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RHODIUM(I) AND IRIDIUM(I) CARBONYL DERIVATIVES WITH ANIONIC CHELATING LIGANDS

R. UGO, G. LA MONICA, S. CENINI AND F. BONATI
Istituto di Chimica Generale dell'Università, via Saldini 50, Milano (Italy)

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INTRODUCTION

Rhodium(I)[1] and iridium(I)[2] dicarbonyl β-diketonates have recently been described. These compounds show in the solid state a metal–metal interaction[3,4] which gives them the anisotropic properties of semiconductors[4], although in solution they are monomeric. The extensive physical data[2–4] indicate that an electronic effect of the substituents of the chelated β-diketonate ring acts on the electronic density on the metal.

We have now extended our work to other asymmetric chelated rings in order to investigate the effect of the nature of the chelated ring on the electronic density on the metal and the properties related to this density such as metal–metal interactions, carbonyl stretching frequencies and some catalytic properties.

PREPARATION AND PROPERTIES OF DERIVATIVES

By reacting $[Rh(CO)_2Cl]_2$ in benzene with asymmetric chelating ligands having N and O as donor atoms, only non-chelated compounds have been obtained with the ligand coordinated through the nitrogen atom[5] (Table 1). However, if the same reaction is carried out in benzene (or, better, methanol) in the presence of barium carbonate, chelated dicarbonyl derivatives have been obtained as follows:

TABLE 1

COMPOUNDS OF FORMULA $(CO)_2Rh(Cl)(ChelH)$

No.	*ChelH*	*Reaction medium and time*	*Isolation (Purification)*	*Formula and colour*	*M.p. (°C)*	*Analyses[a] (%)*		
						C	*H*	*N*
VIII	8-oxy-quinoline	benzene 2 h	filtration	$C_{11}H_7NO_3ClRh$ green-violet[b] [c]	115	38.82 (38.73)	2.06 (1.88)	4.12 (4.50)
IX	salicyl-aldoxime	benzene + $BaCO_3$ 1 h	evaporation (C_6H_6 + pet.ether)	$C_9H_7NO_4ClRh$ brown[b]	106–110	32.6 (33.10)	2.12 (2.30)	4.24 (4.48)
X	benzoin-oxime	benzene + $BaCO_3$ 1 h	evaporation (C_6H_6 + pet.ether)	$C_{16}H_{13}NO_4ClRh$ dark-brown[b]	190	45.6 (46.10)	3.1 (3.40)	3.32 (3.53)

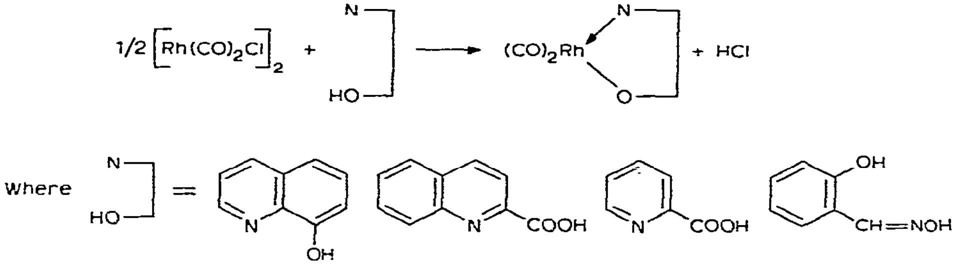
[a] Calcd/(found); [b] yellow in $CHCl_3$ soln.; [c] dichroic.

