

COMPLEXES OF RHODIUM(I) WITH 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE

SYNTHESIS AND REACTIONS OF CATIONIC CARBONYL DERIVATIVES

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Summary

The synthesis and reactions of Rh^{I} carbonyl complexes of the type $[\text{RhChel}(\text{CO})_2]^+$ and RhChelCOX (Chel = Bipy, Phen; X = Cl, Br, I) are described. Coordinative, oxidative-addition, and substitution reactions are compared with those of the corresponding Ir^{I} derivatives.

Introduction

It is well known that bidentate chelating systems of the type represented by 2,2'-bipyridine and 1,10-phenanthroline can give stable isostructural complexes, $[\text{M}(\text{Chel})_3]^{n+}$, in which the metals are in different oxidation states [1]. Similar behaviour has also been observed for the complexes $[\text{Co}(\text{Bipy})_2(\text{CH}_3)_2]\text{ClO}_4$ [2], $\text{Co}(\text{Chel})_2\text{CONO}$ and $\text{Fe}(\text{Chel})_2(\text{NO})_2$ [3], (Chel = Bipy or Phen), but not for $[\text{Co}(\text{DPE})_2\text{H}_2]\text{ClO}_4$ [2]. Recently Saito et al. [4] pointed out that in $[\text{M}(\text{Chel})_3]^{n+}$ complexes the stretching frequencies of the M—N bond are little influenced by varying the formal oxidation state, unless the electronic configuration changes from t_{2g}^n to a $t_{2g}^n e_g^m$. These results were explained assuming that σ -bonding becomes weaker and π -bonding stronger as the formal oxidation state is lowered, so that the overall M—N bond strength is approximately constant.

Bidentate (or polydentate) chelating systems with delocalized ground state as supporting ligands in σ - or π -organometallic complexes should allow the study of the reactivity of coordinated organic groups in series of isostructural complexes with the metals in different oxidation states. At present, numerous organometallic complexes with σ -M—C bond are known (e.g. with Ti^{IV} [5], Cr^{III} [6,7], Fe^{II} [8], Co^{II} [3,8], Co^{III} [3,9], Ni^{II} [8], Pd^{II} [10]), but π -organometallic complexes have been little investigated [11,12].

In this paper we describe the synthesis and reactions of rhodium(I) com-

plexes of the type $[\text{Rh}(\text{Chel})(\text{L}-\text{L})]\text{PF}_6$ and $[\text{Rh}(\text{Chel})(\text{CO})_2]\text{PF}_6$ * [$\text{Chel} = \text{Bipy}$ or Phen ; $\text{L}-\text{L} = \text{cis}, \text{cis}-1,5\text{-cyclooctadiene} = \text{COD}$ or $\text{bicyclo}[2.2.1]\text{hepta-2,5-diene} = \text{NBD}$].

Results

Reactions of carbonyl derivatives with unsaturated molecules

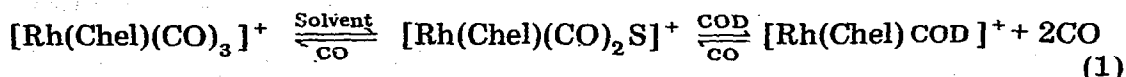
In a previous paper [13] we reported the synthesis of the $[\text{Rh}^{\text{I}}\text{Bipy}(\text{CO})_2]\text{ClO}_4$ complex. A more detailed study of the reaction between $[\text{Rh}(\text{Chel})\text{COD}]\text{PF}_6$ and carbon monoxide has shown that these complexes take up three ligand moles for each mole of complex, to give the pentacoordinated tricarbonyl derivatives $[\text{Rh}(\text{Chel})(\text{CO})_3]\text{PF}_6$ (I). Their IR spectra in methyl cyanide show two bands at 2101 and 2040 cm^{-1} (previously attributed at dicarbonyl derivatives on the basis of other data in the literature [11]), which disappear when nitrogen is bubbled through the solutions, while two new intense bands become evident at 2012 and 1976 cm^{-1} . Resaturation with carbon monoxide restores the original spectra. The cycle can be repeated many times.

