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RHODIUM(I) AND IRIDIUM(I) CARBONYL AND OLEFIN DERIVATIVES OF SALICYLALDIMINE SCHIFF-BASES

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SUMMARY

$[(CO)_2RhCl]_2$ and $[CodMCl]_2$ ($M = Rh^I, Ir^I$; Cod = 1,5-cyclooctadiene) react with bidentate salicylaldimines, HSal=NR (R = alkyl, aryl), in the presence of base to yield the chelate compounds $(CO)_2RhSal{=}NR$ and CodMSal=NR. A more efficient route to these compounds involves bridge-splitting metathetical reaction of the chloro-bridge with the thallium(I) Schiff-base derivatives TlSal=NR. The $(CO)_2IrSal{=}NR$ derivatives were obtained using this method starting from $[Ir(CO)_3Cl]_n$. The potential tetradentate Schiff-base *N,N'*-ethylenebis(salicylaldimine), H_2Salen, yields the novel binuclear derivatives $[(CO)_2M]_2$Salen and $[CodRh]_2$Salen.

INTRODUCTION

In their reactions with protonic ligands such as carboxylic acids[1], β-diketones[2,3], Schiff-bases[4], porphyrins[5], etc., metal carbonyls have recently proven to be extremely useful starting materials for the syntheses of metal complexes of these ligands. The method is particularly useful for preparing complexes of 2nd and 3rd row transition metals which often are difficult to obtain by more conventional routes. As part of a study of Schiff-base chelates of the heavier transition metals we have investigated the reactions of bidentate and tetradentate salicylaldimines with the carbonyl chlorides of rhodium(I) and iridium(I), and also with the related 1,5-cyclooctadiene (Cod) derivatives. In these reactions it is found that the chloro rather than the carbonyl or olefin groups are replaced by the ligand. We have found that the thallium(I) complexes[6] of the Schiff-bases in most cases react more efficiently and under milder conditions than the corresponding free Schiff-bases. Bonati and coworkers have recently described related rhodium(I) and iridium(I) chelates with β-diketones[7], oxines[8] and β-ketoimines[9] but in the main using different synthetic procedures to those described here. The structures of the present chelates have been investigated by IR and NMR spectroscopy. Some reactions of the complexes are described. Preliminary results have been mentioned briefly[6].

RESULTS AND DISCUSSION

Syntheses

The reactions of $[(CO)_2RhCl]_2$ or $(CodMCl)_2$ (M = Rh, Ir; Cod = 1,5-

cyclooctadiene) with bidentate salicylaldimines, HSal=NR, in methanol at room temperature did not produce any isolable products. Addition of the base triethylamine, however, led to replacement of the chloride and chelation of the ligand to produce the complexes $(CO)_2RhSal{=}NR$ and CodMSal=NR ($R = n\text{-}C_3H_7$, C_6H_5, $p\text{-}CH_3C_6H_4$, $p\text{-}ClC_6H_4$). A more efficient method involved the use of salicylaldiminatothallium(I) complexes[6], TlSal=NR, which involved simply filtration of precipitated thallous chloride followed by crystallization of the mother liquor. The $(CO)_2IrSal{=}NR$ derivatives were obtained by this route from $[(CO)_3IrCl]_n$. The complexes are all soluble in organic solvents in which they are monomeric and non-conducting. They are diamagnetic as expected for d^8 Rh^I and Ir^I. In the solid state some of the complexes exhibit red–yellow dichroism. This has been observed in other related systems and has been attributed to metal–metal interactions[8,10].

The tetradentate Schiff-base *N,N'*-ethylenebis(salicylaldimine), (H_2Salen) reacted with $[(CO)_2RhCl]_2$, $[(CO)_3IrCl]_n$ or $(CodRhCl)_2$ in methanol to yield yellow or red complexes with the 2/1 metal to ligand formulations $[(CO)_2M]_2$Salen and $(CodRh)_2$Salen respectively. A Cod–iridium product could not be isolated. The $(CodRh)_2$Salen compound was much more soluble in organic solvents than the carbonyl derivative. The molecular weight determination in chloroform was in agreement with this binuclear formulation and the mass spectrum terminated in the molecular ion. The related ligand *N,N'*-phenylenebis(salicylaldimine), (H_2Salophen), did not show any reaction. The tetradentate β-ketoimine *N,N'*-ethylenebis(acetylacetoneimine), H_2Acacen, reacted with $[(CO)_2RhCl]_2$ to produce, not the Schiff-base chelate, but an ethylenediamine (En) derivative $[(CO)_2RhCl]_2$En. Hydrolysis of the Schiff-base has occurred in the presence of the rhodium(I) complex in the same manner as recently observed[9] with bidentate β-ketoimines. The En complex could be independently synthesized in low yield by reaction with ethylenediamine directly. It

