

Substituted Carbonyl Complexes of Rhodium Containing Amino Acidato Ligands*

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The reactions of halogen, gaseous haloacids, alkyl and aryl amines, 2-2' bipyridyl, 1-10 phenanthroline, tetracyanoethylene on the dicarbonyl amino acidato complexes $\text{Rh}(\text{CO})_2\text{LL}'$ and monocarbonyls $\text{RhCO}(\text{LL}')\text{L}$, where LL' =amino acidato groups and $\text{L}=\text{PPh}_3$, have been reported. The reaction of gaseous haloacids on the dicarbonyls produces $[\text{Rh}(\text{CO})_2\text{X}]_2$ and free amino acids. 1-10 phenanthroline and 2-2' bipyridyl react with the dicarbonyls giving products where both CO groups have been substituted. Chlorination of the monocarbonyl derivatives produce the oxidised products of Rh(III) with a sharp CO absorption bands at ca. 2110 cm^{-1} . Tetracyanoethylene adds to the dicarbonyls giving $\text{Rh}(\text{CO})_2(\text{LL}')\text{TCNE}$. Monodentate nitrogen donor ligands substitutes the cis carbonyls giving $\text{Rh}(\text{LL}')(\text{RNH}_2)_2$. The complexes are characterised by elemental analyses, conductivity measurements, IR and UV-VIS spectra.

A part from catalytic activity, recent investigations show that rhodium compounds exhibit marked tendency to act as antibacterial and antitumor agents¹⁻². Indeed, some neutral Rh(I) complexes having overall square planar geometry do resist the growth of certain tumor by selectively inhibiting the leucine and uridine incorporation into protein². We have found that $\text{Rh}(\text{CO})_2\text{LL}'$ complexes (LL' =glycinato, L-leucinato, L-alaninato and L-phenylalaninato groups) demonstrate significant activity in arresting the growth of certain bacterium with substantial filamentous growth in *E. coli*³. In fact, dicarbonyl leucinatorrhodium(I) has been put to antitumor study in National Cancer Institute, USA. It would therefore be interesting to study the behaviour of these amino acidato complexes of Rh(I) (specially of leucinato derivatives) towards some organic amines, TCNE, halogens and N-heterocyclic ligands.

Results and Discussion

Action of monodentate and bidentate nitrogen donor ligands on the dicarbonyls :

Out of the various amines used (methyl amine, ethyl amine, isobutyl amine and cyclohexyl amine) $\text{Rh}(\text{CO})_2\text{LeuO}$ forms stable yellow compounds with only isobutyl and cyclohexyl amine. These products are neutral (conductivity data) and correspond to the molecular formula $\text{Rh}(\text{LeuO})(\text{RNH}_2)_2$ ($\text{R}=\text{isobutyl}$ and cyclohexyl groups). The parent dicarbonyl shows split νCO bands in the region $2115\text{-}1970\text{ cm}^{-1}$ whereas the amine substituted products did not absorb in this region. The relatively broad absorption bands in the region 3400

and 3200 cm^{-1} have been assigned to νNH on the basis of the well established literature data⁴. Similarly the region around 1600 cm^{-1} is relatively less resolved due to the overlapping of $\nu_{\text{As}}\text{COO}$ and three δNH_2 bands. In the parent compounds, however, these bands appear as distinct absorptions. The UV-VIS spectra of the amine substituted compounds exhibit broad absorption bands in the near ultraviolet region with absorption maxima at $35,500\text{ cm}^{-1}$ ($E=9000$) in the cyclohexyl compound and at $32,500\text{ cm}^{-1}$ ($E=9000$) for the isobutyl amine compound. These bands may be attributed to the MLCT bands as observed for other Rh(I) complexes⁵⁻⁶.

The action of 1-10 phenanthroline and 2-2' bipyridyl (N-N) on $\text{Rh}(\text{CO})_2\text{LeuO}$ produce dark green and brown hygroscopic products which show no CO bands. The analytical data of the complexes conform to their molecular formula $\text{Rh}(\text{LeuO})(\text{N-N})$. The UV-VIS spectra exhibit relatively broad band at ca. $28,000\text{ cm}^{-1}$ and an unresolved band at ca. $31,000\text{ cm}^{-1}$ characteristic of Rh(I) compounds⁵⁻⁶. From these data and from the non-conducting nature of the compounds it appears that these compounds are most probably square planar. These results indicate that the cis CO groups can be replaced by nitrogen donor ligands keeping the metal in the same oxidation state which is of great practical importance in bio-inorganics².