TABLE 2

COMPOUNDS OF FORMULA LL'(M)Chel

No.	*M*	*L/L'*	*Chel*	*Reaction medium and time*	*Isolation (Purification)*	*Formula and colour*	*M.p. (°C)*	*Analyses*[a]			
								C (%)	*H (%)*	*N (%)*	*Mol.wt.*
I	Rh	CO	8-oxyquinolate	MeOH	filtration	$C_{11}H_6NO_3Rh$	210	43.6	1.98	4.63	—
		CO		2 h		black-violet[b,d]		(43.78)	(2.16)	(5.0)	
II	Rh	CO	quinaldinate	MeOH	filtration	$C_{12}H_6NO_4Rh$	193	43.5	1.81	4.23	—
		CO		1 h		orange[e]		(43.27)	(1.78)	(4.40)	
III	Rh	CO	α-pyridine-	benzene +	concentration	$C_8H_4NO_4Rh$	200	34.2	1.42	5.0	—
		CO	carboxylate	$BaCo_3$ 1 h	(C_6H_6 + pet. ether)	green-violet[c,d]		(34.35)	(1.38)	(5.20)	
IV	Rh	CO	salicyl-	MeOH +	concentration	$C_9H_6NO_4Rh$	147	36.5	2.03	4.75	—
		CO	aldoximate	$BaCO_3$ 2 h		red-orange[e]		(36.39)	(1.96)	(4.66)	
V	Ir	CO	quinaldinate	MeOH	filtration	$C_{12}H_6NO_4Ir$	250	34.2	1.42	3.33	—
		CO		2 h		dark-green[c,d]		(33.39)	(1.33)	(3.20)	
VI	Ir	CO	α-pyridine-	MeOH	filtration	$C_8H_4NO_4Ir$	240	25.8	1.08	3.77	—
		CO	carboxylate	< 0.1 h		violet[c,d]		(24.70)	(1.04)	(3.50)	
VII	Ir	CO	8-oxyquinolate	isopropanol	filtration	$C_{11}H_6NO_3Ir$	300	33.6	1.53	3.57	—
		CO		< 0.1 h	H_2O washings	black[b]		(32.50)	(1.81)	(3.62)	
XI	Rh	CO	8-oxyquinolate	benzene	evaporation	$C_{28}H_{21}NO_2PRh$	148	62.6	3.91	2.61	537
		Ph_3P		1 h	(C_6H_6 + pet. ether)	yellow		(61.80)	(3.74)	(2.49)	(572)[c]
XII	Rh	CO	8-oxyquinolate	benzene	evaporation	$C_{28}H_{21}NO_2AsRh$	168	57.8	3.61	2.41	—
		Ph_3As		1 h	(C_6H_6 + pet. ether)	yellow		(58.30)	(3.42)	(2.56)	
XIII	Rh	DPE	8-oxyquinolate	benzene	concentrn. + pet. ether	$C_{35}H_{30}NOP_2Rh$	270	65.0	4.65	2.17	645
				10 h reflux		yellow-orange		(64.59)	(4.60)	(2.18)	(613)[c]
XIV	Rh	CO	8-oxyquinolate	benzene	evaporation	$C_{18}H_{18}NO_2Rh$	125	56.4	4.7	3.65	383
		1,3-COD		15 h reflux	(pet. ether washings)	yellow		(56.59)	(4.93)	(3.69)	(380)[c]
XV	Rh	1,5-COD	8-oxyquinolate	benzene	evaporation	$C_{17}H_{18}NORh$	170	57.5	5.08	3.94	355
				3 h reflux	(pet. ether washings)	orange		(56.6)	(4.87)	(4.02)	(375)[c]
XVI	Ir	CO	8-oxyquinolate	benzene	evaporation	$C_{28}H_{21}NO_2PIr$	160	53.6	3.37	2.23	—
		Ph_3P		2 h	(C_6H_6 + pet. ether)	yellow		(53.92)	(3.90)	(2.26)	
XVII	Ir	CO	8-oxyquinolate	toluene	evaporation	$C_{18}H_{18}NO_2Ir$	180	—	—	—	473
		1,5-COD		8 h reflux	(pet. ether washings)	yellow	dec.				(462)[c]

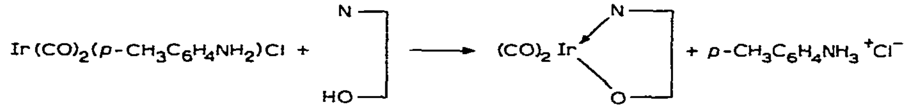
[a] Calcd/(found); [b] yellow-orange in $CHCl_3$ soln.; [c] chloroform; [d] dichroic; [e] yellow in $CHCl_3$ soln.



Some of these compounds (Table 2.) are dichroic in the solid state.