TABLE 1

INFRARED SPECTRA OF RHODIUM(I) AND IRIDIUM(I) CARBONYL SCHIFF-BASE COMPLEXES

Complex	Phase	$\nu(CO)$ (cm^{-1})
$(CO)_2Rh\ Sal{=}N(C_3H_7\text{-}n)$	Nujol mull	2079 s, 2074 (sh), 2054 w, 2001 s, 1975 w
	$CHCl_3$ soln.	2082 s, 2006 s
$(CO)_2IrSal{=}N(C_3H_2\text{-}n)$	Nujol mull	2061 s, 2038 w, 1988 s, 1931 w
	$CHCl_3$ soln.	2070 s, 1989 s
$(CO)_2RhSal{=}N(C_6H_5)$	Nujol mull	2090 s, 2063 w, 2031 s, 2010 w, 1993 w
	$CHCl_3$ soln.	2084 s, 2014 s
$(CO)_2RhSal{=}N(C_6H_4CH_3\text{-}p)$	Nujol mull	2075 s, 2046 w, 1998 s, 1981 w, 1961 w
$(CO)_2IrSal{=}N(C_6H_4CH_3\text{-}p)$	Nujol mull	2057 s, 2032 w, 1977 s, 1963 (sh), 1943 w
	$CHCl_3$ soln.	2071 s, 1997 s
$(CO)_2RhSal{=}N(C_6H_4Cl\text{-}p)$[a]	Nujol mull	2090 s, 2062 w, 2013 s, 1998 w, 1969 w
$(CO)_2RhSal{=}N(C_6H_4Cl\text{-}p)$[b]	Nujol mull	2082 s, 2059 w, 1995 s, 1960 w
$(CO)_2IrSal{=}N(C_6H_4Cl\text{-}p)$	Nujol mull	2058 s, 2035 w, 1981 s, 1942 w
$((CO)_2Rh)_2$Salen	Nujol mull	2070 s, 2065 s, 2052 (sh), 1983 s, 1964 m, 1954 m
$[(CO)_2RhCl]_2$En	Nujol mull	2111 s, 2080 w, 2045 s, 2000 (sh), 1985 (sh)[c]
$[(Ph_3P)(CO)Rh]_2$Salen	Nujol mull	1967 s
$(Ph_3P)(CO)RhSal{=}N(C_6H_4CH_3\text{-}p)$	Nujol mull	1962 s

[a] Red form. [b] Yellow form. [c] γ(NH) 3270 m, 3200 m.

shows slight dissociation in nitromethane solution, $\Lambda_m = 22$ ohm$^{-1}\cdot$cm$^2\cdot$mole^{-1} (1/1 conductors, $\Lambda_m = 80$–90 ohm$^{-1}\cdot$cm$^2\cdot$mole^{-1}).

Spectra and structure

The $(CO)_2MSal{=}NR$ compounds all show two strong ν(CO) frequencies in their solution infrared spectra (Table 1). The mull spectra generally show more complex absorptions in this region due to solid state splitting. The solid state spectra of the red and yellow forms of the $R = p$-ClC_6H_4 compound are different due probably to association via metal–metal bonding or oxygen-bridging in one of the forms[9,10]. The mull spectra of the $[(CO)_2M]_2$Salen compounds display a ν(CO) pattern similar to those of bridged dicarbonylrhodium complexes possessing bridging groups such as acetate[11], suphate[11], nitrate[11] and 8,8′-dihydroxy-5,5-biquinoline[12]. The ν(CO) and ν(NH) bands in the spectrum of $[(CO)_2RhCl]_2$En are in similar positions to those very recently observed in phenylene- and long-chain alkyldiaminerhodium carbonyl chloride complexes. These latter complexes have been formulated[12,13] as possessing bridging diamine groups. The 1700–1200 cm^{-1} region of the spectra of the salicylaldiminato compounds are typical of chelated Schiff-base metal complexes.

