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RHODIUM(I) AND IRIDIUM(I) CARBONYL DERIVATIVES OF SOME SCHIFF BASES OF ACETYLACETONE

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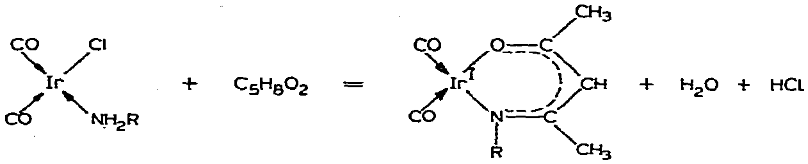
INTRODUCTION

Recent work[1,2,3] has shown that it is possible to synthesize chelated metal carbonyl derivatives where the chelating moiety is a β-diketonato group. However, similar chelated derivatives of a Schiff base have not so far been reported, except for those described in our preliminary note[4]; the Schiff-base derivatives of iron carbonyl described by Pauson[5] are quite different from our type of compounds. We report here syntheses and some properties of chelated dicarbonyl-iridium(I) and dicarbonyl-rhodium(I) compounds, where the chelating group is the anion derived from the condensation product of a primary amine and acetylacetone. This product can exist either in the form of enamine or in the form of a Schiff base; the two forms are in equilibrium, which lies well over towards the ketimine form.

SYNTHESES OF THE COMPOUNDS

Iridium derivatives were prepared from [$(CO)_2$(amine)IrCl][6] and acetylacetone. With aromatic amines (aniline, *p*-toluidine, α-naphthylamine) the reaction gave the corresponding dicarbonyl(2-aryliminopenten-3-olato-4)iridium(I), identified by analyses, IR and NMR spectra:



(I: R=*p*-tolyl; VII: R=phenyl; IX: R=α-naphthyl)

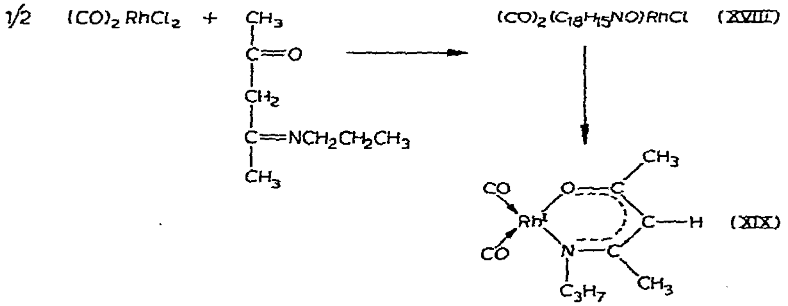
The compounds are soluble in non-polar organic solvents and can be sublimed under vacuum. This afforded a convenient separation from an ionic *cis*-bishalogenocarbonyliridate(I), $[(CO)_2IrX_2]^-$, which was isolated as the tetraphenylarsonium salt. With aliphatic amines, the green derivative of the Schiff base formed when *n*-propylamine was used, whereas isopropylamine gave the golden-yellow, N-free dicarbonyliridium (I) acetylacetonate, (III).

In order to confirm the proposed structures by an independent synthesis, we used the crude product[7] obtained by treating Na_3IrCl_6 with carbon monoxide under pressure, "$Na_2[Ir_2(CO)_4Cl_{4.8}]$". This was treated with excess Schiff base to give the required compound. This synthesis, however, cannot be recommended. When an excess of Schiff base was used, the usual purification by sublimation was very difficult since the ligand has roughly the same volatility as the reaction product. Repeated washing with aqueous alcohol was effective in removing the excess ligand, but this resulted in a heavy loss of product. An excess of ligand could rarely be avoided, since the "purity" of the starting material could not be easily established. Further, the N-free chelate, $[(CO)_2Ir(C_5H_7O_2)]$, (III), was formed because of exposure to moisture and had to be separated by fractional sublimation.

Attempts to obtain derivatives from Schiff bases and $[(CO)_3IrBr]$ were unsuccessful, although the N-free chelate, (III), was prepared in an analogous way from acetylacetone or from a thallium(I)-β-diketonate[2].

