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RHODIUM CARBONYL COMPLEXES WITH TROPOLONES, SALICYLALDEHYDE AND SALICYLALDIMINE SCHIFF BASES

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Summary

The preparation and properties of rhodium complexes of the general formulae $Rh(A)(CO)_2$ and $Rh(A)(CO)L$ (A = tropolone (trop), Me-trop, i-Pr-trop, salicylaldehyde (sal)) are described. The coordinated salicylaldehyde moiety of $[Rh(sal)Y_2]$ (Y_2 = COD, $(CO)_2$, $(CO)PPh_3$) complexes react with primary amines to yield $Rh(sal{=}NR)Y_2$ derivatives. $Rh(sal{=}NMe)(CO)_2$ can be formed by addition of salicylaldehyde to the solution obtained by refluxing $RhCl_3 \cdot xH_2O$ with dimethylformamide.

Introduction

Rhodium(I) complexes with salicylaldehyde, tropolone and related ligands have been little studied [1,2]. In this paper we describe some methods of synthesis of $Rh(A)(CO)_2$ and $Rh(A)(CO)L$ complexes and some related complexes of Schiff bases. Several groups [3—5] have reported rhodium(I) complexes of salicylaldimine Schiff bases, but they mainly used other synthetic methods.

We used as ligands the anionic forms of tropolone (trop), β-methyltropolone (Me-trop), β-isopropyltropolone (i-Pr-trop), salicylaldehyde (sal), salicylaldimines (sal=NMe, sal=NPh), *N,N'*-ethylenebis(salicylaldimine)(salen) and *N,N'*-*p*-phenylenebis(salicylaldimine)(salpphen).

Results and discussion

Tropolone complexes

Complexes of the general formulae $Rh(A)(CO)_2$ (where A = trop, Me-trop,

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i-Pr-trop) were prepared by three methods: (i) Bubbling of carbon monoxide at ordinary pressure through suspensions or solutions of complexes of the type Rh(A)(diolefin) [1] resulted in displacement of the diolefin and formation of the corresponding dicarbonyl derivative (eq. 1).

$$\mathrm{Rh(A)(diolefin)} + 2\,\mathrm{CO} \rightarrow \mathrm{Rh(A)(CO)_2} + \mathrm{diolefin} \qquad (1)$$

(ii) The reaction of $[RhCl(CO)_2]_2$ with TlA gave $Rh(A)(CO)_2$ (eq. 2):

$$1/2[\mathrm{RhCl(CO)_2}]_2 + \mathrm{TlA} \rightarrow \mathrm{Rh(A)(CO)_2} + \mathrm{TlCl} \qquad (2)$$

(iii) In a more direct route, tropolone or its derivatives were added to the solution [6] obtained by refluxing $RhCl_3 \cdot xH_2O$ in dimethylformamide (DMF) (eq. 3).

$$\mathrm{RhCl_3} \cdot x\mathrm{H_2O} \xrightarrow{\mathrm{DMF}} \begin{array}{c}\text{“carbonylated}\\ \text{intermediate”}\end{array} \xrightarrow{\mathrm{HA}} \mathrm{Rh(A)(CO)_2} \qquad (3)$$

The complexes were isolated as stable orange-yellow microcrystalline solids, non-conducting in acetone. Elemental analyses, yields and IR data are listed in Table 1. The ^1H NMR spectra confirm the proposed formulation, showing resonances at 7.2—7.7 ppm (H-ring), along with those of the substituents (Me, 2.5 ppm; i-Pr, 1.3 ppm and 2.9 ppm, $J(CH_3—CH)$ 7 Hz). The complexes show $\nu(CO)$ absorptions in their solution IR spectra as expected for *cis*-dicarbonyl derivatives, but the solids show complex absorptions probably due to rhodium—rhodium interactions [7,8].

We studied in most detail the reactions of $Rh(trop)(CO)_2$. Triarylphosphines or triphenylarsine react with this complex to displace one CO ligand according to eq. 4.

$$\mathrm{Rh(trop)(CO)_2} + \mathrm{L} \rightarrow \mathrm{Rh(trop)(CO)L} + \mathrm{CO} \qquad (4)$$

($L = AsPh_3$, PPh_3, $P(p\text{-}ClC_6H_4)_3$, $P(p\text{-}MeC_6H_4)_3$ and $P(p\text{-}MeOC_6H_4)_3$); the crystal structure of $Rh(trop)(CO)PPh_3$ was reported recently [2].

