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Studies on the reactivity of rhodium(I) dimers with salen as the bridging ligand

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Abstract

Reaction of $[\{Rh(CO)_2\}_2salen]$ (I) with an equimolar amount of MeI or I_2 gives green, weakly paramagnetic, little characterized materials. Use of an excess of the MeI or I_2 reagent leads to decomposition. Reactions of $[\{Rh(CO)L\}_2salen]$ (II) ($L = PPh_3$), with one molar proportion of MeI, I_2, $HgCl_2$, or two molar proportions of AgacO, occurs at one metal centre only, yielding Rh^{III}–Rh^{I} dimers. The Rh^{III}–Rh^{III} dimers can be obtained by use of an excess of reagent and longer reaction times. The ^{31}P NMR spectra give no indication of any metal–metal interaction in the derivatives of II.

Introduction

In addition to giving well-known mononuclear complexes, the quadridentate ligands salen (Fig. 1 (a)) and saloph (Fig. 1 (b)) can act as bridging groups, since they can function as bis-bidentate ligands, to give complexes with two metal centres chelated to the O and N donor atoms of the salicylideneiminato entities [1]. Bridging is achieved by twisting of these two entities by rotation around the C–C (diamine) or the C–N bonds [1–5] (see Fig. 1). Homobimetallic complexes of this type have been reported for cobalt [1], platinum [6], gold [7], palladium [2,3], iridium [4,5,8,9] and rhodium [6,8–10].

However, further rotation of the aforementioned bonds may lead to interaction of the two metal centres. Thus by treatment of $[\{Rh(CO)_2\}_2salen]$ (I) with an excess of ligand, we have obtained a derivative of divalent rhodium, $[Rh_2salen_2]$, in which the oxidation state is stabilized by metal–metal interaction, as shown by the low magnetic moment of the complex [11]. This compound is presumably formed by oxidative addition of the biprotic acid $salenH_2$ to I, followed by reductive elimination of H_2 (detected by GLC [11]) from the dimeric Rh^{III} dihydride that is the likely intermediate:

$$[\{Rh(CO)_2\}_2salen] + salenH_2 \rightarrow [Rh_2salen_2] + H_2 + 4\,CO \qquad (1)$$

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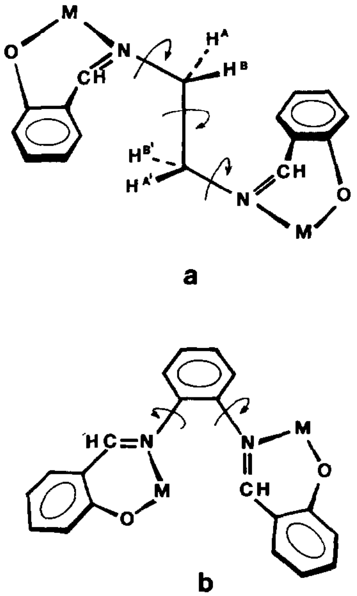


Fig. 1. Bonds rotation in salen (a) and saloph (b) bimetallic complexes.

In this paper we report a study on the reactions of I and of [{Rh(CO)L}$_2$salen] (II) (L = PPh$_3$), with reagents able to provide two or four formal oxidation equivalents, in the hope of throwing light on the factors which may lead to metal–metal interaction in this type of complex.