Similarly, visible spectra of the solutions saturated with carbon monoxide are characterized by a maximum (397 nm, $\text{Chel} = \text{Bipy}$), which is shifted towards higher wavelengths, with a simultaneous increasing of intensity, by sweeping the solutions with nitrogen. Regeneration of starting products is quantitative on resaturating the solutions with carbon monoxide.

This behaviour, which is due to an equilibrium between the tri- and dicarbonyl derivatives, is not observed in the solvents previously used for the synthesis of the carbonyl derivatives (methanol [13] or ethanol [11]).

In the presence of COD all the carbon monoxide can be easily expelled from the solutions of complexes (I) and the complexes $[\text{Rh}(\text{Chel})\text{COD}]\text{PF}_6$ are reformed. This process is also reversible.

The above reactions are collected together in Eqn. 1.



In accord with this, the derivatives $[\text{Rh}(\text{Chel})(\text{L}-\text{L})]\text{PF}_6$ were isolated from the reaction between the tricarbonyl derivatives and $\text{L}-\text{L}$ ($\text{L}-\text{L} = \text{NBD}$ or $1,3,5,7\text{-cyclooctatetraene} = \text{COT}$).

As shown by spectroscopic variations in the visible region, complexes (I) in methyl cyanide also react with activated olefins such as acrylonitrile (AN), fumaronitrile (FUN) and tetracyanoethylene (TCNE), the rate increasing in the order $\text{AN} < \text{FUN} \ll \text{TCNE}$. On addition of TCNE to solutions of the tricarbonyl derivatives, the colour changes immediately from brown to yellow, and evolution of carbon monoxide is evident. The IR spectra of the yellow solutions show that coordinated carbon monoxide is no longer present. Elemental analyses are in agreement with the formulae $[\text{Rh}(\text{Chel})\text{L}]\text{PF}_6$ (II) ($\text{L} = \text{FUN}$,

* The corresponding perchlorate complexes were prepared, but were not further investigated owing to occasional explosions.

TCNE), which can be regarded as tricoordinated species unless cyanoolefins act as bidentate ligands. IR spectra in the solid state show two bands in the 2250-2150 cm^{-1} region, ascribable to the coordinated olefins. The complexes with FUN, but not those with TCNE, react readily with carbon monoxide to give back the starting tricarbonyl compounds, and with COD and NBD to give the $[\text{Rh}(\text{Chel})(\text{L}-\text{L})]\text{PF}_6$ complexes.

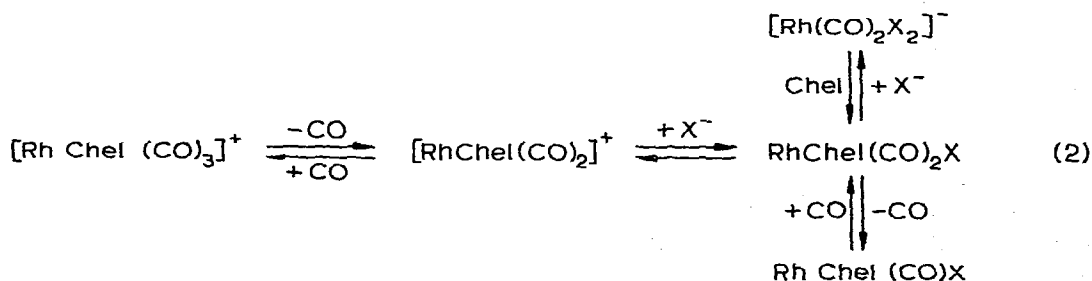
The complexes (II), which are very soluble in methyl cyanide owing to solvation, react with Chel in excess to give the corresponding $[\text{Rh}(\text{Chel})_2\text{L}]\text{PF}_6$ derivatives. The latter complexes can also be prepared by direct action of olefins (AN, FUN, TCNE and MA = maleic anhydride) on the tricarbonyl derivatives, in the presence of an excess of Chel.

Reactions of carbonyl derivatives with X^-

Complexes (I) react under nitrogen in methyl cyanide or acetone with a slight excess of lithium halides to give orange solutions, containing $\text{Rh}(\text{Chel})(\text{CO})\text{X}$ species (III). The visible spectra of solutions of the isolated complexes in methyl cyanide are characterized by a maximum at about 470 nm, slightly sensitive to the nature of the halogen. The IR spectra show an only band in the CO stretching region, at about 1980 cm^{-1} , which moves towards higher frequencies going from iodide to chloride (Table 1).

