Journal of Organometallic Chemistry, 67 (1974) 443—447

SOME CATIONIC CARBONYL COMPLEXES OF RHODIUM(I)

G.K.N. REDDY and B.R. RAMESH

Department of Chemistry, Bangalore University, Bangalore - 560001 (India)

(Received July 30th, 1973)

Summary

A number of cationic rhodium(I) complexes of the type $[Rh(CO)_2(N—N)]ClO_4$, $[Rh(CO)_2L_3]ClO_4$ and $[Rh(CO)(N—N)L_2]ClO_4$, where (N—N) is 2,2′-bipyridine or 1,10-phenanthroline and L is a tertiary phosphine or arsine, have been isolated and their structures assigned. The configuration of the complex ion $[Rh(CO)_2L_3]^+$ appears to depend critically on the size of the ligand L.

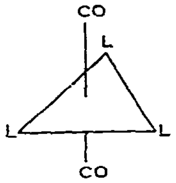
Introduction

We have briefly reported earlier [1] the preparation and characterisation of cationic carbonyl complexes of rhodium(I) of the types $[Rh(CO)_2(N—N)]ClO_4$, $[Rh(CO)_2L_3]ClO_4$ and $[Rh(CO)(N—N)L_2]ClO_4$, where (N—N) is 2,2′-bipyridine (Bipy) or 1,10-phenanthroline (*o*-Phen) and L is Ph_3P or Ph_3As. Some similar or identical compounds have also been reported by other workers [2 - 7]. We have extended our investigations and have isolated new cationic complexes of rhodium(I) of the above types with several other tertiary phosphines and arsines. Details of these investigations are reported here.

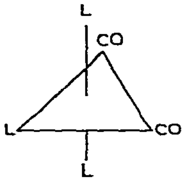
Results and discussions

Rhodium in solution has a high affinity for halide ions [6] and so special methods have to be employed to isolate cationic complexes of rhodium(I) and to avoid the formation of neutral species [3,7 - 9]. With this in view we have used rhodium perchlorate [1] as the starting material for the preparation of our complexes.

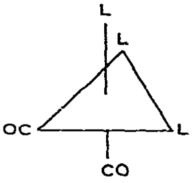
When carbon monoxide is passed through an alcoholic solution of rhodium perchlorate and the nitrogen donor ligands (e.g. Bipy or *o*-Phen) are added to the resulting solution, compounds of the type $[Rh(CO)_2(N—N)]^+ClO_4^-$ separate. The corresponding fluoroborates have also been prepared. These behave as 1/1 electrolytes in nitrobenzene and show two ν(CO) peaks in the



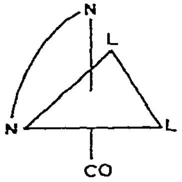
I



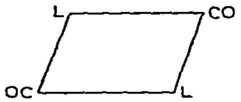
II



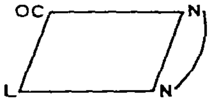
III



IV



V



VI

2000 cm^{-1} region of the infrared; they should have a square planar configuration with the two carbonyls *cis* to each other. Cocevar et al. [2] have reported the preparation of [Rh(CO)$_2$Bipy]ClO$_4$ by a different route.

Addition of one of the monodentate ligands Ph$_3$P, (*p*-CH$_3$C$_6$H$_4$)$_3$P, Ph$_3$As, Ph$_2$MeAs, Ph$_2$EtAs, Ph$_2$PrAs, Ph$_3$Sb, in place of the bidentate nitrogen donor ligands gives a five-coordinate compound of the type [Rh(CO)$_2$L$_3$]-ClO$_4$. Products of this type show a single ν(CO) peak (except Ph$_2$MeAs and Ph$_2$EtAs compounds) and behave as 1/1 electrolytes in nitrobenzene. By analogy with a number of similar cationic complexes of iridium(I) and rhodium(I) reported earlier [5 - 8], these cationic complexes should have trigonal bipyramidal stereochemistry with the carbonyls occupying the axial positions [configuration (I)].