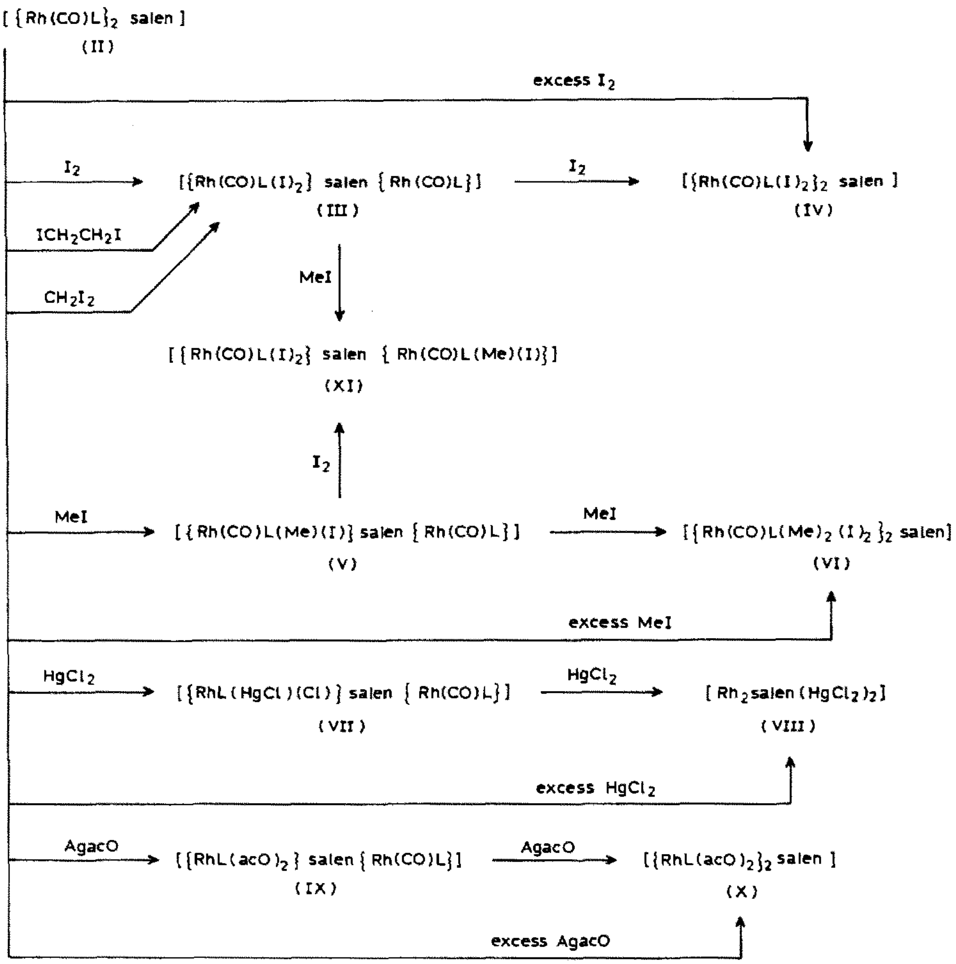
Results and discussion

Reactivity of [{Rh(CO)$_2$}$_2$salen] (I)

When I was treated with two molar proportions of I_2 or MeI, or one of ICH_2CH_2I or CH_2I_2, only decomposition products were obtained, in agreement with previous reports [8]. When a one molar proportion of MeI or I_2 was used, green, weakly paramagnetic materials of approximate formula RhsalenI were isolated. These reactions were not very reproducible, and, as mentioned above, only in the case of reaction of I with salenH$_2$ were we able to obtain [Rh$_2$salen$_2$] in a reproducible way [11]. We were unable to bring about reactions analogous to eq. 1 with other protic acids whose anions are potentially bridging such as CH_3CO_2H, CF_3COOH, acetylacetone, pyrazoles, etc., all of which failed to react. Silver acetate gave uncharacterizable decomposition products.

Reactions of [{Rh(CO)L}$_2$salen] (L = PPh$_3$) (II)

As expected [12], this compounds reacts more easily with oxidative addition reagents. The reactions performed are summarized in Scheme 1; elemental analyses and spectroscopic data are listed in Tables 1 and 2, respectively. With an excess of reagent we obtained the Rh^{III} dimers IV, VI, VIIII and X, whereas use of a one molar proportion of reagent (or two of AgO_2CCH_3) gave the (diamagnetic) compounds III, V, VII and IX, which can be regarded as Rh^{I}–Rh^{III} dimers in which



Scheme 1

there is no interaction between the two metal centres (see below). Acetylacetone, CH_3CO_2H, pyrazoles, and also salenH_2, failed to react with II.