The reaction was more complicated when monovalent rhodium compounds were used. The complex, $[(CO)_2(p\text{-toluidine})RhCl]$, reacted with acetylacetone in benzene; red-green $[(CO)_2Rh(C_5H_7O_2)]$, (XIV), red or yellow dicarbonyl(2-*p*-tolyliminopenten-3-olato-4)-rhodium(I), (XIII), and yellow $[p\text{-}CH_3C_6H_4NH_3]^+$-$[cis\text{-}(CO)_2RhCl_2]^-$, (XV), were isolated. No simpler reaction was obtained by treating $[(CO)_2RhCl]_2$ with 2-*p*-tolylimino-penten-3-ol-4. When petroleum ether was used as a solvent, both (XIII) and (XV) were isolated; when benzene was added, to improve the solubility of the reagents, some $[(CO)_2(p\text{-toluidine})RhCl]$, (XXIII), was formed after a short time, probably owing to the presence of moisture in the solvent, and the compound (XIII) was only isolated later. The latter reaction was used successfully to obtain the N-phenyl derivative, (XI). However, the sterically-hindered condensation product from 2,6-dimethylaniline and acetylacetone reacted with $[(CO)_2RhCl]_2$ to give $[(CO)_2(2,6\text{-dimethylaniline})RhCl]$, (XXI), because of moisture in the solvent, but only an intractable oil was isolated when an anhydrous solvent was used. The complex, $[(CO)_2(2,6\text{-dimethylaniline})RhCl]$, reacted with acetylacetone or its thallium(I) derivative to give a quantitative yield of $[(CO)_2Rh(C_5H_7O_2)$, (XIV): the corresponding N-containing chelate was never isolated when this amine was used.

The reaction of $[(CO)_2RhCl]_2$ with 2(n-propylimino)penten-3-ol-4 gave an intermediate, yellow compound which analysed as the 1:1 adduct of monomeric rhodium carbonyl chloride and the organic ligand.



The adduct, (XVIII), is unstable and could be converted into the N-containing chelate, (XIX), when heated in solution. Compound (XIX) was not isolated when $[(CO)_2RhCl]_2$ was treated with the corresponding Schiff base or when $[(CO)_2(C_3H_7NH_2)$-

RhCl] was treated with acetylacetone in benzene: in all cases a small quantity of the N-free chelate, (XIV), was found, together with a large amount of dark oil, probably a decomposition product of the adduct (XVIII), formed as an intermediate.

The formation of the different reaction products can be explained by assuming that the following equilibrium exists in solution:

$$\text{(B)}\quad [(CO)_2(\text{amine})MX] + n(\text{solvent}) \rightleftharpoons [(CO)_2(\text{solvent})_n MX] + \text{amine}$$

There is evidence for this from the electronic spectra[8]. A similar equilibrium had been observed also[9] by us with the analogous $[(CO)_2(\text{nitrile})RhCl]$ complexes. The solvated species, $[(CO)_2(\text{solvent})_n MX]$, may react either with acetylacetonate (acac) or with chloride ion or with a Schiff base, yielding $[(CO)_2M(\text{acac})]$ or $[(CO)_2MX_2]^-$ or a 1:1 adduct such as (XVIII):

$$\text{(C)}\quad \begin{aligned} &[(CO)_2(\text{solvent})_n MX] + \text{acac}^- = n\ \text{solvent} + [(CO)_2M(\text{acac})] + X^- \\ &[(CO)_2(\text{solvent})_n MX] + X^- = n\ \text{solvent} + [(CO)_2MX_2]^- \\ &[(CO)_2(\text{solvent})_n LX] + (C_8H_{15}NO) = n\ \text{solvent} + [(CO)_2(C_8H_{15}NO)RhX] \end{aligned}$$

The 1:1 adduct then cyclizes according to reaction (A) and the β-ketoiminate is formed. The other product of the equilibrium reaction (B), reacts with acetylacetone

$$CH_3COCH_2COCH_3 + H_2NR = H_2O + CH_3COCH_2C(=NR)CH_3$$

to give the corresponding Schiff base. This reaction may go through a template mechanism.

