted complexes $Rh_2(\mu\text{-}SR)_2(CO)_2(PR'_3)_2$ by addition of two equivalents of the appropriate phosphine PR'_3.

During the last decade, a great attention has been paid to the effects arising from interaction of two (or more) metal atoms in the same complex. Much of the interest relates to the sometimes advantageous influence of such an arrangement on the reactivity of both metal centres, and even on their catalytic activities [1].

In this context we are studying di-rhodium systems, of general formula $[Rh(\mu\text{-}SR)(CO)(PR'_3)]_2$, which show novel properties in catalytic hydroformylation of olefins. Hitherto, such complexes had to be prepared by the stepwise sequence:

$$\underset{(I)}{RhCl_3{,}3H_2O} \rightarrow \underset{(II)}{[RhCl(CO)_2]_2} \rightarrow \underset{(III)}{[Rh(\mu\text{-}SR)(CO)_2]_2} \rightarrow \underset{(IV)}{[Rh(\mu\text{-}SR)(CO)(PR'_3)]_2}$$

The limiting step in this synthesis is the reduction of I into the (μ-chloro)dicarbonylrhodium(I) dimer II. This has been carried out previously by Wilkinson's procedure [2], which has the disadvantages of being lengthly and of possibly giving insoluble and inactive anhydrous rhodium trichloride, and is not generally appliable to large scale preparations (over 3–5 g). Since we use complex II only as precursor of other compounds, we decided to scale a more direct route to complex III.

Twenty years ago Chatt and Shaw [3] prepared complexes of general formula $Rh(Cl)(CO)L_2$ by direct carbonylation of rhodium trichloride in alcoholic media. James and Rempel [4] followed the reduction of rhodium(III) species by treatment

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with CO, and showed that this gave the anion $[RhCl_2(CO)_2]^-$. This anionic complex had been prepared before by Vallarino [5] by reaction of HCl with II, and so we decided to try adding the appropriate thiol HSR to this anion in the hope of obtaining compound III directly:

$$2[RhCl_2(CO)_2]^- + 2\ HSR \xrightarrow{ROH} III + 2\ HCl + 2\ Cl^-$$

Complex II is readily obtained from I in alcoholic media by the action of carbon monoxide. In ethanol, carbonylation occurs at 79 ° C under one atmosphere pressure of CO, but it is necessary to have a stoichiometric amount of hydrochloric acid or chloride salt (such as LiCl) present in order to control the carbonylation. In the presence of HCl or LiCl the formation of the anion is quantitative, whereas in their absence the reaction often gives metallic rhodium. However, the best results are obtained in methanol in which the reaction is slower but does take place at lower temperature, is quantitative, and does not need added acid or chloride ion, since metallic rhodium is not formed.

The reaction can be monitored by IR spectroscopy. At the beginning of carbonylation, a sharp and intense ν(CO) band appears at 2105 cm^{-1}, and is assigned to the complex $[RhCl_4(CO)(MeOH)]^-$ since the solid state spectrum of this species shows a very sharp ν(CO) bond at 2103 cm^{-1}.

Two small ν(CO) bands appear slowly at 2070 and 1993 cm^{-1}; these are characteristic of Vallarino's anion $[RhCl_2(CO)_2]^-$ and grow progressively during the reaction as the 2105 cm^{-1} bond slowly decreases. The end of the reaction is marked by the complete disappearance of the 2105 cm^{-1} band. The appropriate thiol is then added. The formation of III occurs immediately. The IR spectrum of the solution shows that the bands from the Vallarino anion have disappeared and have been immediately replaced by a pattern of three ν(CO) bands, characteristic of complex III.

The tetracarbonyl complex III is easily isolated since it separates out spontaneously above concentrations of ca. 0.1 *M*. Almost total recovery can be achieved by concentration of the solution under vacuum followed by cooling. The crystalline solid III is then filtered off.

It should be noted that the carbonylation may be autocatalytic, since the higher the concentration of rhodium, the faster the carbonylation and the easier the recovery. For example this reaction requires 24 h with $[Rh] \simeq 10^{-2}\ M$ but only 12 to 15 h for $[Rh] \simeq 10^{-1}\ M$. James and Rempel [6] observed previously that the reaction is first order to both rhodium and carbon monoxide.