We have reported earlier [1] that the triphenylphosphine and -arsine derivatives show two very closely spaced ν(CO) peaks (Table 1). We now find that the triphenylphosphine derivative may be obtained in two forms, orange and yellow, with a slight alteration in the experimental conditions. While the orange form [5] shows a single ν(CO) peak the yellow form shows two closely spaced peaks (a split band). This difference between the two forms, we feel, is due to a difference in the way the ions are packed in the crystals rather than to any difference in the stereochemistry of the cations. Warming the orange form in alcohol transforms it into the yellow form. Unfortunately, these compounds undergo slow decomposition in most of the common organic solvents in which they are soluble and so it is not possible to observe meaningful infrared solution spectra.

The diphenylmethylarsine analogue, however, shows two sharp ν(CO) bands at 1979 and 2023 cm^{-1} (Table 1) and hence should have configuration (II) or (III) (infrared data cannot distinguish between these two configurations). We have also obtained the proton NMR spectrum of this compound (in CDCl$_3$) which shows a single methyl resonance at 8.13τ, suggesting configuration (I). It is likely that this result is due to a rapid exchange of the arsines or

TABLE 1

PROPERTIES OF CATIONIC CARBONYL COMPLEXES OF RHODIUM(I)

Compound Colour	M.p. or dec.p. (°C)	Λ[a]	ν(CO) (cm^{-1})[b]	Analyses, found (calcd.) (%)		
				C	H	N
$[Rh(CO)_2Bipy]ClO_4$[c] yellow	200 - 205	30.1	2108 2050	34.77 (34.76)	2.29 (1.95)	6.93 (6.76)
$[Rh(CO)_2\textit{o}\text{-}Phen]ClO_4$[c] yellow	195 - 200	28.1	2105 2042	38.60 (38.34)	2.50 (1.84)	4.70 (6.39)
$[Rh(CO)_2Bipy]BF_4$ green	> 300	22.3	2108 2050	36.90 (35.86)	2.75 (2.01)	6.91 (6.97)
$[Rh(CO)_2o\text{-}Phen]BF_4$ green	> 300	23.1	2112 2050	39.54 (39.38)	2.02 (1.89)	6.84 (6.56)
$[Rh(CO)_2(Ph_3P)_3]ClO_4$ orange	166-170	23.2	2018	64.69 (64.88)	4.67 (4.33)	
$[Rh(CO)_2(Ph_3P)_3]ClO_4$[c] yellow	160 - 162	28.1	2025 2012	64.60	4.32	
$[RhL(CO)_2(Ph_3As)_3]ClO_4$[c] yellow	198 - 199	25.9	2020 2010	57.72 (57.49)	4.00 (3.95)	
$[Rh(CO)_2(Ph_3Sb)_3]ClO_4$ yellow	176 - 178	23.7	2006	50.77 (51.02)	3.59 (3.44)	
$[Rh(CO)_2(Ph_2MeAs)_3]ClO_4$ yellow	143 - 145	21.4	2023 1979	49.25 (49.69)	4.04 (3.97)	
$[Rh(CO)_2(Ph_2EtAs)_3]ClO_4$ greenish yellow	122 - 125	23.8	2025 2012 1965	51.18 (51.17)	4.51 (4.39)	
$[Rh(CO)_2(Ph_2PrAs)_3]ClO_4$ orange	170 - 173	23.4	1991	52.78 (52.51)	4.70 (4.78)	
$[Rh(CO)_2(\textit{o}\text{-}Tolyl_3P)_2]ClO_4$ yellow	183 - 186	23.7	2040	60.28 (60.92)	4.98 (4.88)	
$[Rh(CO)_2(\textit{p}\text{-}Tolyl_3P)_3]ClO_4$ yellow	170 - 172	22.6	2020	66.37 (66.65)	5.58 (5.42)	
$[Rh(CO)Bipy(Ph_3P)_2]ClO_4$[c] yellow	150 - 152	29.9	1920	61.65 (61.97)	4.88 (4.21)	4.70 (3.08)
$[Rh(CO)\text{-}\textit{o}\text{-}Phen(Ph_3P)_2]ClO_4$[c] yellow	148 - 153	27.9	1940	62.47 (62.94)	4.32 (4.10)	3.78 (3.00)
$[Rh(CO)Bipy(Ph_3As)_2]ClO_4$[c] yellow	205 - 208	28.0	1920	56.94 (56.50)	4.11 (3.83)	
$[Rh(CO)Bipy(\textit{o}\text{-}Tolyl_3P)]ClO_4$ orange-yellow	192 - 193	21.8	2100	54.98 (55.62)	4.37 (4.23)	3.92 (4.05)
$[Rh(CO)\textit{o}\text{-}Phen(\textit{o}\text{-}Tolyl_3P)]ClO_4$ orange yellow	228 - 230	26.8	1994	56.54 (57.11)	4.12 (4.08)	3.89 (3.92)
$[Rh(CO)Bipy(\textit{p}\text{-}Tolyl_3P)_2]ClO_4$ orange yellow	211 - 215	25.3	1954	63.79 (63.96)	5.08 (5.06)	3.01 (2.81)
$[Rh(CO)\textit{o}\text{-}Phen(\textit{p}\text{-}Tolyl_3P)_2]ClO_4$ orange yellow	185 - 187	24.8	1947	64.13 (64.85)	4.93 (4.95)	2.77 (2.75)