The 1:1 adduct may then either cyclize as in (A) or revent to the starting materials or undergo hydrolysis; the last possibility would explain the formation of $[(CO)_2Rh(\text{amine})Cl]$ from $[(CO)_2RhCl]_2$ and a Schiff base, which alone cannot be hydrolyzed so easily. The relative contribution of the two mechanisms to the reaction course cannot at present be evaluated; it must be strongly solvent dependent.

A reaction course proceeding through: (1) intermediate formation of an acetylacetonate, (2) opening of the chelated ring, (3) reaction with amine and (4) final formation of a chelated β-ketoiminate, can be excluded. Indeed, $[(CO)_2Rh(C_5H_7O_2)]$ did not react with *p*-toluidine, even in boiling xylene.

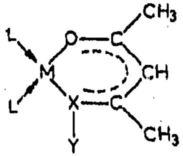
PROPERTIES AND REACTIONS

All the chelated compounds are air-stable, crystalline solids. They are soluble in organic solvents, in which they are monomeric and diamagnetic, and insoluble in water; they can be sublimed under a good vacuum.

The reactivity of iridium and rhodium N-containing chelates was rather different. Compound (XIII) reacted easily with triphenylphosphine and with a chelating diolefin, such as 1,5-cyclooctadiene, to yield the corresponding yellow compounds, (XVI) and (XVIII), having one and no remaining carbonyl group, respectively. Compound (I) reacted with triphenylphosphine to yield either (IV) or (V), but did not react with the diene, even under forcing conditions, although the expected reaction product is known to exist and to be stable: $[(\text{diene})Ir(C_5H_7O_2)]$ was obtained[12] from the chloride and thallium(I) acetylacetonate. Clearly, compound (I) has to be considered as kinetically inert. This behaviour is seen also in the lack of reaction of

TABLE 1

COMPOUNDS WITH CHELATED RING



No.	M	L	L	X	Y	Formula and colour	m.p.	Analyses[f]			
							(°C)	C	H	N	Mol. wt.
I	Ir	CO	CO	N	4-$CH_3C_6H_4$	$C_{14}H_{14}IrNO_3$[d] yellow[e]	153[e]	38.4 (38.7)	3.3 (3.4)	3.2 (3.4)	437 (450)[b,c]
III	Ir	CO	CO	O	—	$C_7H_7IrO_4$ golden yellow	158 decomp.	24.2 (23.9)	1.7 (2.3)	0.0 (0.0)	347 (362)[a]
IV	Ir	CO	Ph_3P	N	4-$CH_3C_6H_4$	$C_{31}H_{29}IrNO_2P$ yellow	184	55.4 (55.7)	4.4 (4.6)	2.1 (2.0)	672 (680)[c]
V	Ir	Ph_3P	CO	N	4-$CH_3C_6H_4$	$C_{31}H_{29}IrNO_2P$ yellow	134	55.4 (55.8)	4.4 (4.4)	2.1 (2.1)	672 (708)[c]
VII	Ir	CO	CO	N	C_6H_5	$C_{13}H_{12}IrNO_3$ red	139	36.9 (36.8)	2.9 (2.8)	3.3 (3.4)	423 (409)[b]
IX	Ir	CO	CO	N	α-$C_{10}H_7$	$C_{17}H_{14}IrNO_3$ pale yellow	134	43.1 (43.6)	3.0 (3.3)	3.0 (3.1)	473 (457)[b]
X	Ir	CO	CO	N	n-C_3H_7	$C_{10}H_{14}IrNO_3$ green	109	31.0 (31.3)	3.6 (3.4)	3.6 (3.7)	389 (385)[b]
XI	Rh	CO	CO	N	C_6H_5	$C_{13}H_{12}NO_3Rh$ yellow[e]	124	46.9 (47.0)	3.6 (3.9)	4.2 (4.3)	339 (323)[b]
XIII	Rh	CO	CO	N	4-$CH_3C_6H_4$	$C_{14}H_{14}NO_3Rh$ yellow[e]	133[e]	48.4 (48.9)	4.1 (4.3)	4.0 (4.3)	347 (267)[b]
XIV	Rh	CO	CO	O	—	$C_7H_7O_4Rh$ red-green[e]	153	32.6 (32.3)	2.7 (2.8)	— —	258 (253)[b]
XVI	Rh	CO	Ph_3P	N	4-$CH_3C_6H_4$	$C_{31}H_{29}NO_2PRh$ yellow[e]	170	64.0 (64.5)	5.0 (5.2)	— —	— —
XVII	Rh	1,5-cyclooctadiene		N	4-$CH_3C_6H_4$	$C_{20}H_{22}NORh$ yellow	206	60.8 (60.5)	6.6 (6.7)	3.5 (3.6)	— —
XIX	Rh	CO	CO	N	n-C_3H_7	$C_{10}H_{14}NO_3Rh$	101	40.2 (39.7)	4.7 (4.5)	4.7 (4.4)	299 (299)