Those complexes can also be prepared from the solution obtained by refluxing $RhCl_3 \cdot xH_2O$ with dimethylformamide [6] (eq. 5).

$$\mathrm{RhCl_3} \cdot x\mathrm{H_2O} \xrightarrow{\mathrm{DMF}} \begin{array}{c}\text{“carbonylated}\\ \text{intermediate”}\end{array} \xrightarrow[\mathrm{PR_3}]{\mathrm{Htrop}} \mathrm{Rh(trop)(CO)PR_3} \qquad (5)$$

The complexes obtained by both methods are yellow air-stable solids at room temperature. Table 1 lists the analytical data for these complexes, whose IR spectra show a single band due to the $\nu(CO)$ vibration in the 1960—1975 cm^{-1} region, along with the characteristic bands of the tropolonate ligands [1].

$Rh(trop)(CO)_2$ reacted with diphos, bipy or phen to yield poorly characterized products which still contain some coordinated carbon monoxide. On the other hand, when it was refluxed in acetone in the presence of an excess of diolefin, the formation of Rh(trop)(diolefin) was observed. Thus, the reaction is reversible (eq. 6).

$$\mathrm{Rh(trop)(CO)_2} + \mathrm{diolefin} \rightleftharpoons \mathrm{Rh(trop)(diolefin)} + 2\,\mathrm{CO} \qquad (6)$$

Some preliminary experiments show that in the presence of KOH Rh(trop)-

TABLE 1

ANALYTICAL AND IR DATA FOR CARBONYL RHODIUM COMPLEXES WITH TROPOLONES OR SALICYLALDEHYDE

Complex	Found (calcd.) (%)		Colour	Yield (%)	IR spectra (cm^{-1})	
	C	H			CH_2Cl_2 solution	Nujol mulls
Rh(trop)$(CO)_2$	38.55 (38.50)	1.82 (1.79)	orange-red	76 [a]	2080s, 2010s	2070s, 2010s, 1950s
Rh(Me-trop)$(CO)_2$	40.90 (40.85)	2.50 (2.40)	orange	80 [a]	2080s, 2010s	2070s, 2000s, 1950w
Rh(i-Pr-trop)$(CO)_2$	45.76 (44.77)	3.36 (3.35)	orange-red	88 [a]	2080s, 2010s	2070s, 2000s, 1985s, 1970w, 1960w
Rh(trop)(CO)$AsPh_3$	55.94 (55.94)	4.20 (3.61)	yellow	72	1960s	1960s
Rh(trop)(CO)PPh_3	60.62 (60.71)	4.00 (3.90)	yellow	85	1970s	1970s
Rh(trop)(CO)P(*p*-$ClC_6H_4)_4$	50.50 (50.58)	2.80 (3.00)	yellow	83	1975s	1970s
Rh(trop)(CO)P(*p*-$MeC_6H_4)_3$	62.14 (62.53)	4.75 (4.70)	yellow	41	1970s	1965s
Rh(trop)(CO)P(*p*-$MeOC_6H_4)_3$	58.00 (57.55)	4.34 (4.33)	yellow	39	1975s	1965s
Rh(sal)(CO)PPh_3	60.82 (60.72)	4.20 (3.92)	yellow	49	1975s	1980s(br)

[a] DMF method.

$(CO)_2$ and the systems $Rh(trop)(CO)_2 + L$ (L = PR_3, diphos, phen) catalyze hydrogen transfer from isopropanol to acetophenone.

Salicylaldehyde complexes

Bubbling of carbon monoxide at normal pressure through an anhydrous toluene solution of Rh(sal)(COD) causes a decrease in the yellow colour of the solution. The IR spectrum of the solution shows two bands, at 2025 and 2095 cm^{-1}, characteristic of a *cis*-dicarbonyl derivative. These observations suggest the occurrence of the reaction indicated in eq. 7.

$$Rh(sal)(COD) + 2\ CO \rightarrow Rh(sal)(CO)_2 + COD \qquad (7)$$

However, when the carbonylation was performed with solvents which had not been dried, formation of $Rh_6(CO)_{16}$ and salicylaldehyde was observed (eq. 8).

$$6\ Rh(sal)(COD) + 19\ CO + 3\ H_2O \xrightarrow{Me_2CO} Rh_6(CO)_{16} + 3\ CO_2 + 6\ COD + 6\ Hsal \qquad (8)$$

An analogous reaction was previously observed by Chini et al. [9] with $[RhCl(CO)_2]_2$.