It is particularly interesting that compounds(II) and (III) with almost similar donor atoms but chelating ligands of different size are of different colour in the solid state.

Analogous iridium derivatives have been obtained in the following manner:



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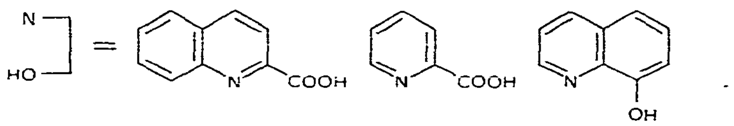
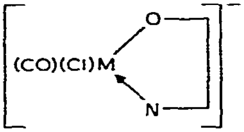


Some of the iridium compounds (Table 2) are also dichroic in the solid state. The quinaldinate derivative (V) is very different in appearance from the analogous rhodium derivative (II), which is not dichroic.

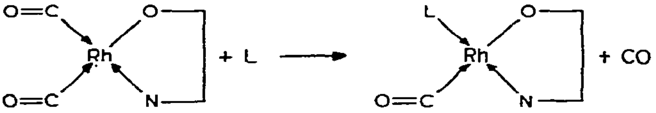
All the rhodium derivatives, and particularly the iridium derivatives, reacted slowly with chloride anion giving methanol-soluble salts of type,



The reaction of a ligand such as benzoinoxime with $[Rh(CO)_2Cl]_2$ did not produce a chelated compound, even in the presence of $BaCO_3$.

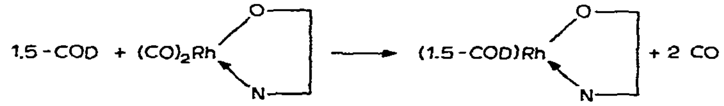
SUBSTITUTION REACTIONS

Rhodium derivatives reacted easily with ligand L ($L = PPh_3, AsPh_3$) as follows:



It is probable that the carbonyl group *trans* to the nitrogen atom is more easily substituted since the tertiary heterocyclic nitrogen has a stronger *trans* effect than oxygen but both isomers were apparently isolated (see infrared spectra). With a chelating diphosphine ($Ph_2P–CH_2CH_2–PPh_2 = DPE$), complete substitution of the carbonyl groups was obtained but this substitution was more difficult in the case of iridium derivatives, as previously found for the β-diketonate compounds[2]. All substitution derivatives were yellow or orange-yellow in the solid state and were not dichroic.

The substitution reactions with chelating diolefins were more interesting. In the case of the reaction of rhodium 8-oxyquinolate derivative (I) and 1,5-cyclooctadiene (1.5–COD) the complete substitution of the two carbonyl groups was easily effected:



With 1,3-cyclooctadiene (1.3–COD), only one carbonyl group was substituted, even under more drastic conditions. However, in the presence of traces of HCl complete substitution of all carbonyl groups was possible under very mild conditions. We have found that a prepared monosubstituted derivative with 1.3–COD changed in the presence of HCl into a yellow compound containing no carbonyl ligand. This compound was identical with that obtained by direct interaction of (I) with 1.5–COD. This shows that in these complexes 1.3–COD cannot isomerize by a hydrogen abstraction[6] mechanism but can rapidly isomerize when HCl is added, possibly by the hydridic mechanism proposed by Cramer[7] for similar compounds. However, when 1.3–COD reacted with (I) in the presence of HCl, (1.5–COD)Rh(8-oxyquinolate) was obtained but the excess of diolefine did not show any appreciable isomerization.

It is possible that compounds such as (1.5–COD)Rh(8-oxyquinolate) substitute the diolefin very slowly so that isomerization cannot be catalytic. In fact, it was found that similar compounds such as $(C_2H_4)_2Rh(\pi\text{-}C_5H_5)$ did not substitute C_2H_4, although similar compounds with acetylacetone did[8].

The substitution of iridium compounds was, as expected[2], more difficult. With 1.5–COD, a monosubstituted derivative was isolated after 8 h of reaction in boiling toluene. The complete substitution of all carbonyl groups was obtained, in very low yield, only after six days of reaction.