[a] Ca $10^{-3}M$ solutions in nitrobenzene at 25° were used to measure molar conductance (ohm^{-1}·cm^2·mole^{-1}). [b] Infrared spectra taken in nujol; compounds show $\nu(ClO_4^-)$ at 1100±5 cm^{-1} or $\nu(BF_4^-)$ at 1066 cm^{-1}. [c] Reported ealier [1].

to a change of the configuration to (I) in solution. Deeming and Shaw [8] and Church et al. [9] have reported similar observations for the cations $[Ir(CO)_2(PMe_2Ph)_3]^+$ and $[Ir(CO)_2(PMePh_2)_3]^+$ respectively. They also assign configuration (II) to these ions.

While the ligand Ph_2MeAs gives a cation of configuration (II) or (III) and Ph_2PrAs gives a cation of configuration (I), the ligand Ph_2EtAs appears to give a mixture of these isomers, as indicated by the infrared. The solid product isolated with this ligand, while giving satisfactory analysis for the formula $[Rh(CO)_2(Ph_2EtAs)_3]ClO_4$, shows three ν(CO) peaks in the infrared at 1965, 2012 and 2025 cm^{-1} (Table 1) suggesting that it is a mixture of isomers. Cationic complexes of rhodium and iridium with the ligands Me_2PhP [8],

$MePh_2P$ [5,9], and Me_2PhAs [8] have also been reported to have structure (II). These observations suggest that the stereochemistry of the cationic complexes of rhodium(I) of the type $[Rh(CO)_2L_3]^+$ is very critically dependent on the size of the ligand L. With more bulky ligands, such as Ph_3P, Ph_3As, Ph_3Sb and $(p\text{-}CH_3C_6H_4)_3P$, configuration (I) is preferred but if one or more of the phenyl groups are replaced by a small alkyl group, configuration (II) or (III) seems to be preferred. If such an alkyl group is sufficiently large, as in the case of Ph_2PrAs, the cation again assumes configuration (I).

We have also prepared cationic complexes of rhodium(I) with the ligand $(o\text{-}CH_3C_6H_4)_3P$. Analysis points to the formula $[Rh(CO)_2\{(o\text{-}CH_3C_6H_4)_3P\}_2]^+\text{-}ClO_4^-$. It shows a single ν(CO) peak and probably has configuration (V) with the carbonyls *trans* to each other. Thus, while tri-*p*-tolylphosphine gives a five-coordinated species of configuration (I), the tri-*o*-tolylphosphine gives a four-coordinated *trans* species. Obviously, because of steric hindrance resulting from the presence of the methyl group in *ortho* position in the phenyl ring of the tri-*o*-tolylphosphine in the cationic complex, the phosphine ligands prefer not to occupy adjacent positions.

Several of these five-coordinate dicarbonyl cations react with Bipy or *o*-Phen to give mixed ligand complexes of the type $[Rh(CO)(N\text{—}N)L_2]ClO_4$, the bidentate nitrogen donor ligand replacing one of the phosphines and a carbonyl group; these cations should have configuration (IV). They can also be prepared by reacting the corresponding cation of the type $[Rh(CO)_2(N\text{—}N)]^+$ with the tertiary phosphine. Attempts to prepare the corresponding tertiary arsine analogues have not been successful, except in the case of triphenylarsine. With the other arsines intractable pastes only result.