On the other hand, the reaction of $[RhCl(CO)_2]_2$ with Tlsal appears to give $Rh(sal)(CO)_2$ species (observed in solution by IR spectra) along with some rhodium metal. The addition of an equimolecular amount of PPh_3 to a solution of $Rh(sal)(CO)_2$ gives $Rh(sal)(CO)PPh_3$. An alternative route is provided by the following reaction:

$$\tfrac{1}{2}[RhCl(CO)PPh_3]_2 + Tlsal \rightarrow Rh(sal)(CO)PPh_3 + TlCl \qquad (9)$$

Salicylaldimine-Schiff-base complexes

An unexpected reaction was observed when salicylaldehyde was added to the solution obtained by refluxing $RhCl_3 \cdot xH_2O$ in dimethylformamide. The complex precipitated by addition of water was $Rh(sal{=}NMe)(CO)_2$, which was characterized by elemental analyses, IR and ^1H NMR spectra (4.0 ppm (NMe); 6.0—7.0 ppm (H-ring); 7.4 ppm (H-ald), $(CD_3)_2CO$). The formation of this product suggests that carbonylation of $RhCl_3 \cdot xH_2O$ in dimethylformamide involves formation of amines, and some methylamine reacts with the salicylaldehyde group, to form the corresponding Schiff base. $Rh(sal{=}NMe)(CO)_2$ exhibits green-blue dichroism, and the solid has a complex IR spectra probably because of metal—metal interactions.

As expected [10], the addition of Schiff-base ligands to the solution obtained by refluxing $RhCl_3 \cdot xH_2O$ in dimethylformamide, leads to formation of $Rh(sal{=}NMe)(CO)_2$, $Rh(sal{=}NPh)(CO)_2$ [5], $Rh_2(salen)(CO)_4$ * [5] and $Rh_2(salphen)(CO)_4$, but the yield of the binuclear derivatives is rather low (<25%). The new

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* This product was contaminated with about 5% of $Rh(sal{=}NMe)(CO)_2$, implying cleavage of the salen ligand.

TABLE 2

ANALYTICAL AND IR DATA FOR CARBONYL RHODIUM COMPLEXES WITH SALICYLALDIMINE SCHIFF-BASES

Complex	Found (calcd.) (%)			Colour	Yield (%)	IR spectra	
	C	H	N			CH_2Cl_2 solution	Nujol mull
Rh(sal=NMe)$(CO)_2$	41.03 (40.98)	2.72 (2.75)	4.74 (4.78)	green-blue	23 [a]	2080s, 2010s	2080s, 2050m, 2010s, 1970w
Rh(sal=NPh)$(CO)_2$	50.73 (51.47)	2.84 (2.85)	3.94 (4.06)	orange-red	58 [a]	2080s, 2010s	2080s, 2055m, 2030s, 2005w, 1990w
Rh(sal=NMe)(CO)PPh_3	60.80 (61.49)	4.25 (4.40)	2.64 (2.66)	yellow	57	1960s	1960s(br)
Rh(sal=NPh)(CO)PPh_3	64.84 (65.20)	4.48 (4.28)	2.39 (2.38)	yellow	71	1965s	1970s, 1960s
Rh_2salen$(CO)_4$	41.84 (41.13)	2.51 (2.42)	4.99 (4.80)	yellow	22 [a]	—	2070s, 2050(sh), 1985s, 1965m, 1955m
Rh_2salphen$(CO)_4$	45.17 (45.60)	2.37 (2.23)	4.49 (4.43)	red	61 [b]	—	2090s, 2060m, 2010s, 1990m, 1960w
Rh_2salphen$(COD)_2$	58.01 (58.74)	5.28 (5.20)	3.97 (3.81)	yellow	83 [b]	—	—

[a] DMF method. [b] Prepared from $[RhClY_2]_2$.

complexes Rh_2(salphen)$(CO)_4$ and Rh_2(salphen)$(COD)_2$ can be prepared in high yield by treating $[RhCl(CO)_2]_2$ or $[RhCl(COD)]_2$ with salphen in the presence of triethylamine.