TABLE 2

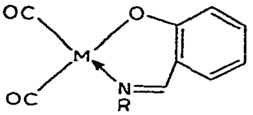
^{1}H NMR SPECTRA

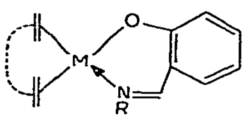
Complex		δ values (relative to TMS: ppm)						
M	R	Schiff-Base					Cod	
		Aromatic	CH=N	CH_2	CH_2	CH_3	$(CH{=}CH)_2$	$(CH_2)_4$
$(CO)_2M$ Sal=NR								
Rh	n-C_3H_7	6.52–7.47	8.01d	3.89t	1.92m	0.95t		
Ir	n-C_3H_7	6.58–7.61	8.20	4.21t	1.94m	0.95t		
Rh	C_6H_5	6.58–7.49	8.13d					
Ir	C_6H_5	6.61–7.70	8.36					
Rh	p-$CH_3C_6H_4$	6.54–7.52	8.15d			2.37		
Ir	p-$CH_3C_6H_4$	6.64–7.69	8.31			2.38		
Ir	p-ClC_6H_4	6.68–7.70	8.33					
Cod M Sal=NR								
Rh	C_6H_5	6.42–7.38	7.94d				3.18	1.5 –2.1
							4.57	2.1 –2.5
Ir	C_6H_5	6.55–7.55	8.30				2.97	1.45–1.9
							4.43	1.93–2.3
Rh	p-$CH_3C_6H_4$	6.40–7.40	7.96d			2.32	3.20	1.5 –2.1
							4.55	2.1 –2.5
Ir	p-$CH_3C_6H_4$	6.52–7.52	8.30			2.37	3.02	1.54–1.96
							4.42	1.96–2.30
Rh	p-ClC_6H_4	6.42–7.42	7.89d				3.12	1.5 –2.1
							4.57	2.1 –2.6
Ir	p-ClC_6H_4	6.55–7.65	8.30				2.94	1.42–1.97
							4.47	1.97–2.35
$(Cod\,Rh)_2$ Salen		6.28–7.41	7.65d	3.37[a]			3.67	1.55–2.02
							4.5	2.02–2.62

[a] Sharp singlet; d doublet $J(^{103}Rh$–$^1H) \sim 2$ Hz; t triplet J 7 Hz; m multiplet.

The ^1H NMR spectra of the $(CO)_2MSal{=}NR$ complexes show resonance positions typical of chelated salicylaldimine ligands (Table 2). The CH=N resonance at $\delta \sim 8.15$ ppm is split symmetrically by about 2 Hz in the rhodium spectra due, possibly, to $^{103}Rh{-}^1H$ coupling. This CH=N resonance appeared at higher field than in the corresponding iridium spectra. The ^1H NMR spectra of the 1,5-cyclooctadiene compounds, CodMSal=NR, display two different olefin absorptions on the Cod ring (Table 2). This arises due to the unsymmetrical nature of the Sal=NR group. The related symmetrical compound CodRhAcac shows[13] only one CH=CH absorption, at δ 4.12 ppm.

In the NMR spectrum of $(CodRh)_2Salen$, apart from the broad olefin and methylene absorption of the Cod ring, a very sharp singlet is observed at δ 3.37 ppm. We assign this resonance to the C_2H_4 group of a bridging Salen structure (Fig. 1c). The C_2H_4 resonance in planar tetradentate Salen complexes is normally observed[15] as a broad or structured A_2B_2 absorption.


(a)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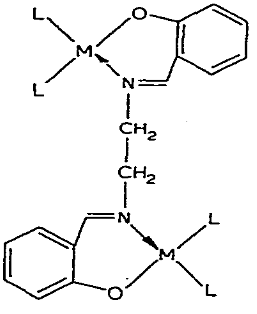
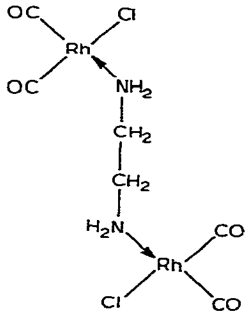


(c)


(d)

The evidence thus far presented is compatible with square planar structures for the $(CO)_2MSal{=}NR$ and CodMSal=NR chelates as shown in Fig. 1a, b. This structural unit is known for other bidentate chelating ligands[7-9]. The complexes with the potential tetradentate ligand appear to contain Salen in an unusual bridging bidentate configuration, though each $(CO)_2M\begin{smallmatrix}\swarrow N\\ \searrow O\end{smallmatrix}$ or Cod $M\begin{smallmatrix}\swarrow N\\ \searrow O\end{smallmatrix}$ moiety retains a square planar structure (Fig. 1c).