The four-coordinate tri-*o*-tolylphosphine derivative on reaction with Bipy or *o*-Phen gives four-coordinate substitution products of the type $[Rh(CO)(N\text{—}N)L]ClO_4$, which should have configuration (VI).

Experimental

The infrared and NMR measurements were carried out with Carl Zeiss UR 10 spectrophotometer and Varian T-60 instruments, respectively. Conductivity measurements were made using Toshniwal Instruments conductivity bridge type CLO1.02.

Dicarbonyl-2,2'-bipyridine (or 1,10-phenanthroline)rhodium(I) perchlorate (or tetrafluoroborate), $[Rh(CO)_2(N\text{—}N)]^+ClO_4^-$ (or BF_4^-)

Carbon monoxide was passed through a refluxing alcoholic solution of rhodium perchlorate for 2 h. To this solution a calculated amount of Bipy (or *o*-Phen) was added and passage of carbon monoxide was continued when yellow crystals of the perchlorate separated.

The tetrafluoroborate derivatives were made by passing carbon monoxide through an alcoholic solution of rhodium trichloride and adding excess $NaBF_4$, followed by a calculated amount of Bipy or *o*-Phen at ice temperature, when the required compound separated.

Dicarbonyltris(tertiary phosphine or arsine or stibine)rhodium(I) perchlorate, $[Rh(CO)_2L_3]ClO_4$

Carbon monoxide was passed through a refluxing alcoholic solution of rhodium perchlorate for 1 h. A calculated amount of the ligand was added to the solution, and bubbling of CO was continued for another hour. The resulting solution, on evaporation under reduced pressure, deposited crystals of the required compound. In the case of the compound $[Rh(CO)_2(PPh_3)_3]ClO_4$, if reaction is carried out at room temperature orange-yellow crystals are obtained, if higher temperatures are used an yellow crystalline material separates.

The dicarbonyl bis(tri-*o*-tolylphosphine) compound $[Rh(CO)_2L_2]ClO_4$ was also prepared in the same way.

Carbonyl-2,2'-bipyridine (or 1,10-phenanthroline)bis(tertiary phosphine or arsine)rhodium(I) perchlorate, $[Rh(CO)(N{-}N)L_2]ClO_4$

To an alcoholic suspension of $[Rh(CO)_2(N{-}N)]ClO_4$ or $[Rh(CO)_2L_3]$-ClO_4 a calculated amount of the ligand L or (N—N) in alcohol is added and the resulting solution, on evaporation under vacuum, deposits the required compound.

The carbonyl 2,2'-bipyridine (or 1,10-phenanthroline) tertiary phosphine rhodium(I) perchlorate compounds $[Rh(CO)(N{-}N)L]ClO_4$ were made in a similar way.

Acknowledgements

The authors thank Dr. R.J.H. Clark, University College, London, for microanalysis, Prof. A.R.V. Murthy, I.I.Sc., Bangalore, for infrared and NMR spectra, the U.G.C., Government of India for financial assistance (to B.R.R.) and the Chemical Society, London, for a grant from the Research Fund (to G.K.N.R.).

References

1 G.K.N. Reddy and C.H. Susheelamma, J. Chem. Soc. D, (1970) 54.
2 C. Cocevar, G. Mestroni and A. Camus, J. Organometal. Chem., 35 (1972) 389.
3 J.V. Kingston, F.T. Mohmoud and G.R. Scollary, J. Inorg. Nucl. Chem., 34 (1972) 3197.
4 G. Mestroni and A. Camus, Inorg. Nucl. Chem. Lett., 9 (1973) 261.
5 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 93 (1971) 2397.
6 J.T. Mague, Inorg. Chem., 11 (1972) 2558.
7 J. Peone and L. Vaska, Angew. Chem., Int. Ed. Engl., 10 (1971) 511.
8 A.J. Deeming and B.L. Shaw, J. Chem. Soc. A, (1970) 2705.
9 M.J. Church, M.J. Mays, R.N.S. Simpson and F.P. Stefanini, J. Chem. Soc. A, (1970) 2909.