INFRARED SPECTRA

All unchelated and chelated compounds showed two strong carbonyl absorptions (Tables 3 and 5). The position of these shifted very little on changing the chelated ring. However, there was a slight difference at higher frequencies with amminoacid ligands [compounds (II), (III), (V), (VI)] compared with 8-oxyquinoline [compounds (I), (VII)]. A shift of nearly 5–10 cm^{-1} at lower frequencies was found between rhodium and iridium compounds, as for the corresponding β-diketonato derivatives[2].

In the solid state, all compounds gave a complex spectrum pattern in the carbonyl stretching region, showing that the site symmetry of the molecules in the crystals was more complex than in solution, possibly because of a metal–metal interaction. In the monosubstituted compounds, the carbonyl bands shifted at lower frequencies as expected (Table 4). The iridium compounds, however, showed higher values for the carbonyl stretching frequency than those of the related rhodium compounds. This

TABLE 3

INFRARED SPECTRA OF COMPOUNDS OF FORMULA $(CO)_2M(Chel)$

	M	*Chel*	*ν(C=O)(nujol)(cm^{-1})*	*ν(C=O) ($CHCl_3$ soln.)(cm^{-1})*	*Other absorptions (nujol)(cm^{-1})*
(I)	Rh	8-oxyquinolate	2070s, 2054vs, 2010sh 1995s, 1989s, 1952w	2073vs, 2006s	1579–1570
(II)	Rh	quinaldinate	2102s, 2092s, 2022s	2093vs, 2015s	1682 ν_{as}(C=O), 1601–1572
(III)	Rh	α-pyridinecarboxylate	2093s, 2067w, 2037s 2007w, 1979vw	2095vs, 2023s	1676 ν_{as}(C=O) 1609
(IV)	Rh	salicylaldoximate	2083s, 2013s, 1973w	2088vs, 2018s	1603 ν(C=N)
(V)	Ir	quinaldinate	2078s, 2058sh, 2008s 1970sh	2085vs, 2003s	1708 ν_{as}(C=O) 1590–1578
(VI)	Ir	α-pyridinecarboxylate	2083s, 2015s (broad)	2085vs, 2002s	1680 ν_{as}(C=O) 1608
(VII)	Ir	8-oxyquinolate	—	2072vs, 1991s	—

TABLE 4

INFRARED SPECTRA OF COMPOUNDS OF FORMULA $(CO)LM(Chel)$

M	*Chel*	*L*	*ν(CO) ($CHCl_3$ soln.)(cm^{-1})*	*Other absorptions (nujol)(cm^{-1})*
Rh	8-oxyquinolate	PPh_3	1965	1569
Rh	8-oxyquinolate	$AsPh_3$	1950	1570
Rh	8-oxyquinolate	1.3–COD	1981	1565
Ir	8-oxyquinolate	PPh_3	2000	1573
Ir	8-oxyquinolate	1.5–COD	2006	1570

TABLE 5

INFRARED SPECTRA OF COMPOUNDS OF FORMULA $(CO)_2Rh(Cl)(ChelH)$

	ChelH	*ν(CO)(nujol)(cm^{-1})^{a}*	*Other absorptions(nujol)(cm^{-1})*
(VIII)	8-oxyquinoline	2075vs, 2010s	1600, 3250 ν(OH)(broad)
(IX)	salicylaldoxime	2087vs, 2030s	1598 ν(C=N), 3200 ν(OH)(broad)
(X)	benzoinoxime	2080s, 2010s	1600, 3400–3200 ν(OH)(broad)

[a] All these bands are asymmetric.

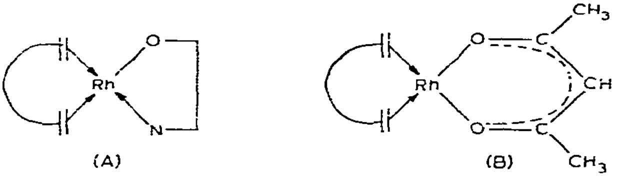
unusual behaviour can be explained by assuming that the two metals gave different isomers (with the ligand *trans* to O or N).