Compounds III and V can be described as Rh^I–Rh^{III} dimers on the basis of the following observations. The ^{31}P NMR spectra show two sets of resonances (in a 1/1 ratio) with δ and J(P–Rh) values attributable to Rh^I- and Rh^{III}-bound phosphine [13,14]. These resonances are "clean" doublets ruling out any metal–metal interaction. There is more than one doublet in the region of phosphorous bound to Rh^{III}, suggesting the presence of more than one geometrical isomer (see below). The non-equivalence of the Rh atoms is also reflected by the presence in the ^1H NMR spectra of two sets of resonances (doublets of doublets, again in the ratio 1/1) due to the azomethine protons; their chemical shifts and their H–Rh and H–P coupling constants can be attributed to Rh^I and Rh^{III} coordinated azomethine groups by comparison with the corresponding values for the wholly-reduced and wholly-oxidized dimers.

Table 1. Analytical data for complexes III–XI

Complex	Molecular formula	Found (calc) (%)			
		C	H	N	Rh
[{Rh(CO)L(I)$_2$}salen{Rh(CO)L}] (III)	$C_{54}H_{44}N_2I_2O_4P_2Rh_2$	49.41 (49.63)	3.26 (3.37)	2.20 (2.14)	15.05 (15.76)
[{Rh(CO)L(I)$_2$}$_2$salen] (IV)	$C_{54}H_{44}N_2I_4O_4P_2Rh_2$	41.31 (41.55)	2.75 (2.82)	2.01 (1.80)	13.84 (13.19)
[{Rh(CO)L(Me)(I)}salen{Rh(CO)L}] (V)	$C_{55}H_{47}N_2IO_4P_2Rh_2$	54.95 (55.29)	4.02 (3.94)	2.57 (2.35)	17.73 (17.24)
[{Rh(CO)L(Me)(I)}$_2$salen] (VI)	$C_{56}H_{50}N_2I_2O_4P_2Rh_2$	50.59 (50.31)	3.89 (3.74)	2.00 (2.10)	15.90 (15.40)
[{RhL(HgCl),(Cl)}salen{Rh(CO)L}] (VII)	$C_{53}H_{44}N_2Cl_2HgO_3P_2Rh_2$	49.20 (49.10)	3.30 (3.40)	2.31 (2.16)	15.15 (15.89)
[Rh$_2$salen(HgCl$_2$)$_2$] (VIII)	$C_{16}H_{14}N_2Cl_4Hg_2O_2Rh_2$	18.76 (18.92)	1.51 (1.38)	2.66 (2.76)	19.81 (20.28)
[{RhL(acO)$_2$salen{Rh(CO)L}] (IX)	$C_{57}H_{50}N_2O_7P_2Rh_2$	60.12 (59.90)	4.45 (4.38)	2.37 (2.45)	17.69 (18.02)
[{RhL(acO)$_2$}$_2$salen]·H$_2$O (X)	$C_{60}H_{58}N_2O_{11}P_2Rh_2$	57.10 (57.61)	4.73 (4.64)	2.19 (2.24)	16.90 (16.47)
[{Rh(CO)L(Me) (I)}salen{Rh(CO)L(I)$_2$}] (XI)	$C_{55}H_{47}N_2I_3O_4P_2Rh_2$	45.83 (45.60)	3.40 (3.25)	1.95 (1.93)	13.95 (14.21)

Table 2. Relevant spectroscopic data [a]