Complexes (III) react reversibly in methyl cyanide with carbon monoxide to give the corresponding pentacoordinated adducts in equilibrium with complexes (I). These adducts are characterized by a group of bands in 1900 - 1800 cm^{-1} region [14]. On the other hand, if the reaction with carbon monoxide is carried out in the presence of halides, Chel is displaced and the known complexes $[\text{Rh}(\text{CO})_2\text{X}_2]^-$ are formed. In the IR spectra the band at 1980 cm^{-1} disappears, and two new bands, whose frequencies decrease slightly from chloride to iodide, appear at about 2060 and 1990 cm^{-1} *. The reaction is reversible, as can be seen by sweeping the solutions with nitrogen, but becomes irreversible on addition of HClO_4 , owing to the protonation of the Bipy [16].

The observed reactions are shown in Eqn. 2.



Complexes (III) react also with the activated olefins AN, FUN, TCNE, and also with acetylene, to give the corresponding pentacoordinated adducts, some

* The complex $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ made by James and Ng's method [15a], shows two bands at the same frequencies in methyl cyanide. Furthermore addition of triphenylphosphine to the solution of our chloride derivative gives the known complex $\text{Rh}(\text{PPh}_3)_2\text{COCl}$ [15b] in high yield.

TABLE 1
CARBONYL STRETCHING FREQUENCIES^a

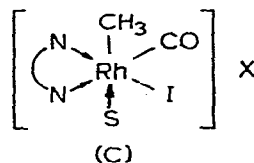
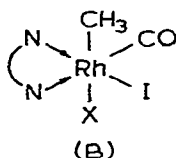
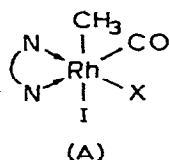
Compound	$\nu(\text{CO})$	Solvent	Compound	$\nu(\text{CO})$	Solvent
[RhBipy(CO) ₂]PF ₆	2012, 1976	(CH ₃ CN)	RhBipy(CO)FUNI	2057	(CH ₃ CN)
[RhBipy(CO) ₃]PF ₆	2101, 2040	(CH ₃ CN)	RhBipy(CO)ANI	2035	(CH ₃ CN)
RhPhen(CO)Cl	1989	(CHCl ₃)	RhBipy(CO)CH≡CHI	2026	(CH ₃ CN)
PhPhen(CO)Br	1989	(CHCl ₃)	RhBipy(CO)CH ₃ CH	2084	(CH ₃ CN)
RhPhen(CO)I	1990	(CHCl ₃)	RhBipy(CO)CH ₃ BI	2077	(CH ₃ CN)
RhBipy(CO)Cl	1977	(CH ₃ CN)	RhBipy(CO)CH ₃ I ₂	2068	(CH ₃ CN)
RhBipy(CO)Br	1976	(CH ₃ CN)			
RhBipy(CO)I	1974	(CH ₃ CN)	[Rh(CO) ₂ Cl ₂] ⁻	2066 1990	(CH ₃ CN)
RhBipy(CO)FUNCI	2066	(CH ₃ CN)	[Rh(CO) ₂ Br ₂] ⁻	2064 1989	(CH ₃ CN)
RhBipy(CO)FUNBr	2062	(CH ₃ CN)	[Rh(CO) ₂ I ₂] ⁻	2057 1986	(CH ₃ CN)

^a The frequencies are not appreciably different for the corresponding Phen derivatives.

of which were isolated. All these complexes show a single CO stretching, which moves towards higher frequencies on going from acetylene to AN and FUN, and from iodide to chloride (Table 1). With the FUN and AN adducts, reversible dissociation of the coordinated olefin occurs. Complexes (III) also react with cyclooctene and cyclohexene, but these reactions were not investigated in detail. Complexes (III) also react, but irreversibly, with molecular oxygen. The CO band disappears, and we cannot exclude the possibility that carbonato complexes [17] are formed.