Action of tetracyanoethylene on the dicarbonyls :

When a solution of TCNE in benzene is added to a solution of the dicarbonyls in 1 : 1 mole ratio, the yellow solution immediately turns red which on

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keeping overnight gives either brilliant blue green or brown yellow products. The TCNE adducts exhibit two distinct sharp carbonyl bands (ca. 2090 and 2020 cm^{-1}) due to two cis CO groups instead of much split bands as observed in parent dicarbonyls. The characteristic CN band of TCNE is found at ca. 2220 cm^{-1} . These adducts might exist as either trigonal pyramidal (with TCNE occupying the apex) or quasi-octahedral compounds containing "metal cyclopropane ring"^{7,8,9}. This type of adduct formation of TCNE to other square planar Rh(I) complexes have been reported⁸⁻¹⁰. The leucinato complex shows a broad band in UV-VIS spectra with absorption maxima at ca. 30,000 cm^{-1} and three poorly resolved absorption maxima at ca. 16,000 cm^{-1} . The other products containing glycinate and phenylalaninato groups show similar absorption bands but only in the higher wave length region. Thus in these compounds a broad band is observed at ca. 43,000 cm^{-1} which has a tendency to split and two poorly resolved bands around 26,000 cm^{-1} . These bands indicate that Rh(I) is probably oxidised to Rh(III). Moreover, the unsymmetrical appearance (twin structure) of the bands at ca. 26,000 cm^{-1} may be due to the distortion of the quasi-octahedral structure. Further in TCNE itself a strong band appears at 40,000 cm^{-1} due probably to molecular π -transitions which is either absent in the TCNE derivatives or appears as a very weak absorption. This probably indicated that TCNE is bonded to the central metal atom through the involvement of the C=C.

Action of chlorine on substituted monocarbonyls :

When dry chlorine is passed through a suspension of $\text{Rh}(\text{CO})(\text{LL}')\text{L}_2$ in CCl_4 the compounds go into solution finally forming the reddish yellow product $\text{RhCO}(\text{LL}')\text{Cl}_3$. The compounds show a ν_{CO} peak at ca. 2100 cm^{-1} . The increased ν_{CO}

value from 1965 cm^{-1} (parent compounds) to 2100 cm^{-1} is characteristic of carbonyl complexes of Rh(III)¹¹⁻¹³. The compounds contain about three chlorine atoms per rhodium atom. To account for this and to preserve 18 electron rule for Rh(III) carbonyl derivatives we invoke the idea of amino acidato ligands undergoing chlorine substitution. This type of halogenation of quinoline-8-olato group in $\text{Rh}(\text{Oxq})(\text{CO})_2$ when treated with halogen has been reported¹⁴. It is also found from NMR studies that the methylene groups in glycinate type of ions become activated upon chelation and in fact the substitution of methylene proton of coordinated amino acidato groups in Copper(II) and Cobalt(III) complexes have been reported¹⁵⁻¹⁸. Therefore in $\text{Rh}(\text{CO})\text{L}(\text{R}-\text{CH}(\text{NH}_2)\text{COO})\text{Cl}_3$ it is probable that one of the three chlorines displaces the proton of the activated methylene group (alkyl substituted for the above case) thus suggesting the formula $\text{Rh}(\text{CO})\text{L}(\text{R}-\text{CCl}(\text{NH}_2)\text{COO})\text{Cl}_2$. The chloro substituted methylene group will obviously influence the position of ν_{AsCOO} which is actually observed in the shifts of these absorptions to higher region (see Table 1).