Complex IV is readily and quantitatively prepared by addition of a stoichiometric amount of a phosphine to a solution of III at room temperature. The reaction is immediate, and the complex is of type IV and isolated by concentration of the solution under vacuum followed by filtration. The overall yield is nearly quantitative [7]. If the reaction is conducted on the initial alcoholic solution, the product is contaminated by small amounts of Rh^{III} species arising from decomposition of IV by residual traces of hydrochloric acid.

We found that our procedure is suitable for non-functional thiols (e.g. HS^tBu, HSPh, etc.) but all attempts with functional ones (e.g. HS-pyridine, cysteine, etc.) failed, and we obtained mixtures of various complexes. We also observed that, as previously noted [8], it was not possible to obtain $[Rh(CO)(PR'_3)(SC_6F_5)]_2$.

Table 1

Characterization of compounds

[Rh(CO)$_2$(SR)]$_2$ R =	IR (cm^{-1}) in hexane	^{31}P NMR: δ(J(P–Rh))	Yield (%)
^{t}Bu	2062m 2044vs 1991vs		97
Me	2069m 2051vs 2005vs		97
Ph	2073m 2058vs 2013vs		100
CH$_2$Ph	2062m 2045vs 2000vs		100
C$_6$F$_5$	2087m 2070vs 2025vs		98
[Rh(CO)(SR)(PPh$_3$)]$_2$ R =			
^{t}Bu	1063vs 1945vs(KBr)	35.8 ppm (153 Hz)	95
Ph	1986vs 1975vs(acetone)	38 ppm (159 Hz) 37 ppm (151 Hz)	80
CH$_2$Ph	1973vs 1963vs	38.1 ppm (159 Hz) 37.1 ppm (156 Hz)	85

The IR spectra of all di-phosphinated complexes IV show two terminal ν(CO) bands separated by ca. 15 cm^{-1}, which shows the presence of one carbonyl group per rhodium atom in a dinuclear complex.

The ^{31}P NMR spectra of the complexes show one doublet, with a ^1J(Rh–P) coupling constant appropriate for Rh^I, but in some cases, a second doublet of similar coupling values and differing in height from experiment to experiment is observed very near the first one ($\leqslant$ 1 ppm). In such cases, the spectroscopic data do not allow us to decide whether we have obtained *cis/trans* or *endo/exo* isomers.

Experimental

Synthesis of [Rh(CO)$_2$(S^{t}Bu)]$_2$

To 0.4 g of RhCl$_3$ · 3H$_2$O (= 1.5 × 10^{-3} g atom of Rh) contained under nitrogen in a flask fitted with a reflux condenser, 90 ml of deoxygenated methanol were added, to give a clear red-brown solution. The solution was stirred as CO was bubbled through the mixture and the temperature was raised slowly (3 h) to 65°C. The solution became yellow during the carbonylation, which was complete in ca. 15 h. After this time the IR spectrum of the solution showed two ν(CO) bands at 2073 and 1995 cm^{-1}, and the solution was then allowed to cool to room temperature and the flow of CO replaced by that of nitrogen, in order to remove the hydrochloric acid. The thiol (HS^tBu; 0.1353 g; 1.5×10^{-3} equiv.) was subsequently added at room temperature with stirring and bright red microcrystals appeared immediately. The mixture was kept at −5 °C overnight and the solid then filtered off, washed with cold methanol, and dried under vacuum; 0.36 g (97%) of the tetracarbonylrhodium dimer was obtained.

II. Synthesis of $[Rh(\mu\text{-}S^tBu)(CO)(PPh_3)]_2$

A solution of 0.99 g (2×10^{-3} mole) of $[Rh(\mu\text{-}S^tBu)(CO)_2]_2$ in 10 ml of hexane was made up at room temperature with stirring and 1.05 g (4×10^{-3} mole) of triphenylphosphine was then added. The di-substituted compound began to separate immediately. The mixture was kept overnight at −5 °C, and the product then filtered off, washed with cold hexane, and dried under vacuum to give 1.85 g (95%) of yellow microcrystals.

Similar procedures were used for all the related compounds. Satisfactory analytical data were obtained for all elements present.

Conclusion

A useful new procedure is described for which the only trouble that has to be taken involves checking by IR spectroscopy that the solution obtained by CO reduction of $RhCl_3 \cdot 3H_2O$ no longer contains any Rh^{III} species, $[RhCl_4(CO)(MeOH)]^-$. Addition of a stoichiometric amount of HSR to Vallarino's anion leads quantitatively to $Rh_2(\mu\text{-}SR)_2(CO)_4$ complexes when simple thiols are used.

There is no limit an the amount of rhodium trichloride that can be used.

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