Complexes (III) react with methyl iodide to give the corresponding organometallic derivatives $\text{RhChel}(\text{CO})\text{CH}_3(\text{X})\text{I}$. Their IR spectra in methyl cyanide show a band at about 2070 cm^{-1} , whose frequency changes on varying the halide in the same direction as with the tetra and pentacoordinated derivatives (Table 1). The intensity of the CO stretching bands decreases with time, with a rate increasing in the order $\text{Phen} > \text{Bipy}$ and $\text{Cl} > \text{Br} > \text{I}$. At the same time (Chel = Bipy and X = Br) a new band appears at about 1700 cm^{-1} , very probably due to an acyl group formed by methyl migration to the carbonyl group.

The NMR spectra of the complexes $\text{RhBipy}(\text{CO})\text{CH}_3(\text{X})\text{I}$ in deuterated DMF show resonances corresponding to a methyl group σ -bonded to rhodium, as indicated by the observation of $^1\text{H}-^{103}\text{Rh}$ coupling of the order of 2.0 Hz [18]. When X = I, there is a doublet centred at about $\tau\ 8.5$; when X = Br or Cl, two partially overlapped doublets of comparable intensity are present at about $\tau\ 8.45$ and 8.4 , respectively. In addition, all the compounds show a much smaller doublet at about $8\ \tau$, which after 48 h has significantly increased at the expense of the lowest one in the case of chloro and bromo derivatives. Tentatively, we assume for these products the structures (A), (B) + (C).



This is in agreement with the experimental evidence: (a), the presence of a single CO stretching frequency, (b), the migration of methyl to the carbonyl group; (c), the presence of two doublets, very near to each other, when $\text{X} \neq \text{I}$.

The higher field doublets are attributed to the structure (A), with the iodide *trans* to the methyl group, while the doublets at $8\ \tau$ are attributed to the dissociation of the halide in the *trans* position in structure (B), and consequent formation of species (C). Conductivity measurements confirm the formation of ionic complexes.

Conclusions

The reported results show that in general the behaviour of Bipy and Phen derivatives is similar, but Bipy, which can exist in a *trans*-conformation, dissociates more easily, and can thus be monodentate, sometimes assuming the function of a bridging ligand between two metal atoms. For example, while the

(continued on p. 126)

TABLE 2

ANALYTICAL DATA FOR THE ISOLATED COMPLEXES

Number	Complex	Colour	Analysis found (calcd.) (%)		
			C	H	N
(1)	[RhPhenCOD]PF ₆	Orange-red	44.8 (44.80)	3.8 (3.76)	5.2 (5.22)
(2)	[RhPhenCOD]B(Ph) ₄	Orange-red	74.3 (74.37)	5.5 (5.67)	4.2 (3.94)
(3)	RhPhenCODI	Orange-red	45.8 (45.36)	3.8 (3.89)	5.2 (5.40)
(4)	RhBipyCODI	Red	43.8 (43.75)	4.1 (4.08)	5.7 (5.67)
(5)	[RhBipyNBD]ClO ₄	Orange	44.6 (45.31)	3.4 (3.58)	6.2 (6.22)
(6)	[RhBipyNBD]PF ₆	Orange	40.3 (41.15)	3.0 (3.25)	5.7 (5.64)
(7)	[RhPhenNBD]ClO ₄	Orange	47.5 (48.09)	3.4 (3.39)	5.8 (5.90)
(8)	[RhPhenNBD]PF ₆	Orange	43.5 (43.87)	3.0 (3.10)	5.7 (5.38)
(9)	RhPhen(NBD)I	Red-violet	45.1 (45.45)	3.0 (3.21)	5.7 (5.58)
(10)	[RhBipy(CO) ₃]PF ₆	Yellow			
		(CH ₃ OH)			
		Green			
(11)	[RhPhen(CO) ₃]PF ₆	(CH ₃ CN)	32.4 (31.99)	1.8 (1.65)	6.0 (5.74)
		Violet black			
		(CH ₃ OH)			
		Red-brown			
		(CH ₃ CN)	34.9 (35.18)	1.8 (1.57)	5.9 (5.47)
(12)	[RhBipyFUN]ClO ₄	Yellow	38.2 (38.52)	2.6 (2.31)	13.7 (12.83)
(13)	[RhBipyFUN]PF ₆	Yellow	35.9 (34.88)	2.7 (2.09)	12.2 (11.62)
(14)	[RhPhenFUN]PF ₆	Yellow	38.0 (37.97)	2.4 (1.99)	11.2 (11.07)
(15)	[RhBipyTCNE]PF ₆	Yellow-orange	35.4 (36.11)	2.0 (1.50)	15.5 (15.80)
(16)	[RhPhenTCNE]PF ₆	Yellowgreen	39.0 (38.87)	2.0 (1.45)	15.3 (15.12)
(17)	[Rh(Bipy) ₂ AN]PF ₆	Orange	44.6 (45.04)	3.2 (3.12)	11.2 (11.42)
(18)	[Rh(Bipy) ₂ FUN]PF ₆	Yellow	45.1 (45.16)	2.8 (2.84)	13.4 (13.17)