Rhodium(I) salicylaldimine-Schiff-base complexes can be prepared by reaction of the coordinated salicylaldehyde moiety with primary amines (eq. 10).

$$\mathrm{Rh(sal)Y_2 + RNH_2 \rightarrow Rh(sal{=}NR)Y_2 + H_2O} \qquad (10)$$

$(Y_2 = \mathrm{COD}, (\mathrm{CO})_2, (\mathrm{CO})\mathrm{PPh_3}; R = \mathrm{Me, Ph})$

This method was also used for the preparation of the homologous binuclear complexes with salen and salphen.

Other related reactions observed for these complexes are indicated in eqs. 11 and 12.

$$\mathrm{Rh(sal{=}NPh)(COD) \xrightarrow{CO} Rh(sal{=}NPh)(CO)_2 \xrightarrow{PPh_3} Rh(sal{=}NPh)(CO)PPh_3} \qquad (11)$$

$$\mathrm{Rh_2salen(COD)_2 \xrightarrow{CO} Rh_2salen(CO)_4 \xrightarrow{PPh_3} Rh_2salen(CO)_2(PPh_3)_2} \qquad (12)$$

All the salicylaldimine-Schiff-base complexes (Table 2) are stable in air at room temperature. Their IR spectra show absorptions characteristic of the chelate-Schiff-base compounds in the range 1700—1200 cm^{-1}. In particular, the new complexes $Rh(sal{=}NR)(CO)PPh_3$ (R = Me, Ph) in dichloromethane show a strong band ν(CO) at 1960—1965 cm^{-1}. In the solid state, this band is broad in the case of the sal=NMe complex and split in the case of the sal=NPh complex, probably due to lattice effects in the solid.

Experimental

The C, H and N analyses were made with a Perkin—Elmer 240 microanalyzer, the IR spectra were recorded on a Perkin—Elmer 567 spectrophotometer (over the range 4000—200 cm^{-1}) using Nujoll mulls between KBr discs, polyethylene sheets, or dichloromethane solutions. The ^1H NMR spectra were recorded on a Varian XL-100 instrument.

β-Methyltropolone and the Schiff bases were prepared by published procedures [4,11,12].

Preparation of complexes of the type Rh(A)(CO)₂ (A = trop, Me-trop, i-Pr-trop)

The compounds were prepared by the three general routes described below.

(i) Carbon monoxide was bubbled through a solution of the complex Rh(A)-(COD) in dichloromethane at room temperature for 15 min. The resulting solution was evaporated and the complex was precipitated by adding n-pentane or petroleum ether.

(ii) A mixture of $[RhCl(CO)_2]_2$ and the stoichiometric amount of TlA (except A = β-methyltropolone) was refluxed with methanol with stirring for 1 h. The formed TlCl was filtered off through kieselguhr and the filtrate was evaporated to dryness. The solid obtained was recrystallized from CH_2Cl_2/petroleum ether. The complex $Rh(trop)(CO)_2$ was purified by sublimation (60—80°C, 0.1 mmHg).

(iii) A solution of $RhCl_3 \cdot xH_2O$ in dimethylformamide was refluxed with stirring for approximately 30 min. The resulting yellow solution was treated with a slight excess of the ligand HA and the mixture was stirred for 15 min. Addition of distilled water precipitated the complex which was washed with water, dried in vacuo and crystallized from CH_2Cl_2/petroleum ether.

Preparation of complexes of the type Rh(trop)(CO)L (L = $AsPh_3$, PPh_3, $P(p\text{-}ClC_6H_4)_3$, $P(p\text{-}MeC_6H_4)_3$ and $P(p\text{-}MeOC_6H_4)_3$)

The addition of a stoichiometric amount of phosphine to a solution of $Rh(trop)(CO)_2$ in dichloromethane caused rapid evolution of carbon monoxide. The solution was stirred at room temperature for 1 h and evaporated to ca. 3—4 ml, and crystallization was induced by the addition of petroleum ether. The crystals thus obtained were recrystallized from CH_2Cl_2/petroleum ether.

When L = $AsPh_3$ the dichloromethane solution was stirred under reflux for 1 h, using an excess of $AsPh_3$ (L/Rh 2/1) .

Preparation of $Rh(sal)(CO)PPh_3$

A slurry of 85.73 mg (0.1 mmol) of $[RhCl(CO)PPh_3]_2$ and 66.50 mg (0.2 mmol) of Tlsal in acetone was stirred for 1 h, at room temperature. The TlCl was removed by filtration through kieselguhr and the yellow solution obtained was evaporated to dryness. The residue was crystallized from CH_2Cl_2/pentane.