Compound	IR (cm^{-1})		^{31}P NMR, δ (ppm) (J(P–Rh), Hz)	^{1}H NMR; δ (ppm) (J, Hz)	
	CO	C=N		H-C=N	CH$_2$CH$_2$
I	1980	1610			
	2056				
II	1951	1605	41.1 (158)	8.38 (dd, 11.5, 2.1)	4.70 (s)
III	1946	1605	41.8 (157)	8.36 (dd, 11.5, 2)	4.5 (b)
	2066	1618	9.7 (94), 10.5 (94), 11.0 (94) [b]	8.50 (dd, 21.0, 1.5)	
IV	2067	1619	11.0 (94)	8.50 (dd, 21.0, 1.5)	4.55 (dd, 2.2, 2.2) [c]
V	1945	1602	41.0 (157)	8.37 (dd, 21.0, 1.5)	4.66 (b) [d]
	2064	1620	20.4 (113), 20.8 (112), 21.8 (112) [b]	8.96 (dd, 18.4, 1.7)	
VI	2048	1619	20.4 (112)	8.96 (dd, 18.4, 1.5)	3.92 (d, 11), 5.21 (d, 11) [e,f]
VII	1955	1606	41.0 (157)	8.37 (d, b, 10)	4.7 (b)
			27.8 (130), 29.0 (127) [b]	8.6 (b)	
VIII		1639			[g]
IX	1955	1607	41.7 (156)	8.55 (d, b, 10)	4.68 (s)
			28.7 (127)		
X		1610	28.0 (129)	8.5 (b)	4.30 (b)
XI	2050	1620	10.7 (94), 21.6 (114)	8.50 (dd, 21, 1.5)	4.50 (b) [h]
	2065			8.95 (dd, 18.4, 1.5)	

[a] IR spectra as KBr disks, NMR spectra as CDCl$_3$ solutions. ^{31}P NMR spectra: δ values vs. 85% H$_3$PO$_4$, as external reference;, all resonances are doublets. ^{1}H NMR spectra: δ values vs. Me$_4$Si; s, singlet; d, doublet; dd, doublet of doublets; b, broad. The integrations of the azomethine and ethylenediamine protons are in the correct ratio 1/2. [b] The integrals of the signal due to Rh^{I}- and the total integration of the signals of the Rh^{III}-bound phosphine are in the ratio 1/1. [c] Broadens at −30 °C. [d] CH$_3$-Rh: 1.44 (dd, 3, 3); 1.48 (dd, 3, 2). Total integration three protons. The values of ^2J(H–Rh) and ^3J(H–P) are in the range reported for a similar compound [12]. [e] These two doublets coalesce at 70 °C in toluene solution. [f] CH$_3$-Rh: 1.47 (dd, 3, 2). Integrates for six protons. [g] Not recorded because of the low solubility. [h] CH$_3$-Rh: 1.42 (dd, 3, 2). Integrates for three protons.

The IR spectra of compounds III and V present two bands attributable to Rh^I- and Rh^{III}-bound carbon monoxide. There are also two C=N stretches, and we assign the higher frequency band to the azomethine bound to Rh^{III}, by comparison with the values for compounds II and IV, and VI. The stretching frequency of the carbon monoxide bound to the unreacted Rh^I centre is slightly lower than that for the parent Rh^I dimer II, suggesting a small increase in the electron density on one metal centre upon oxidation of the other. This is consistent with the fact that such an atom can also undergo oxidative addition, although under slightly more vigorous conditions involving use of an excess of reagent and longer reaction times (see Experimental). Compounds IV and VI can also be obtained by reaction of III and V with an excess of substrate and, moreover, treatment of III or V with an excess, respectively, of MeI or I_2 yields $[\{Rh(CO)LMe(I)\}salen\{Rh(CO)L(I)_2\}]$ (XI) (see Scheme 1). This behaviour contrasts with that of another Rh^I–Rh^I system in which oxidation of one metal centre deactivates the second rhodium atom towards further oxidative addition [15].

Reaction of dimeric Rh^I complexes with mercury chloride can give Hg-bridged dimers [16–18]. When II was treated with an equimolar amount of $HgCl_2$, we obtained compound VII, to which we assign the formula $[\{RhL(HgCl)(Cl)\}salen\{Rh(CO)L\}]$, formally a Rh^I–Rh^{III} dimer, on the basis of the ^{31}P NMR data. One CO ligand is lost, probably from the Rh^{III} centre (as judged from the IR spectrum) which is apparently unsaturated. This compound could not be further characterized because its ^{31}P resonances are again clean doublets, with no sign of metal–metal interaction, and any ^{31}P–^{199}Hg coupling was probably hidden by the noise. Use of an excess of $HgCl_2$ gave a compound of stoichiometry $[Rh_2salen(HgCl_2)_2]$ (VIII). We were unable to detect any signal in the ^{199}Hg NMR spectra of either compound.