Some typical ligand absorptions changed very little on passing from the free to the chelated ligands (Tables 3 and 5). The 1600 cm^{-1} absorption,characteristic of the heteroaromatic ring of chelating ligands used, showed no shift. In the case of the salicylaldoximate, the ν(C=N) band was shifted nearly 30 cm^{-1} towards lower frequencies. Substitution of a carbonyl group with PPh_3, $AsPh_3$, 1.5–COD or 1.3–COD, lowered the 1600 cm^{-1} absorption band of the 8-oxyquinolate ligand by nearly 20–30 cm^{-1} (Table 4).

The asymmetric ν(C=O) band of the carboxylic group was found in the region 1670–1680 cm^{-1}, as expected for an unchelated carboxylic group[9], so that a possible pentacoordination can be ruled out. This value is higher than that found in more polar carboxylate[9] complexes indicating that the metal–oxygen bond is highly covalent. All the unchelated compounds showed very broad OH absorptions (Table 5) which confirmed the proposed non-chelated structures; the shift at 1598 cm^{-1} of the ν(C=N) band of the salicylaldoximate derivative showed that the ligand was coordinated by the nitrogen atom.

NMR SPECTRA*

The NMR spectra of 1.5-cyclooctadiene (1.5–COD)Rh(Chel) derivatives with 8-oxyquinoline as chelating ligand showed clearly a different distribution of the electronic density *trans* to oxygen or nitrogen (A). The rhodium derivative gave at room temperature two broad peaks at $\tau = 5.70$ and $\tau = 5.12$, corresponding to two different types of olefin bound to the metal.



A symmetrical derivative such as (1.5–COD)Rh($C_5H_7O_2$) (B) showed only one signal at τ 5.88. We can thus assign the signal at τ 5.70 of the 8-oxyquinoline derivative to the olefinic bond *trans* to the oxygen. It appears then that the position *trans* to the tertiary nitrogen has less electronic density than the position *trans* to the oxygen and a different reactivity of the two positions can therefore be predicted.

CONCLUSIONS

The results confirm that the metal–metal interaction[3,4] in d^8 complexes of type $(CO)_2M$(Chel) (M = Rh, Ir) is probably present also when the symmetrical chelated ring of β-diketonate ligands[1,2] is substituted with the asymmetric chelated ring of aminoacids or aminophenols (where nitrogen is in a heterocyclic ring), or other ligands with N and O as donor atoms. The presence of a metal–metal interaction is demonstrated by the dark colours and the dichroism of these compounds and by their complex infrared spectra in the solid state. However, in the case of 8-oxyquinolate compounds, a π charge transfer interaction[10] in the solid state between the nonbonding electrons on the metal and the π-acceptor system of the ligand, cannot be ruled out, particularly for the iridium compound.

The strength of the metal–metal interaction seems to be affected by two factors: the electronic density[3] on the metal and steric effects. The necessity of steric requirements is demonstrated by comparing the rhodium derivatives of quinaldic and α-pyridine carboxylic acids. In both cases, the electronic density on the metal atom should be the same, but although the α-pyridine carboxylate is dichroic in the solid state, the quinaldinate is not. Iridium quinaldinate, however, is dichroic showing

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* A full study of NMR spectra at different temperatures of these, and similar 1.5-cyclooctadiene, compounds will be reported in another paper.

that in the iridium atom the electronic density in the direction of the metal–metal interaction is higher than that in the rhodium atom[4] so that this interaction is easier despite the steric properties of the chelated ligand. The balance between electronic and steric effects gives the conformation of these molecules in the solid state. We believe that steric requirements are often more important in dictating the presence of a metal–metal interaction. In fact, on substituting a carbonyl group by a ligand like PPh_3 or $AsPh_3$, which should increase the electronic density on the metal, any metal–metal interaction disappeared in every case[2,3]. Clearly, the bulky dimensions of PPh_3 and $AsPh_3$ do not allow metal–metal interaction despite the higher electronic density on the metal.

EXPERIMENTAL

Preparation of the compounds

All reactions were carried out in air, with good yields in every case (~60%). Evaporation was always carried out under reduced pressure (10–50 mm Hg), unless otherwise stated. Melting points were determined in air and are uncorrected. Molecular weights were measured on a Mechrolab Osmometer. Infrared spectra were taken on a Perkin–Elmer model 237 instrument. Proton NMR resonance spectra were recorded with a Perkin–Elmer R 10 machine, operating at 60.0 Mc; $CDCl_3$ was used as solvent and tetramethylsilane as internal standard.