The formation of such a bridged complex would explain the otherwise puzzling failure of $H_2Salophen$ to react with $[(CO)_2MCl]_2$ and $(CodMCl)_2$. This ligand is unable to twist about the C–C bond of the phenylene ring in contrast to salen and therefore would seem unable to adopt a configuration comparable to that shown in Fig. 1c. A bridging configuration has just been confirmed for a tetradentate Schiff-base ligand by an X-ray single crystal study[16] on the compound $Co_2(3\text{-}CH_3O{-}Salen)_3$.

We have also observed it[17] in compounds of the type M_2Salen_3 ($M = Cr^{III}$, Fe^{III}).

There should, however, be no steric hindrance to the coordination of Acacen as a bridging ligand. The observed hydrolysis to produce the compound $[(CO)_2RhCl]_2En$ can be associated with the tendency for $H_2Acacen$ to bond to the metal in the keto–amine tautomeric form[9,18–20] in contrast to the enolic form for the salicylaldimines. Thus the C–N bond in the former case readily undergoes nucleophilic displacement by water (in the solvent) to yield coordinated ethylenediamine and free acetylacetone. In contrast the CH=N bond in the salicylaldimine complexes would require an initial S_N1 displacement by water to give –CH(OH)–NH– followed by addition of another mole of water catalysed by acid or metal.

The slight conductance of the complex in nitromethane solution favours the ethylenediamine bridging structure for this complex (Fig. 1d), rather than an ionic salt of the type $[(CO)_2RhEn][(CO)_2RhCl_2]$. As mentioned above, this type of bridging has recently been suggested for other diamines[12,13]. It is worth pointing out, however, that there is some conflict in the literature[11–14] between bridging and ionic structures for Cod and carbonyl rhodium(I) complexes with secondary amines, bipyridine and phenanthroline.

Reactions

Some oxidative addition and substitution reactions of the complexes were studied. All attempts to convert the square-planar Rh^I and Ir^I chelates into octahedral Rh^{III} and Ir^{III} derivatives, by reaction with X_2, HX and RX (X = halogen, R = alkyl) were unsuccessful. Decomposition appeared to occur in all cases and no stable product could be isolated. There are no previous reports of oxidative additions to Rh^I and Ir^I complexes which contain bidentate ligands other than chelating diphosphines[21]. It is known[22,23] that the ability of d^8 complexes to undergo oxidative addition reactions is highly dependent on the nature of the attached ligands. The present Schiff-bases can presumably be classed as deactivating.

$[(CO)_2M]_2Salen$ and $(CO)_2MSal{=}NR$ (M = Rh, Ir) react readily with excess 1,5-cyclooctadiene in methanol to give the corresponding diene complexes $(CodM)_2Salen$ and CodMSal=NR. Reactions with excess triphenylphosphine in benzene led to substitution of only one of the carbonyl groups to yield the complexes $[Ph_3P(CO)M]_2Salen$ and $(Ph_3P)(CO)MSal{=}NR$. This partial substitution has been observed in related systems[7–9]. Attempts to replace both CO groups in $(CO)_2RhSal{=}NR$ by reaction with excess 1,2-bis(diphenylphosphino)ethane (Diphos) yielded a poorly characterized product which still contained CO. The Diphos derivative from $(CO)_2RhOx$ (Ox = oximato) has, however, been isolated[8]. It was thought that the monophosphine Schiff-base derivatives might undergo oxidative addition reactions with alkyl halides more readily than the parent carbonyl compounds, but again no isolable products could be obtained. More detailed studies of the reactions of these chelate compounds are currently in progress including the effect of variation of the attached phosphine.