Reactions with silver acetate were performed with the hope of obtaining acetato-bridged Rh^{II} compounds [19], but in this case also "chemical" oxidation occurred separately at the two metal centres, again with concomitant loss of carbon monoxide. The ^{31}P NMR spectra of compounds IX and X show no sign of metal–metal interaction. Hexacoordination around the Rh^{III} centres is probably achieved through chelation of one acetato group per Rh^{III} atom, as suggested by the appearance in the IR spectra of bands at 1560 and 1465 cm^{-1} characteristic of chelated acetato groups [20].

Finally, reaction of II with ICH_2I or CH_2I_2 gave only compounds III and IV depending on the reagents ratio. These reactions were not investigated further.

The geometry of the oxidative addition reactions described above is of interest. The Rh^I–Rh^{III} dimers show in the Rh^{III}-phosphine region, two or three ^{31}P resonances whose total integration equals that of the signals due to the Rh^I-bound phosphine. In the ^1H NMR spectrum of compound V there are also two resonances due to CH_3-Rh. These observations suggest the presence of various geometrical isomers involving the Rh^{III} centres. The data in Table 2 are for freshly prepared solutions, since the number of the isomers and their ratio changes upon heating or ageing the solutions, and eventually only one doublet, due to the Rh^{III}-bound P, is obtained. This appears at the same frequency of the only doublet shown by the corresponding Rh^{III} dimer. Clearly isomerisation around Rh^{III} in the Rh^I–Rh^{III} derivatives tends to lead to the most stable isomer, which is the same as the Rh^{III} dimer.

Conclusions

In the observed reactions of II the two metal centres react separately. Oxidation of one metal centre makes reaction at the other slightly more difficult, and this makes possible the isolation of the Rh^{I}–Rh^{III} derivatives. In no case did the ^{31}P NMR spectra give any indication of metal–metal interaction, even in the case of the apparently unsaturated compounds VII, IX and X, or in the presence of the potentially bridging acetato ligands. We believe that the formation of the Rh^{I}–Rh^{III} compounds III, V, VII and IX, rather than the dimeric Rh^{II} derivatives, must be ascribed to the difficulty of forming metal–metal bonds in this system.

It is likely that the bulky phosphine ligands help to stabilize a conformation of the bridging salen which prevents metal–metal interaction. In the case of compound VI, such a conformation is rather rigid. In its ^{1}H NMR spectrum at room temperature the four protons of the ethylenediamine moiety give rise to two doublets (J 11 Hz) at δ 3.92 and 5.21 ppm. Either doublet becomes a broad singlet upon irradiation of the other doublet. The doublets coalesce to a singlet at δ 4.60 ppm at 70 °C (80 MHz, toluene solution). This pattern can be accounted for on the assumption that at room temperature the molecule is fixed in a conformation similar to that shown in Fig. 1a, in which protons A′ and B′ experience different magnetic environments because of their different spatial orientations with respect to the azomethine or the benzene rings, and in which the dihedral angle ACCB′ is such that $J(AB')$ and $J(A'B)$ are approximately zero, and the geminal protons (A and B, or A′ and B′) show a normal coupling constant of about 11 Hz. The other compounds show a broad resonance at 4.65–4.80 ppm at room temperature.

Since I is less sterically hindered, some metal–metal interaction in its derivatives might be expected, but apart from the isolation [11] of the Rh^{II} derivative $[Rh_2salen_2]$, compound I either fails to react or decomposes under the reaction conditions.

Experimental

Microanalyses (Table 1) were by the Microanalytical Laboratory of the University, Milan. Infrared spectra were recorded on a Nicolet MX1 FT IR. NMR spectra were obtained on a Bruker WP 80.

All the reactions were performed under dry nitrogen by standard Schlenk techniques. $[\{Rh(CO)_2\}_2salen]$ (I) and $[\{Rh(CO)L\}_2salen]$, ($L = PPh_3$) (II) were obtained as described in Ref. 8.