[a] Acetone; [b] benzene; [c] chloroform; [d] found: Ir, 43.1; O, 10.5; calcd.: Ir, 44.0; O, 10.5%; [e] see text; [f] calcd./(found).

TABLE 2

COMPOUNDS WITHOUT CHELATED RING

No.	*Compound*	*m.p.*	*Formula and colour*	*C*[d]	*H*	*N*	*Cl*
II	$[Ph_4As][Ir(CO)_2Cl_2]$[a]	214–5 (decomp.)	$C_{26}H_2OAsIrO_2Cl_2$ white	45.1 (41.1)	2.8 (3.1)	— —	— —
VI	$[Ir(CO)_2(PhNH_2)Cl]$	190 (decomp.)	$C_8H_7ClIrNO_2$ green-violet	25.4 (25.7)	1.9 (2.1)	3.7 (3.8)	— —
XII	$[Rh(CO)_2(PhNH_2)Cl]$[14]	140 (decomp.)	$C_8H_7ClNO_2Rh$ green-violet	33.4 (33.05)	2.5 (2.6)	4.9 (4.6)	— —
XV	$[p\text{-}CH_3C_6H_4NH_3][Rh(CO)_2Cl_2]$[b]	151	$C_9H_{10}Cl_2NO_2Rh$ yellow	32.0 (32.2)	3.0 (3.2)	4.1 (4.6)	— —
XVIII	$[Rh(CO)_2(C_8H_{15}NO)Cl]$	[c]	$C_{10}H_{15}ClNO_3Rh$ yellow	35.8 (35.5)	4.5 (4.4)	4.2 (4.4)	10.6 (11.2)
XX	$[Rh(CO)_2(iso\text{-}C_3H_7NH_2)Cl]$	63	$C_5H_9ClNO_2Rh$ greenish-brown	— —	— —	— —	14.0 (13.7)
XXI	$[Rh(CO)_2(2,6\text{-}(CH_3)_2C_6H_3NH_2)Cl]$	104 (decomp.)	$C_{10}H_{11}ClNO_2Rh$ yellow	— —	— —	— —	11.2 (11.3)
XXII	$[Rh(CO)_2(n\text{-}C_3H_7NH_2)Cl]$	129 (decomp.)	$C_5H_9ClNO_2Rh$ yellow-green	— —	— —	— —	14.0 (14.2)
XXIII	$[Rh(CO)_2(p\text{-}CH_3C_6H_4NH_2)Cl]$	141	$C_9H_9ClNO_2Rh$ yellow	35.9 (36.0)	3.0 (3.0)	4.7 (4.7)	11.8 (11.8)

[a] $\Lambda(PhNO_2, 10^{-3}\ M)$: 21 ohm^{-1} cm^{2}mole^{-1} at 20°; [b] $\Lambda(PhNO_2, 10^{-3}\ M)$: 17.4 ohm^{-1} cm^{2}mole^{-1} at 25°; [c] gradual decomp. [d] calcd./(found).

(I) with triphenylarsine, and is different also from the easy reactivity of the N-free rhodium chelate, (XIV).