	[Rh(Phen) ₂ FUN]F ₆	Yellow-green	49.5	(48.93)	2.0	(2.04)	15.9	(15.22)
(20)	[Rh(Phen) ₂ FUN]F ₆	Yellow-green	49.5	(48.93)	2.2	(2.19)	7.8	(7.93)
(21)	[Rh(Phen) ₂ TCNE]PF ₆	Yellow	47.3	(47.62)	2.8	(2.57)	8.4	(8.68)
(22)	[Rh(Phen) ₂ MA]PF ₆	Black	40.0	(40.97)	2.5	(2.50)	7.5	(7.63)
(23)	RhBipy(CO)Cl	Black	35.7	(36.00)	2.2	(2.19)	8.2	(8.07)
(24)	RhBipy(CO)Br	Red-violet	44.6	(45.06)	2.4	(2.32)	7.0	(7.16)
(25)	RhPhen(CO)Cl	Red-violet	40.0	(39.93)	2.15	(2.06)	6.4	(6.39)
(26)	RhPhen(CO)Br	Black	35.7	(35.65)	1.90	(1.84)	8.3	(7.99)
(27)	RhPhen(CO)I	Light yellow	40.7	(41.11)	2.5	(2.30)	7.4	(7.10)
(28)	RhBipy(CO) ₂ Cl	Yellow	36.1	(36.49)	2.0	(2.04)	6.4	(6.39)
(29)	RhBipy(CO) ₂ Br	Deep Yellow	31.9	(32.91)	1.9	(1.84)	13.2	(12.60)
(30)	RhBipy(CO) ₂ I	Yellow	41.3	(40.48)	2.4	(2.26)	6.2	(6.04)
(31)	RhBipy(CO)FUNBr	Red	38.3	(38.82)	2.1	(2.17)	5.9	(6.03)
(32)	RhPhen(CO)(CH≡CH)I	Yellow	29.6	(31.03)	2.1	(2.38)	5.5	(5.50)
(33)	RhBipy(CO)CH ₃ Cl	Yellow	27.9	(28.33)	2.1	(2.18)	5.0	(5.04)
(34)	RhBipy(CO)CH ₃ Br	Yellow	25.7	(25.93)	1.9	(1.95)	5.3	(4.83)
(35)	RhBipy(CO)CH ₃ I	Yellow-orange	29.3	(28.99)	2.0	(1.91)		
(36)	RhPhen(CO)CH ₃ I ₂	Yellow						

reaction between Bipy and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ in methyl cyanide gives the complex RhBipyCOCl , the reaction between Bipy and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ in benzene affords the binuclear species $[\text{Rh}(\text{CO})_2\text{Cl}]_2\text{Bipy}$ [14].

From the data shown in Table 1, it can be seen that, as expected, the CO stretching frequencies are shifted towards higher values and are more and more dependent on the nature of the ligand on going from tetra- to penta- to hexacoordinated structures. Furthermore a comparison between *trans*- $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{X}$ [19] and $\text{Rh}(\text{Chel})(\text{CO})\text{X}$ shows that the $\nu(\text{CO})$ frequencies move in the opposite direction, but are slightly influenced either by the nature or the position of the halide, while the differences in $\nu(\text{CO})$ in $\text{RhChel}(\text{CO})\text{Cl}$ and $\text{RhDPE}(\text{CO})\text{Cl}$ are in agreement with the larger *trans*-influence of phosphorus in comparison with nitrogen.