Action of HX on the dicarbonyls :

Previously¹⁹ we reported that gaseous HCl reacts with the dicarbonyls producing the parent dimer with the simultaneous release of free amino acids which is a reversible process. Now it is found that when fumes of HBr is passed over any of the solid amino acidato dicarbonyls, the bromobridged dimer is produced which is an easy method for the preparation of the bromobridged dimer from the chloro bridged one via the amino acidato derivatives. These results are in agreement with those of Burlex *et al.*²⁰ who have shown that HX (X=Cl or Br) reacts with the square planar Rh(I) complexes $\text{Rh}(\text{acac})\text{COL}$ (L=PPh₃ or AsPh₃) to give

TABLE I—IMPORTANT IR AND UV-VIS SPECTRAL DATA OF THE RHODIUM COMPOUNDS

Compound	E_{max} in μm^{-1}	Extinction coefficient $\text{M}^{-1}\text{cm}^{-1}$ (principal band)	ν_{CO} cm^{-1}	ν_{CN} cm^{-1}	ν_{NH} cm^{-1}	ν_{AsCOO} cm^{-1}	δ_{NH_2} cm^{-1}
$\text{Rh}(\text{CO})_2(\text{GlyO})\text{TCNE}$	4.8, 2.7, 2.55	8289	2085s 2010s	2200s	3200- 3100br	1625- 1600br	
$\text{Rh}(\text{CO})_2(\text{PheO})\text{TCNE}$	4.75, 2.65, 2.55	7014	2080s 2015s	2220s 2165sh	3200br	1600br	
$\text{Rh}(\text{CO})_2(\text{LeuO})\text{TCNE}$	3.0, 1.67, 1.57, 1.4	6012	2090s 2020s	2225s	3200br	1650br	1600br
$\text{Rh}(\text{LeuO})(\text{Cha})$	3.55	9175	—	—	3350br 3200br	1625- 1575br	
$\text{Rh}(\text{LeuO})(\text{Iba})$	3.25	9050	—	—	3300- 3200br	1600br	
$\text{RhCO}(\text{PPh}_3)(\text{LeuO}-\text{Cl})\text{Cl}_2$	—	—	2105s	—	3400br 3200br	1625br*	1575br
$\text{RhCO}(\text{PPh}_3)(\text{PheO}-\text{Cl})\text{Cl}_2$	—	—	2104s	—	3350br	1625br*	1565br
$\text{RhCO}(\text{PPh}_3)(\text{TrpO}-\text{Cl})\text{Cl}_2$	—	—	2107s	—	3350br 3150tr	1725br*	1610br

GlyO = glycinate, PheO = L-phenylalaninato, LeuO = L-leucinato, TrpO = L-tryptophanato, s = sharp, br = broad, sh = shoulder.

* For the respective parent compounds the ν_{AsCOO} are at 1610, 1606 and 1670 cm^{-1} respectively.
Cha = cyclohexyl amine, Iba = isobutyl amine.

the halobridged dimer $[\text{RhXCOL}]_2$ and of Ukhin *et al.*²¹ who have also established that $\text{Rh}(\text{CO})_2\text{L}$ (HL = acetylacetonone) reacts with HLL (HLL = CF_3COOH , $\text{C}(\text{CH}_3)_2\text{FCOOH}$, HCN) to give $[\text{Rh}(\text{CO})_2\text{LL}]_2$.

Experimental

The parent compounds were prepared following published methods^{19,22}. The important IR and UV-VIS spectral bands of the reported compounds are given in Table 1.

$\text{Rh}(\text{LL}')(\text{RNH}_2)_2$: An acetone solution of 0.1 g of the dicarbonyl $\text{Rh}(\text{CO})_2\text{LeuO}$ was treated with excess of the amines. The solution was kept for one week in vacuum which on evaporation under reduced pressure gave yellow products.

Leucinatobis (cyclohexyl amine) rhodium(I): RhLeuO(Cha)₂:

Yellow compound. (Found Rh, 23.4; C, 41.4; H, 8.5; N, 9.4; Calc. for $\text{RhC}_{18}\text{H}_{38}\text{N}_3\text{O}_2$: Rh, 23.8; C, 41.1; H, 8.8; N, 9.7%).

Leucinatobis (isobutyl amine) rhodium(I). RhLeuO(Iba)₂:

Yellow compound. (Found: Rh, 23.4; C, 44.0; H, 8.5; N, 10.9; Calc. for $\text{RhC}_{14}\text{H}_{34}\text{N}_3\text{O}_2$: Rh, 23.8; C, 44.3; H, 8.9; N, 11.08%).