EXPERIMENTAL

Syntheses

$[(CO)_2RhCl]_2$[24], $(CodRhCl)_2$[14], $(CodIrCl)_2$[25] and the thallium(I) Schiff-

TABLE 3

ANALYTICAL DATA AND MOLECULAR WEIGHTS

Complex	Formula	Colour	Analyses (%)								Mol.wt.		
			Found				Calcd.				Found		Calcd.
			C	H	N	X	C	H	N	X	In $CHCl_3$[a]	m/e[b]	
$[(CO)_2Rh]_2$Salen	$C_{20}H_{14}N_2O_6Rh_2$	Yellow	41.68	2.83	5.13		41.11	2.42	4.80				584
$Rh_2(CO)_4EnCl_2$	$C_6H_8Cl_2N_2O_4Rh_2$	Green/violet	16.44	2.26	6.39	16.1	16.05	1.80	6.24	15.80			449
$(CodRh)_2$Salen	$C_{32}H_{38}N_2O_2Rh_2$	Yellow	55.97	5.67	3.94		55.82	5.56	4.07		685	688	688
$(CO)_2RhSal{=}N(C_6H_4CH_3\text{-}p)$	$C_{16}H_{12}NO_3Rh$	Yellow	52.25	3.21	3.70		52.06	3.28	3.80		375	369	369
$(CO)_2RhSal{=}N(C_3H_7\text{-}n)$	$C_{12}H_{12}NO_3Rh$	Yellow	45.01	4.08	4.22		44.90	3.77	4.36			321	321
$(CO)_2RhSal{=}N(C_6H_5)$	$C_{15}H_{10}NO_3Rh$	Red	50.22	2.97	4.23		50.75	2.84	3.95		364	355	355
$(CO)_2RhSal{=}N(C_6H_4Cl\text{-}p)$	$C_{15}H_9ClNO_3Rh$	Yellow	46.36	2.11	3.64		46.25	2.31	3.60			390	390
$(CO)_2RhSal{=}N(C_6H_4Cl\text{-}p)$	$C_{15}H_9ClNO_3Rh$	Red	46.28	2.15	3.58		46.25	2.31	3.60		382	390	390
$CodRhSal{=}N(C_6H_4CH_3\text{-}p)$	$C_{22}H_{24}NORh$	Yellow	62.54	6.03	3.25		62.72	5.74	3.33			421	421
$CodRhSal{=}N(C_6H_5)$	$C_{21}H_{22}NORh$	Yellow	61.82	5.67	3.53		61.93	5.44	3.44		384	407	407
$CodRhSal{=}N(C_6H_4Cl\text{-}p)$	$C_{21}H_{21}ClNORh$	Yellow	56.86	4.66	3.22	8.09	57.10	4.79	3.17	8.02	436	442	442
$(CO)_2IrSal{=}N(C_6H_4CH_3\text{-}p)$	$C_{16}H_{12}IrNO_3$	Red	41.58	2.40	2.97		41.91	2.64	3.06		465	458	458
$(CO)_2IrSal{=}N(C_3H_7\text{-}n)$	$C_{12}H_{12}IrNO_3$	Red	34.90	2.81	3.60		35.12	2.95	3.41		455	410	410
$(CO)_2IrSal{=}N(C_6H_5)$	$C_{15}H_{10}IrNO_3$	Green/violet	40.69	2.36	3.31		40.53	2.27	3.16			444	444
$(CO)_2IrSal{=}N(C_6H_4Cl\text{-}p)$	$C_{15}H_9ClIrNO_3$	Red	37.49	1.83	2.89		37.62	1.89	2.92			479	479
$[(CO)_2Ir]_2$Salen	$C_{20}H_{14}Ir_2N_2O_6$	Red	31.25	1.82	3.72		31.49	1.85	3.67				763
$CodIrSal{=}N(C_6H_4CH_3\text{-}p)$	$C_{22}H_{24}IrNO$	Orange	51.45	4.62	2.77		51.75	4.74	2.74		548	511	511
$CodIrSal{=}N(C_6H_5)$	$C_{21}H_{22}IrNO$	Orange	50.87	4.29	2.74		50.79	4.47	2.82			497	497
$CodIrSal{=}N(C_6H_4Cl\text{-}p)$	$C_{21}H_{21}ClIrNO$	Orange	48.33	3.97	2.49	7.90	47.50	3.99	2.64	6.68		531	531
$[(CO)(PPh_3)Rh]_2$Salen	$C_{54}H_{44}N_2O_4P_2Rh_2$	Yellow	61.16	4.43	2.65[c]		61.55	4.21	2.66[c]				
$(CO)(PPh_3)RhSal{=}N(C_6H_4CH_3\text{-}p)$	$C_{33}H_{27}NO_2PRh$	Yellow	65.66	4.53	2.34		65.69	4.51	2.32				