Coordinative and oxidative addition reactions occur less easily for the $[\text{Rh}^{\text{I}}(\text{Chel})\text{L}_2]^+$ than for the corresponding iridium(I) complexes [20], and are favoured as L_2 changes from COD to CO, i.e. with the increasing σ -donor and decreasing π -acceptor power of the ligand. For example, carbon monoxide gives a very unstable $[\text{Rh}(\text{Chel})(\text{COD})\text{CO}]^+$ adduct and reacts reversibly with $[\text{RhBipy}(\text{CO})_2]^+$, while the $[\text{Ir}(\text{Chel})\text{COD}]^+$ complex takes up carbon monoxide reversibly and $[\text{Ir}(\text{Chel})(\text{CO})_2]^+$ does so irreversibly [20]. Furthermore the $[\text{Ir}(\text{Chel})(\text{CO})_2]^+$ complex, but not the corresponding rhodium derivative, reacts with molecular hydrogen. As for the exchange reactions with unsaturated substrates, the rhodium(I) complexes react more easily than the corresponding iridium(I) derivatives. This may be due to the fact that in penta-coordinated complexes the Ir-olefin and Ir-CO bonds are more stable than those in the rhodium compounds: (e.g. $[\text{Rh}(\text{Chel})(\text{CO})_3]^+$, $\nu(\text{CO})$ 2101 - 2040 cm^{-1} ; $[\text{Ir}(\text{Chel})(\text{CO})_3]^+$, $\nu(\text{CO})$ 2089 - 2023 cm^{-1}). Because of the higher instability of the rhodium(I) pentacoordinated adducts, formation of the bond between the metal and the entering ligand should occur at the expense of weakening the preexisting bond, as shown by the fact that in this type of complexes, the entering ligands usually displace the coordinated ligands of similar nature [13].

In general, the rhodium(I) complexes with Bipy or Phen undergo coordinative addition reactions more easily than analogous complexes containing other bidentate chelating systems. Thus, whereas the $[\text{Rh}(\text{Chel})(\text{CO})_2]^+$ derivatives take up carbon monoxide reversibly, the complexes $\text{Rh}(\text{Acac})(\text{CO})_2$ [21] and $\text{Rh}(\text{Sal}=\text{NR})(\text{CO})_2$ [22] do not react. The behaviour of $\text{Rh}(\text{DPE})\text{COCl}$ or $\text{Rh}(\text{TDPME})\text{COCl}$ [17] in this respect, is likewise in contrast with that of $\text{Rh}(\text{Chel})\text{COCl}$.

The difference in behaviour between Chel and DPE is explained in terms of the stronger π -acceptor capacity of DPE, as observed in complexes $\text{M}(\text{CO})_4\text{L}_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [1], while in the case of Acac and $\text{Sal}=\text{NR}$ it can be related either to the higher electronegativity of oxygen in comparison with nitrogen or to the degree of π -bonding, which is larger in hexa-atomic than in penta-atomic chelate rings.

Experimental

Unless otherwise specified, preparations were performed at room tempera-

ture under nitrogen, using deaerated solvents. Analytical data are collected in Table 2.

[Rh(Phen)COD]PF₆ (1)

Phen (0.59 g; 3 mmoles) were added to a suspension of 0.49 g (1 mmole) of [Rh(COD)CL]₂ in methanol (50 ml). After 15 min the red solution was filtered and treated dropwise with concentrated aqueous solution of NH₄PF₆. Recrystallization was from hot methanol.

[Rh(Phen)COD]B(Ph)₄ (2)

(2) was prepared as above, using B(Ph)₄⁻ as precipitating agent, and recrystallization from acetone/water.

Rh(Phen)(L-L)I L-L = COD (3) or NBD (9)

Solid NaI (0.1 g) was added to 1 mmole of (1) or (8) dissolved in methyl cyanide (25 ml). The crystalline compounds were filtered off and thoroughly washed with water. (3) gives a violet solution in dichloromethane.

Rh(Bipy)(COD)I (4)

(4) was obtained from [Rh(Bipy)COD]PF₆ [13], by the above procedure.

[Rh(Chel)NBD]X Chel = Bipy, Phen, X⁻ = ClO₄⁻, PF₆⁻ (5) - (8)

[Rh(Chel)(CO)₃]X (1 mmole) suspended in methanol was treated with an excess of NBD (2 ml), and the mixture was kept for 1 h with nitrogen bubbling through. The crystals were filtered off and thoroughly washed with ether.