$\text{Rh}(\text{CO})_2(\text{LL}')\text{TCNE}$: A solution of TCNE in benzene was treated with a solution of amino acidato dicarbonyls in 1:1 mole ratio. The solution was kept overnight for complete reaction. Evaporation of the solution under vacuum gave yellow brown to brilliant blue green compounds. The compounds are soluble in chloroform or alcohol.

$\text{Rh}(\text{CO})_2(\text{GlyO})\text{TCNE}$: Yellow brown amorphous compound. (Found: C, 32.5; H, 1.15; N, 19.1; Calc. for $\text{RhC}_{10}\text{H}_4\text{N}_5\text{O}_4$: C, 33.2; H, 1.1; N, 19.3%).

$\text{Rh}(\text{CO})_2(\text{PheO})\text{TCNE}$: Brown crystalline compound. (Found: C, 45.0; H, 2.0; N, 15.2; Calc. for $\text{RhC}_{17}\text{H}_{10}\text{N}_5\text{O}_4$: C, 45.2; H, 2.2; N, 15.5%).

$\text{Rh}(\text{CO})_2(\text{LeuO})\text{TCNE}$: Brilliant blue green crystal. (Found: C, 39.6; H, 2.9; N, 16.4; Calc. for $\text{RhC}_{14}\text{H}_{13}\text{N}_5\text{O}_4$: C, 40.2; H, 3.07; N, 16.7%).

$\text{Rh}(\text{CO})\text{L}(\text{LL}'\text{-Cl})\text{Cl}_2$: A stream of dry chlorine gas was passed through a suspension of 0.1 g of the monocarbonyls $\text{RhCO}(\text{LL}')\text{L}_2$ in CCl_4 for one hour. The compound dissolves and a reddish precipitate

slowly separated from the solution. Filtered, washed with chloroform and finally dried.

$\text{Rh}(\text{CO})\text{PPh}_3(\text{LeuO-Cl})\text{Cl}_2$: Yellow compound. (Found: C, 47.3; H, 4.1; N, 2.1; Cl, 15.0; Calc. for $\text{RhC}_{25}\text{H}_{27}\text{NCl}_3\text{PO}_3$: C, 47.7; H, 4.3; N, 2.2; Cl, 15.2%).

$\text{Rh}(\text{CO})\text{PPh}_3(\text{TrpO-Cl})\text{Cl}_2$: Yellow compound. (Found: C, 50.8; H, 3.9; N, 3.7; Cl, 14.8; Calc. for $\text{RhC}_{30}\text{H}_{26}\text{N}_2\text{Cl}_3\text{PO}_3$: C, 51.2; H, 4.1; N, 3.9; Cl, 15.1%).

$\text{Rh}(\text{CO})\text{PPh}_3(\text{PheO-Cl})\text{Cl}_2$: Reddish compound. (Found: C, 50.6; H, 3.77; N, 1.9; Cl, 15.6; Calc. for $\text{RhC}_{28}\text{H}_{28}\text{NCl}_3\text{PO}_3$: C, 50.6; H, 3.77; N, 2.1; Cl, 15.9%).

$\text{Rh}(\text{LeuO})(\text{N-N})$: To an acetone solution of 0.1 g of the dicarbonyl $\text{Rh}(\text{CO})_2\text{LeuO}$ was added solid 1-10 phenanthroline or 2-2' bipyridyl (N-N) in 1:1 mole ratio. An immediate separation of solid dark green to brown products took place with evolution of CO gas. Filtered and washed with acetone on filter, collected and preserved under vacuum.

L-Leucinatophenanthrolinerhodium(I); $\text{Rh}(\text{LeuO})\text{-Phen}$:

Dark green hygroscopic product. (Found: C, 51.5, H, 4.2; Rh, 24.2; Calc. for $\text{RhC}_{18}\text{H}_{20}\text{N}_3\text{O}_2$: C, 52.3; H, 4.8; Rh, 24.8%).

L-Leucinatobipyridylrhodium(I): $\text{Rh}(\text{LeuO})\text{-Bipy}$:

Brown hygroscopic product. (Found: C, 48.6; H, 5.1; Rh, 26.0; Calc. for $\text{RhC}_{16}\text{H}_{20}\text{N}_3\text{O}_2$: C, 49.5; H, 5.1; Rh, 26.5%).

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