All the compounds synthesized are reported in Tables 1 and 2 and were prepared as in the following examples, modified according to the data given in the Tables.

Dicarbonyl(8-oxyquinoline)rhodium(I) chloride (*VIII*). A benzene solution (30 ml) of 8-oxyquinoline (0.145 g) was added slowly with stirring to a benzene solution (20 ml) of $[Rh(CO)_2Cl]_2$ (0.194 g). A yellow compound was suddenly formed; this changed to a green-violet colour. After 2 h, the compound was collected by filtration.

Dicarbonyl(8-oxyquinolate)rhodium(I) (*I*). A methanolic solution (30 ml) of 8-oxyquinoline (0.290 g) was added with stirring to a methanolic solution (30 ml) of $[Rh(CO)_2Cl]_2$ (0.194 g). A black-violet compound suddenly precipitated. After 2 h, the compound was collected by filtration and washed with petroleum ether.

Dicarbonyl(8-oxyquinolate)iridium(I) (*VII*). An isopropanol solution (50 ml) of 8-oxyquinoline (0.145 g) was added with stirring to a solution (20 ml) in the same solvent of $[Ir(CO)_2(p\text{-}CH_3C_6H_4NH_2)Cl]$[11] (0.392 g). A black compound suddenly precipitated. It was collected by filtration, washed several times with water and dried under vacuum.

Carbonyl(triphenylphosphine)(8-oxyquinolate)rhodium(I) (*XI*). Triphenylphosphine (0.131 g) was added to a benzene suspension (50 ml) of dicarbonyl(8-oxyquinolate)rhodium(I) (0.151 g). Gas was evolved. After 1 h, the yellow-orange solution was evaporated to dryness and the residue crystallized from benzene and petroleum ether.

(1,5-cyclooctadiene)(8-oxyquinolate)rhodium(I) (*XV*). Freshly-distilled 1,5-cyclooctadiene (1 ml) was added to a benzene suspension (50 ml) of dicarbonyl-(8-oxyquinolate)rhodium(I) (0.303 g). The solution was refluxed for 3 h and then evaporated to dryness. The residue was washed with a small quantity of petroleum ether, to yield an orange-coloured compound. The IR spectrum did not show any carbonyl stretching band.

(1,5-cyclooctadiene)(8-oxyquinolate)iridium(I) (XVIII). Freshly-distilled 1,5-cyclooctadiene (2 ml) was added to a toluene suspension of dicarbonyl(8-oxyquinolate)iridium(I) (0.393 g). The solution was refluxed for 7 days and then evaporated to dryness. The residue was washed with petroleum ether to yield an impure yellow-brown compound. This compound did not show any carbonyl stretching band in the IR spectrum but the NMR spectrum showed the presence of a coordinate diolefin. All attempts to purify it were unsuccessful.

Reaction of (I) with 1,3-cyclooctadiene in the presence of HCl. Freshly-distilled 1,3-cyclooctadiene (2 ml) was added to a methanolic suspension (30 ml) of (I) (0.303 g) in the presence of traces of hydrochloric acid. After 1 h, the yellow solution was evaporated to dryness and the residue extracted with benzene; the extract was dried over $MgSO_4$. On evaporation to dryness, the completely substituted compound identical with (XV) was obtained. The distilled excess of diolefin did not show any appreciable isomerisation, however. The same compound was also obtained by allowing (XIV) to react in benzene solution with traces of hydrogen chloride.

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SUMMARY

The preparation and properties of compounds of formula $[(CO)_2M(Chel)]$ (M = Rh, Ir; Chel = 8-oxyquinolate, quinaldinate, α-pyridinecarboxylate, salicylaldoxymate) are reported. The substitution reactions with PPh_3, $AsPh_3$, 1,5-cyclooctadiene and 1,3-cyclooctadiene are described and compared. Infrared and NMR spectra are discussed.

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