Preparation of $Rh(sal{=}NMe)(CO)_2$

(i) A dimethylformamide solution of $RhCl_3 \cdot xH_2O$ was refluxed for 30 min. The yellow solution was cooled to room temperature, and a slight excess of salicylaldehyde was added. The mixture was stirred for 60 min, then distilled water was added to precipitate a green-blue solid, This was filtered off, washed with water, dried in vacuo, and recrystallized from CH_2Cl_2/pentane.

(ii) Carbon monoxide was bubbled through a solution of Rh(sal)(COD) in acetone or methanol, which had been previously saturated with gaseous methylamine or treated with $MeNH_2 \cdot HCl/Et_3N$. The yellow solution was treated with water, and the complex which separated was recrystallized from methanol/water.

Similar procedures were used in the preparation of the complexes $Rh(sal{=}NPh)(CO)_2$ and $Rh_2salen(CO)_4$. The precipitated $Rh_2(salen)(CO)_4$ complex was contaminated with ca. 5% of $Rh(sal{=}NMe)(CO)_2$, which could be eliminated by washing with Et_2O.

Preparation of complexes of the type $Rh(sal{=}NR)(CO)PPh_3$ (R = Me, Ph)

(i) To a solution of $Rh(sal{=}NR)(CO)_2$ in dichloromethane was added a stoichiometric amount of triphenylphosphine. The yellow solution was stirred at room temperature for 30 min, then evaporated to small volume. The monocarbonylated complexes were precipitated by adding n-pentane.

(ii) A solution of $Rh(sal)(CO)PPh_3$ in methanol solution was treated with an excess of methylamine at room temperature or aniline at reflux temperature. Careful addition of distilled water caused precipitation of a yellow solid, which was recrystallized from CH_2Cl_2/Et_2O.

The above methods were also used for preparation of the complex $Rh_2salen(CO)_2(PPh_3)_2$.

Preparation of Rh_2*salphen(CO)*$_4$ *and* Rh_2*salphen(COD)*$_2$

(i) A slight excess of the ligand salphen was added to the solution obtained by refluxing $RhCl_3 \cdot xH_2O$ in dimethylformamide. Addition of distilled water gave a red solid in low yield (12%).

(ii) A solution of $[RhCl(CO)_2]_2$ in methanol was treated with the stoichiometric amount of salphen in the presence of a slight excess of triethylamine. An insoluble red solid was obtained.

The related complex Rh_2salphen$(COD)_2$ was prepared by use of $[RhCl(COD)]_2$ as starting material.

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References

1 M. Valderrama, H. Rafart and L.A. Oro, Transition Met. Chem., in press.
2 J.G. Leipoldt, L.D. Bock, S.S. Basson and H. Meyer, Inorg. Chim. Acta, 42 (1980) 105.
3 J.T. Mague and M.O. Nutt, J. Organometal. Chem., 166 (1979) 63.
4 N. Platzer, N. Goasdone and R. Bonnaire, J. Organometal. Chem., 160 (1978) 455.
5 R.J. Cozens, K.S. Murray and B.O. West, J. Organometal. Chem., 27 (1971) 399.
6 (a) A. Rusina and A.A. Vlcek, Nature, 206 (1965) 295; (b) Yu.S. Varshavskii and T.G. Cherkasova, Russ. J. Inorg. Chem., 12 (1967) 1709.
7 R. Ugo, G. La Monica, S. Cenini and F. Bonati, J. Organometal. Chem., 11 (1968) 159.
8 P.W. DeHaven and V.L. Goedken, Inorg. Chem., 18 (1979) 827.
9 P. Chini and S. Mantinengo, Inorg. Chim. Acta, 3 (1969) 315.
10 Yu.S. Varshavskii, T.G. Cherkasova, O.A. Osipov, N.P. Bednyagina, A.D. Garnovskii, R.I. Oglobina, G.K. Mitina and G.N. Liponova, Russ. J. Inorg. Chem., 17 (1972) 726.
11 R.D. Haworth and J.D. Hobson, J. Chem. Soc., (1951) 561.
12 E. Hasty, L.J. Wilson and D.N. Hendrickson, Inorg. Chem., 17 (1978) 1834.