Infrared data are reported in Tables 3 and 4. Strong carbonyl stretching frequencies were observed; their position in the N-containing iridium chelates is at slightly lower frequencies than in the corresponding acetylacetonate. No significant difference was detectable with rhodium compounds; similarly, no significant change was observed on changing the group bonded to nitrogen. The only apprenable low-frequency shift was that observed on passing to the triphenylphosphine derivative, as expected. The presence of the chelated ring was supported by the presence of medium bands in the region 1500–1600 cm^{-1}, due to $C\overset{\cdots}{-}C$, $C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}N$ stretching. The amine complexes showed strong and sharp carbonyl stretchings and rather broad bands due to N–H stretching in the 3200 cm^{-1} region; the latter are absent in the *p*-toluidinium salts, (XV).

NMR spectra support the proposed formulae (Table 5). No satellite band due to ^{103}Rh $(I=\frac{1}{2})$ or ^{191}Ir$(I=\frac{3}{2})$ or ^{193}Ir $(I=\frac{3}{2})$ was observed, in agreement with the quadruple moment on the iridium nuclei and with the distance between the observed protons and the rhodium. The absence of coupling between ^{103}Rh and the middle hydrogen on the ring rules out an alternative structure with a direct Rh–C bond, as found quite recently for some rhodium chelates[13]; besides, a similar structure had already been ruled out by the molecular weight measurements, which showed that our compounds are monomeric.

Some of the compounds exist in two different crystalline forms with different colours and different IR spectra in the solid state, but with the same spectrum in solution. Compound (I) can be isolated either as red needles or as yellow crystals: the former were obtained by sublimation at 100°/0.1 Torr and were converted to the yellow form by heating, even under nitrogen, above 120°: the m.p. is that of the yellow form (155°). The change from the red to the yellow form took place slowly also at lower temperatures, *e.g.* at 100° in a few hours, at room temperature in a few months. This indicates that the yellow form is the stable one; it is even more stable in the related rhodium complexes, (XI) and (XII) (see experimental part). The solutions of either the red or yellow crystals afforded a yellow residue, especially on rapid evaporation of the solvents under vacuum.

A possible explanation for the existence of two forms, as in dicarbonylrhodium(I)-3-allylacetylacetonate[1], is that the red form can associate in the solid state (like nickel(II) acetylacetonate[10]) by a tricoordinated oxygen (or nitrogen), or (like $[(CO)_2Rh(C_5H_7O_2)]$[1], or [(CO)$_2$(aniline)IrCl][6]) by means of a metal–metal bond. An intramolecular association through a tricoordinated oxygen atom would be in agreement with the observation that rather bulky substituents on the nitrogen atom in the ring, such as phenyl or a *p*-tolyl group, do not hinder the appearance of dimorphism. However, only an X-ray structural determination could settle the question unambiguously.

EXPERIMENTAL

All the initial reactions were carried out under nitrogen, but the working up of the products was carried out under atmospheric conditions. Melting points were determined in air and are uncorrected. Molecular weights were determined on a

Mechrolab Osmometer and are reported in Tables 1 and 2. In Tables 3 and 4 are recorded the relevant infrared data obtained with Perkin-Elmer 137 and 237 instruments. Proton NMR resonance spectra (Table 5) were recorded with a Perkin-Elmer R10 machine, operating at 60.0 Mc; unless stated otherwise, $CDCl_3$ was used as solvent and tetramethylsilane as internal standard. Evaporation was always carried out under reduced pressure (10–50 mm Hg), unless stated otherwise. Nearly all the analytical data are in Tables 1 and 2.