[a] Osmometric. [b] Mass spectrum. [c] Found: P, 5.7. Calcd.: P, 5.88%.

base complexes[6] were prepared as described previously. $[Ir(CO)_3Cl]_n$, obtained from Strem Chemicals Inc., was used without further purification. Analytical figures and other properties are given in Table 3.

$(CO)_2RhSal{=}NR$ ($R = n\text{-}C_3H_7$, C_6H_5, $p\text{-}CH_3C_6H_4$, $p\text{-}ClC_6H_4$). These compounds could be prepared by two routes, involving either the thallium(I) Schiff-base complexes, or triethylamine as base. The thallium complex route resulted in higher yields and greater purity of product.

(*a*). An equimolar amount of the thallium(I) Schiff-base complex was added as a solid to an ethanolic solution of $[(CO)_2RhCl]_2$, and the resultant solution stirred under an atmosphere of nitrogen for about 1 h at room temperature. The precipitated thallous chloride was filtered off, and the products crystallized by evaporation of the solution [$R = C_6H_5$, $p\text{-}CH_3C_6H_4$, $p\text{-}ClC_6H_4$ (yellow form)] or by addition of a little water followed by evaporation ($R = n\text{-}C_3H_7$). The red form of $(CO)_2RhSal{=}N(C_6H_4Cl\text{-}p)$ was obtained by recrystallization from chloroform/methanol. All the products could be recrystallized from chloroform/methanol ($R = C_6H_5$, $p\text{-}CH_3C_6H_4$, $p\text{-}ClC_6H_4$) or from ethanol/water ($R = n\text{-}C_3H_7$). Yields 70–80%.

(*b*). A small excess of triethylamine was added to a methanolic solution of $[(CO)_2RhCl]_2$ and an equimolar amount of the Schiff-base ligand, HSal=NR ($R = p\text{-}CH_3C_6H_4$, $p\text{-}ClC_6H_4$), yielding a yellow solution from which yellow crystals of $(CO)_2RhSal{=}NR$ were obtained by careful evaporation. The reaction was carried out at room temperature, under an atmosphere of nitrogen. The products were recrystallized from chloroform/methanol. Yields 50–60%.

$(CO)_2IrSal{=}NR$ ($R = n\text{-}C_3H_7$, C_6H_5, $p\text{-}CH_3C_6H_4$, $p\text{-}ClC_6H_4$). Equimolar amounts of $[Ir(CO)_3Cl]_n$ and the thallium(I) Schiff-base complex were refluxed in ethanol, under an atmosphere of nitrogen, for about 1 h. The thallous chloride was filtered off, and the products crystallized by evaporation of the solution ($R = p\text{-}CH_3C_6H_4$, $p\text{-}ClC_6H_4$) or by addition of water followed by evaporation ($R = n\text{-}C_3H_7$, C_6H_5). For $R = p\text{-}CH_3C_6H_4$, $p\text{-}ClC_6H_4$, products were recrystallized from methylene chloride/ethanol. For $R = n\text{-}C_3H_7$, C_6H_5 the products were recrystallized from ethanol/water. Yields 70–80%.

CodMSal=NR ($M = Ir, Rh$; $R = C_6H_5$, $p\text{-}CH_3C_6H_4$, $p\text{-}ClC_6H_4$). The thallium(I) Schiff-base complex was added as a solid, in a 2/1 molar ratio, to a degassed methylene chloride solution of $(CodRhCl)_2$ or a degassed benzene solution of $(CodIrCl)_2$, and the mixtures stirred under an atmosphere of nitrogen, at room temperature, for 1 h. The thallous chloride was filtered off, and the products crystallized by the addition of degassed ethanol, followed by careful evaporation of the solution. All the products were recrystallized from degassed methylene chloride/ethanol. The iridium complexes were quite air-sensitive as solids, and were stored under nitrogen. Yield 70–90%.