[Rh(Bipy)(CO)₃]PF₆ (10)

(a). [Rh(Bipy)COD]PF₆ [13] (0.51 g; 1 mmole) were suspended in methanol (25 ml). The vessel was evacuated and refilled with carbon monoxide. The starting product disappeared slowly, and a new microcrystalline solid was formed; this was separated and washed repeatedly with methanol.

(b). [Rh(Bipy)COD]PF₆ (0.51 g; 1 mmole) were dissolved in methyl cyanide (20 ml). The vessel was evacuated and refilled with carbon monoxide. After 15 min the product was precipitated by addition of ether (10 ml), filtered off, and washed with methanol.

[Rh(Phen)(CO)₃]PF₆ (11)

Passage of carbon monoxide through a suspension of 0.53 g (1 mmole) of (1) in methyl cyanide (30 ml) gave a red-brown solution. The crystalline compound, precipitated by ether addition, was filtered off and washed with ether.

[Rh(Chel)FUN]X Chel = Bipy X⁻ = ClO₄⁻ (12), PF₆⁻ (13), Chel = Phen X⁻ = PF₆⁻ (14)

FUN (0.16 g; 2 mmoles) were added to 1 mmole of the corresponding [Rh(Chel)(CO)₃]⁺ complexes, suspended in methyl cyanide (40 ml). The vessel was evacuated and the mixture set aside overnight. The products were precipitated by ether from the yellow solutions, then separated and washed with ether.

[Rh(Chel)TCNE]PF₆ Chel = Bipy (15), Phen (16)

TCNE (0.2 g; 1.5 mmoles) were added to 1 mmole of (10) or (11), suspended in methyl cyanide (40 ml). After a few minutes a yellow-orange solution was obtained, from which the complexes were precipitated by ether addition.

[Rh(Chel)₂L]PF₆ Chel = Bipy, Phen; L = AN (17)(19), FUN (18)(20) TCNE (21), MA (22)

0.5 Mmoles of (10) or (11), suspended in methanol (30 ml) were treated with a slight excess of Chel. After 10 min, 0.1 g L were added and allowed to react for 3 h. The solids were filtered off and washed with methanol.

Rh(Chel)COX Chel = Bipy, Phen; X⁻ = Cl⁻ (23) (25), Br⁻ (24) (26), I⁻ (27)

0.5 Mmoles of (10) or (11) were dissolved in methyl cyanide (100 ml) or acetone (70 ml). The solution was saturated with LiX and nitrogen was bubbled through for 3 h. The moist compounds are air sensitive.

[Rh(Bipy)(CO)₂X] X⁻ = Cl⁻ (28), Br⁻ (29), I⁻ (30)

(10) (0.48 g; 1 mmole) was dissolved in methyl cyanide (20 ml) and carbon monoxide was bubbled through the solution. Saturation with LiX precipitated the corresponding complexes, which were isolated and washed with water and ether.

The same products can be also prepared by treating RhChel(CO)X with carbon monoxide in methyl cyanide.

Rh(Bipy)CO(FUN)Br (31)

FUN (0.16 g; 2 mmoles) were added to 0.41 g (1 mmole) of (29) suspended in methyl cyanide (30 ml). The vessel was then evacuated to remove the evolved carbon monoxide. After 12 h the new solid was filtered off and washed with ether. Recrystallization was from acetone in the presence of FUN.

Rh(Phen)COCH≡CHI (32)

(27) (0.22 g; 0.5 mmoles) were suspended in methyl cyanide (40 ml) and the solution was saturated with acetylene. When the starting material had disappeared, the new solid formed was filtered off and dried in vacuo.