Reactivity of $[\{Rh(CO)_2\}_2salen]$ *(I)*

Typically a solution of equimolar amounts of this compound and MeI in benzene was refluxed for 24 h. The dark green precipitate formed was filtered off and washed with Et_2O. Analysis: C, 38.00; H, 3.00; N, 6.10. [RhsalenI] calc: C, 38.73; H, 2.83; N, 5.65%. IR data: no CO stretch, ν(C=N) 1623 cm^{-1}; $\chi = 2–4 \times 10^{-6}$ cm^3 g^{-1} depending on the batch. A material with very similar analytical and spectroscopic data was obtained by reaction with an equimolar amount of iodine in refluxing benzene for 2 h.

[{Rh(CO)L(I)$_2$}salen{Rh(CO)L}] (III)

130.0 mg of II were treated with 31.4 mg of I_2 in 15 ml of CH_2Cl_2 for 3 h at room temperature. The red solution was concentrated and treated with Et_2O to give a violet precipitate.

[{Rh(CO)L(I)$_2$}$_2$salen] (IV)

This was obtained by reaction of II with I_2 (molar ratio 1/2.5), or of III with a 50% excess of iodine, in CH_2Cl_2 for 8 h at room temperature, followed by precipitation as above.

[{Rh(CO)L(Me)I}salen{Rh(CO)L}] (V)

This was obtained by reaction of II and MeI (molar ratio 1/1) in CH_2Cl_2 at room temperature for 10 h. Addition of hexane yielded a dark yellow precipitate.

[{Rh(CO)L(Me)I}$_2$salen] (VI)

A solution of 200.5 mg of II and 55.3 mg of MeI (molar ratio 1/2) in CH_2Cl_2 (5 ml) was kept at room temperature for 10 h, after which an aliquot of the solution was treated with ether, to give a precipitate that contained some V (identified by IR). Additional MeI (30 mg) was therefore added to the remaining solution, which was left at room temperature for 4 more hours. Addition of ether gave the desired product as a bright yellow solid.

[{RhL(HgCl)(Cl)}salen{Rh(CO)L}] (VII)

59.8 mg of $HgCl_2$ were added to a solution of 230.0 mg of II in 10 ml of THF. The brown solution was allowed to stand overnight at room temperature, then filtered, concentrated, and treated with ether, to give VII as a brown precipitate.

[Rh$_2$salen(HgCl$_2$)$_2$] (VIII)

The brown-red slurry of 254.0 mg of II and 131.3 mg of $HgCl_2$ in 10 ml of THF, was stirred for 2 d at room temperature. The orange precipitate was filtered off and washed with ether. Shorter reaction times gave VIII containing VII.

[{RhL(acO)$_2$}salen{Rh(CO)L}] (IX)

A mixture of 202.0 mg of II, 64.2 mg of AgacO, and 10 ml of CH_2Cl_2 was kept, in the dark at room temperature, for 10 h. The solution was filtered and ether was added to the filtrate to give IX as a brown solid.

[{RhL(acO)$_2$}$_2$salen] (X)

An excess of silver acetate was stirred with II in CH_2Cl_2 for 24 h at room temperature in the dark. The brown compound was precipitated by addition of ether to the filtered solution.

[{Rh(CO)L(Me) (I)}salen{Rh(CO)L(I)$_2$}] (XI)

This was obtained at room temperature in dichloromethane, either by reaction of III with an excess of MeI for 12 h or by reaction of V with I_2 for 8 h. The latter reaction gave a purer product.

Reaction with ICH_2CH_2I

149.4 mg of II were treated with 40.1 mg of ICH_2CH_2I (molar ratio 1/1) in CH_2Cl_2 to give a red solution. After 4 h and upon addition of ether gave a violet precipitate. Elemental analysis, IR, and NMR data showed that was compound III.

Reaction with CH_2I_2

This was performed as above, but a longer time (12 h) was required to yield a product with analytical and spectroscopic data identical with those of III.

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