TABLE 3

IR DATA OF COMPOUNDS WITH CHELATED RING

No.		*Carbonyl region*[a]	*1500–1600 cm^{-1} region*[a]
I	H	2062, 1990	—
	N[b]	2062w. 2046, 1991w, 1973	1576sh, 1564m, 1553sh, 1522sh
	N[c]	2060, 2049sh, 1998, 1944w	1518, 1512, 1502
III	H	2087, 2002	—
	N	2061sh, 2046, 1986	1570sh, 1562, 1531
IV	D	1960	—
V	D	1962	—
VII	D	2070, 1995	1565w, 1525m
	N	2063m, 2040, 1990m, 1971	1562w, 1550w, 1512m, 1483m
IX	D	2060, 1981	—
	N	2055, 1990	1587m, 1557m, 1523, 1497m
X	H	2062, 1972	—
	N	2057w, 2034, 1966, 1922w	1595w, 1586w, 1565w, 1581m, 1493w
XI	H	2078, 2050vw, 2005, 1975vw, 1965vw	—
	D	2073 2005	1595w, 1568w, 1557sh, 1515m
	N[c]	2065, 2043sh, 2005, 1960m	1591sh, 1572m, 1541w, 1512
XIII	N[c]	2087m, 2068, 2057m, 2030m, 2000, 1990, 1950w	1582m, 1562m, 1543w, 1518m, 1502m
	N[b]	2078m, 2068, 2058, 2030w, 2010, 2000, 1985m	—
XIV	H	2083, 2066w, 2015, 1987w	1553, 1513 (CCl_4)
	N	2085w, 2071, 2050w, 2010, 1970w, 1960w	1582w, 1567sh, 1562m, 1550sh, 1523
XVI	D	1976	1578sh, 1573w, 1514m, 1503
XVII	D	empty	1575sh, 1567m, 1518, 1504
XIX	D	2085, 2075, 2015, 2005	1570sh, 1565, 1530, 1510sh
	N	2070, 2050, 2003, 1982	1586, 1576, 1516, 1494

[a] H: hexane solution; D: dichloromethane solution; N: nujol mull. Strong bands, unless stated; [b] red form; [c] yellow form.

Preparation of starting materials

Compounds with the general formula $[(CO)_2(amine)RhCl]$ and $[(CO)_2(amine)IrCl]$ were prepared from $[Rh(CO)_2Cl]_2$ and from halogenocarbonyliridates according to literature methods[6,14] or extensions of them.

Crude "$Na[Ir_2(CO)_4Cl_{4.8}]$" was prepared[7] by heating sodium hexachloroiridate(III) at 120° under 200 atm of carbon monoxide in the presence of copper wire for 3 h. Schiff bases and amines were distilled or crystallized before use.

TABLE 4

IR DATA OF COMPOUND WITHOUT CHELATED RING

Compound	*Carbonyl region*[a]	*1500–1600 region*	*Other data*
VI	2090, 2052, 2024 m 2000, 1983, 1961 w 1950 w; 2075, 1995 (CH_2Cl_2)	1620 w, 1609 m, 1568 m	3250 m, 3196 sh
XII	2100, 2070, 2035 2015, 2002 m, 1995 w 1970 w	1605 m, 1568 m, 1498 m	3235, 3200
XV	2092, 2028	1583 w, 1563 w, 1556 w 1514 w, 1500	
XVIII	2059, 1994, 1970 w	1601, 1580, 1570 1549, 1537, 1505	3200 w
XX	2086, 2066 m, 2030 1992 m	1560 sh, 1554 m 1540 sh	3275 m, 3225 m
XXI	2081, 2046 m, 2010 1963 m	1596 m, 1583 m, 1570 m	3270, 3230, 3140
XXII	2095, 2060, 2027 2018, 1985, 1960 w	1570 sh, 1564	3275 m, 3235 m
XXIII	2095, 2066 m, 2055 m 2035, 1997 m, 1980 w	1612 w, 1550 w, 1513	3347

[a] Nujol mull and strong bands, unless stated.

TABLE 5

PROTON MAGNETIC RESONANCE DATA

Compound	*Signal position and area*[a] *Ring* CH_3	*Ring CH*	*Group on the nitrogen*
I	8.23 [3], 7.87 [3],	4.59 [1],	7.62 [3], 2.97 [4] quartet
III[b]	8.18 [6]	4.33 [1],	—
VII	8.22 [3], 7.83 [3]	4.57 [1],	2.46–3.07 [5] complex
X	7.94 [3], 7.89 [3],	4.77 [1],	*ca.* 7.8–9.1 complex
XIV	7.89 [6]	4.48 [1],	—

[a] $CDCl_3$ soln.; [b] CS_2 soln.