Rh(Chel)COCH₃XI Chel = Bipy, X⁻ = Cl⁻ (33), Br⁻ (34), I⁻ (35) Chel = Phen, X⁻ = I⁻ (36)

1 Mmole of (10) or (11) was dissolved in methyl cyanide (40 ml) and saturated with LiX, and nitrogen was bubbled through for 0.5 h. The solution then turned slowly to yellow when 2 ml of methyl iodide was added. The iodo compounds precipitated spontaneously; water addition and evaporation to a small volume under reduced pressure were necessary to give crystals of the chloro and bromo complexes. The compounds were washed with water and ether. Conductivity in DMF* of 0.001 M solutions: Rh(Bipy)COCH₃ClI after 0.5 h $\Lambda = 18.2 \text{ mho}\cdot\text{mol}^{-1}\cdot\text{cm}^2$, after 48 h $\Lambda = 42.7 \text{ mho}\cdot\text{mol}^{-1}\cdot\text{cm}^2$; Rh(Bipy)COCH₃BrI after 0.5 h $\Lambda = 15.9 \text{ mho}\cdot\text{mol}^{-1}\cdot\text{cm}^2$, after 48 h $\Lambda = 37.7 \text{ mho}\cdot\text{mol}^{-1}\cdot\text{cm}^2$.

* Typical conductivity for 1/1 electrolytes is 60–80 mho·mol⁻¹·cm² [23].

Techniques

IR spectra were recorded with a Perkin - Elmer 225 spectrophotometer, electronic spectra with a Perkin - Elmer 356 spectrophotometer and NMR spectra at 60 MHz with a Jeol JNM-C-60 HL spectrometer.

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References

- 1 W.R. McWhinnie and J.D. Miller, in H.J. Emeleus and A.G. Sharpe (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 12, Academic Press, New York, 1969, p. 135.
- 2 A. Camus, C. Cocevar and G. Mestroni, *J. Organometal. Chem.*, 39 (1972) 355.
- 3 R.E. Dessy, J.C. Charkoudian and A.L. Rheingold, *J. Amer. Chem. Soc.*, 94 (1972) 738.
- 4 Y. Saito, J. Takemoto, B. Hutchinson and K. Nakamoto, *Inorg. Chem.*, 11 (1972) 2003.
- 5 K.H. Thiele and J. Müller, *Z. Chem.*, 4 (1964) 273.
- 6 M. Tsutsui, *Z. Chem.*, 2 (1962) 214.
- 7 R.P.A. Sneeden and H.H. Zeiss, *J. Organometal. Chem.*, 47 (1973) 125.
- 8 A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida and A. Misono, *J. Amer. Chem. Soc.*, 87 (1965) 4652.
- 9 B. Wozniak, I.D. Ruddick and G. Wilkinson, *J. Chem. Soc. A*, (1971) 3116.
- 10 G. Calvin and G.E. Coates, *J. Chem. Soc.*, (1960) 2008.
- 11 G. Reddy and L. Susheeleemma, *Chem. Commun.*, (1970) 54; J.V. Kingston and G.R. Scollary, *Chem. Commun.*, (1970) 670; B.C. Hui and B.R. James, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 367.
- 12 Ts. Ito, S. Hasegawa, Y. Takahashi and Y. Ishii, *J. Chem. Soc., Chem. Commun.*, (1972) 629.
- 13 C. Cocevar, G. Mestroni and A. Camus, *J. Organometal. Chem.*, 35 (1972) 389.
- 14 D.N. Lawson and G. Wilkinson, *J. Chem. Soc.*, (1965) 1900.
- 15 (a) B.R. James and F.T.T. Ng, *Chem. Commun.*, (1970) 908;
(b) B.R. James and G.L. Rempel, *Chem. Commun.*, (1967) 158.
- 16 Yu.S. Varshavskii, N.V. Kiseleva and N.A. Buzina, *Russ. J. Inorg. Chem.*, 16 (1971) 862.
- 17 W.O. Siegl, S.J. Lapporte and J.P. Collman, *Inorg. Chem.*, 10 (1971) 2158.
- 18 P.R. Branson and M. Green, *J. Chem. Soc., Dalton Trans.*, (1972) 1303.
- 19 L. Vaska and J. Peone Jr., *Chem. Commun.*, (1971) 418.
- 20 G. Mestroni and A. Camus, *Inorg. Nucl. Chem. Lett.*, 9 (1973) 261.
- 21 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, (1964) 3156.
- 22 R.J. Cozens, K.S. Murray and B.O. West, *J. Organometal. Chem.*, 27 (1971) 399.
- 23 J.E. Fergusson and J.H. Hickford, *Austr. J. Chem.*, 23 (1970) 453.