No products of the type $CodMSal{=}N(C_3H_7\text{-}n)$ could be prepared, using either the thallium(I) complex, or the free ligand with added triethylamine as base. These reactions led only to decomposition products.

$[(CO)_2M]_2$Salen and $(CodM)_2$Salen ($M = Rh, Ir$). $[(CO)_2Rh]_2$Salen was obtained in high yield as an insoluble yellow product on mixing methanolic solutions of $[(CO)_2RhCl]_2$ and the ligand in a 1/1 mole ratio.

The Cod analog with Rh^I could be synthesized either by (*a*) addition of a small excess of triethylamine to a 1/1 mole ratio mixture of $(CodRhCl)_2$ and the ligand in degassed methanol, followed by addition of ether to bring about crystallization, or (*b*) by use of Tl_2Salen. Both routes result in comparable yields (60–70%) and purity of product. The product is much more soluble in organic solvents than is the carbonyl analog.

$[(CO)_2Ir]_2$Salen was obtained as an insoluble red solid by the addition of a small excess of triethylamine to a refluxing ethanolic mixture of $[(CO)_3IrCl]_n$ and the ligand.

Attempts to prepare related compounds with the tetradentate ligand H_2-Salophen were unsuccessful in all cases.

The reaction of $[(CO)_2RhCl]_2$ with H_2Acacen in methanol at room temperature yielded dichroic green-violet crystals after evaporation of the yellow solution. The analytical figures corresponded to the formulation $[((CO)_2RhCl)_2En]$; the N–H stretching vibration of ethylenediamine appeared in the IR spectrum (Table 1). The complex was independently prepared from the carbonyl chloride and ethylenediamine mixed in 2/1 mole ratio.

Attempted oxidative addition reactions

1. *With halogens.* The Schiff-base complexes $(CO)_2$RhSal=NR were treated with quantitative amounts of iodine in THF, or bromine in CCl_4, and while most reactions resulted in complete dissolution of the initial complex, no halogen-substituted derivatives could be isolated.

2. *With hydrogen halides.* The complexes $(CO)_2$RhSal=NR were treated with quantitative, and subsequently excess aqueous HCl or HBr in methanol, but again decomposition occurred.

3. *With alkyl halides.* The Schiff-base complexes were reacted with methyl iodide under three different conditions: (*a*). equivalent amounts of alkyl halide and complex in benzene, (*b*) excess alkyl halide in benzene, and (*c*) alkyl halide as solvent in a sealed tube at 60–70°. In general, the $[(CO)_2M]_2$Salen and $(CO)_2$MSal=NR derivatives showed some evidence of reaction, but again no stable products could be isolated. The Cod complexes of Rh^I and Ir^I failed to react.

Ligand replacement reactions

1. *With 1,5-cyclooctadiene.* $[(CO)_2M]_2$Salen and $(CO)_2$MSal=NR were refluxed with excess Cod in methanol, under nitrogen, for about 30 min or until all the insoluble reactant had dissolved. The products $(CodM)_2$Salen and CodMSal=NR were isolated by cooling and carefully evaporating the alcohol solution.

2. *With triphenylphosphine.* $[(CO)(PPh_3)M]_2$Salen and $(CO)(PPh_3)$MSal=NR were readily prepared by refluxing the appropriate Schiff-base complex with a quantitative amount of PPh_3, in a small volume of benzene, for about 1 h, or until all the insoluble reactant had dissolved. The light yellow products were precipitated by the addition of light petroleum, and recrystallized from ether/heptane.

3. *With Diphos.* The Schiff-base complexes $[(CO)_2M]_2$Salen and $(CO)_2$M-Sal=NR were treated with diphos in the same manner as for PPh_3, but with extended reaction times. However, infrared spectra showed that only partial replacement of the carbonyl groups had occurred.

Instrumentation

Infrared spectra were obtained on a Perkin–Elmer 521 instrument. Scans of the ν(CO) region were recorded on an expanded scale. ^{1}H NMR spectra were measured using Varian A 60 or HA 100 spectrometers. Mass spectral measurements were carried out on a Perkin–Elmer–Hitachi RMU-6E instrument with perfluorokerosene used as a counting calibrant. Solution molecular weight determinations were made using a Mechrolab osmometer. Conductivity measurements were obtained with a Wayne–Kerr bridge. Magnetic measurements were made using the Gouy method.

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