Dicarbonyl[2(p-tolylimino)penten-3-olato-4]iridium(I) (I)

(a) Dicarbonyl(*p*-toluidine)chloroiridium(I) (2.0 g) and pentan-2,4-dione (2.0 ml) were dissolved in benzene (150 ml) and refluxed for *ca.* 5 h. The dark-violet solution was filtered and evaporated to dryness. The residue was extracted again with benzene (2 × 50 and 2 × 30 ml); the extract was evaporated to dryness and the residue sublimed at 100–110°/0.2 Torr. The compound, (I), was obtained as yellow crystals (0.350 g), m.p. 153°; sometimes red crystals or mixtures of red and yellow crystals were produced (see under *properties*). Compound (I) was recovered unchanged (m.p., IR spectrum) after treatment of its solution in petroleum ether with excess

1,5-cyclooctadiene, for *ca.* 4 h at room temperature or in benzene solution for 8 h under reflux, or after treatment with norbornadiene for 48 h under reflux in petroleum ether. Similarly, no gas was evolved on the addition of Ph_3As in petroleum ether and the starting compounds were recovered. The brown residue left after the extraction with benzene was found to be sparingly soluble in CH_2Cl_2, and CS_2, but more soluble in C_2H_5OH. In all cases, a remarkable series of colour changes were observed on dissolving the compound. All these solutions reacted with $[Ph_4As]Br$ or with $[(CH)_3(PhCH_2)N]Cl$, giving yellow solutions; there was no evidence of a reaction when $NaClO_4$ was used. An IR spectrum could not be obtained on the brown residue, owing to complete absorption by the nujol mull. The brown residue was extracted with boiling ethanol and excess $[Ph_4As]Cl$ was added to the yellow solution. After a short time, a yellow-white precipitate formed, m.p. 214–215°; the IR spectrum showed no absorption of a β-diketonato ring. Compound (II) was crystallized from CH_2Cl_2/petroleum ether, m.p. 214–5°, white (Found: C, 43,05; H, 3,05; $C_{26}H_{20}\cdot AsCl_2IrO_2$ calcd.: C, 43.5; H, 2.8%); Λ, (nitrobenzene, 10^{-3} *M*; 20°), 21.0 ohm^{-1} cm^2 $mole^{-1}$.

(b) Crude "$Na[Ir_2(CO)_4Cl_{4.8}]$" (2.3 g) and sodium bicarbonate (2.0 g) were suspended in toluene (200 ml); 2(*p*-tolylimino)-penten-3-ol-4 (1.0 g) was added and the mixture was refluxed for 55 h. The now intensely coloured solution was filtered and evaporated to dryness: the residue was extracted with boiling petroleum ether. The extract was concentrated to small volume to yield a brick-red precipitate, which was filtered off and washed with dilute ethanol (0.77 g). Sublimation (100°/0.2 Torr) yielded yellowish $[(CO)_2Ir(C_5H_7O_2)]$, (III), m.p. 157°, identified by IR spectrum and a mixed m.p. Above 100°, orange and yellow crystals sublimed, m.p. 152°, identified as the product (I) by a mixed m.p. and IR spectrum. When the reaction was carried out with a larger quantity of the Schiff base, or when the washing with aqueous ethanol was omitted, the product formed but was always contaminated with a substantial quantity of the Schiff base which sublimed with the compound.

(c) An attempt to synthesize the compound by refluxing a benzene solution of $[Ir(CO)_3Br]$ and 2(*p*-tolylimino)penten-3-ol-4 for 48 h in the presence of $NaHCO_3$, was unsuccessful.

Carbonyl(triphenylphosphine) (2-p-tolylimino -penten-3-olato-4)iridium(I)[(IV)and (V)]

Triphenylphosphine (29.6 mg) in petroleum ether was added to a saturated solution of (I) (47 mg) in the same solvent and the solution heated for 1 min on a water bath. A pale-yellow crystalline compound, (IV), precipitated. A benzene solution of (I) (107 mg) was allowed to react with a nearly saturated benzene solution of triphenylphosphine (131 mg) in the same solvent until no more gas was evolved. The addition of petroleum ether gave pale-yellow crystals, (V).

Dicarbonyl(2-anilinopenten-3-olato-4)iridium(I) (VII)

(a) Crude dicarbonyl(aniline)chloroiridium(I), (V), pentan-2,4-dione (2 ml) and benzene (*ca.* 80 ml) were heated under reflux for 17 h. The red-violet filtered solution together with the benzene washings were evaporated and the residue was extracted with boiling petroleum ether. The yellow extract on evaporation left a green residue which was then sublimed at 80–90°/0.1 Torr. The first small amount of sublimate was green, the rest was brilliant red, (VII); both had the same IR spectrum in nujol mull.

The benzene-insoluble part (40 mg) was brownish in colour and its IR spectrum could not be recorded owing to complete absorption. It was dissolved in ethanol, some gas being evolved; the filtered yellow solution was treated with $[Ph_4As]Cl$ and a very pale-green precipitate was obtained, m.p. 220°, similar to (II). The product was not investigated further.

(b) The preparation was carried out as for (I)b, using 2-aniline-pentan-3-ol-4. Purification was somewhat more difficult here, since the Schiff base sublimed at 80–90° and the compound at *ca.* 90°. After a rough separation by sublimation, the sublimed product was washed several times with aqueous ethanol and resublimed to yield a brilliant red compound, (VII), m.p. 139°.

Dicarbonyl[2(α-naphthylimino)penten-3-olato-4]iridium(I) (IX)

Crude dicarbonyl(α-naphthylamine)chloroiridium(I), (VIII), benzene (35 ml) and pentan-2,4-dione (0.6 ml) were heated for 6 h at 60–70°. The filtered solution and the benzene extract (10 ml) of the precipitate were evaporated to yield a greenish residue from which a yellow powder was obtained by treatment with petroleum ether. Sublimation (120–130°/0.2 Torr) gave pale-yellow prismatic crystals, (IX).

Dicarbonyl(n-propylaminopenten-3-olato-4)iridium(I) (X)

(a) Crude "$Na_2[Ir_2(CO)_4Cl_{4.8}]$" (6.3 g), n-propylaminopenten-3-ol-4 (2.5 g) and benzene (150 ml) were refluxed for 16 h. The filtered wine-red solution and washings were evaporated to dryness; the residue was extracted with boiling petroleum ether. On evaporation, this orange-yellow solution left a halogen-free crystalline residue which on sublimation (80–90°/0.2 Torr) yielded green crystals with a golden lustre, (X).

(b) Crude "$Na[Ir_2(CO)_4Cl_{4.8}]$" (1.95 g), benzene (80 ml) and n-propylamine (0.28 g) were refluxed for 4 h. The filtered golden-yellow solution was evaporated to dryness, to yield dicarbonyl(n-propylamine)chrorocoiridium(I). This compound was then refluxed for 5 h in benzene (*ca.* 80 ml) in the presence of pentan-2,4-dione (1 ml). The wine-red solution was evaporated and the oily residue extracted with petroleum ether. The extract was evaporated and the residue sublimed as above, green crystals of (X) being obtained.

Dicarbonyl(2-phenyliminopenten-3-olato-4)rhodium(I) (XI)

(a) Aniline (0.36 g) was added to a saturated solution of $[Rh(CO)_2Cl]_2$ (0.73 g) in petroleum ether. The crude precipitate, (XII), which was $[Rh(CO)_2 \cdot (C_6H_5NH_2)Cl]$, was dissolved in benzene (*ca.* 150 ml), pentan-2,4-dione (1.5 ml) was added and the golden-yellow solution refluxed for 3 h. The solution was then evaporated and the residue washed repeatedly with aqueous ethanol (1 : 1). The part that sublimed around 65° was found, by means of a mixed m.p. with an authentic sample, to be 2-phenylimino-penten-3-ol-4.After a second crop of sublimate (in which a small quantity of organic matter could still be seen under the microscope) had been discarded, the product, (XI), was collected at 70–80°; at this temperature all the material that could be sublimed changed from red to yellow and an yellow sublimate was obtained.

When the reaction time was either 3 or 9 h but the washing with aqueous ethanol was omitted, sublimation (65–100°/0.2 Torr) yielded pink-red crystals, m.p. *ca.* 44°. From the m.p., mixed m.p. and IR spectra this product was found to be mainly 2-phenyliminopenten-3-ol-4 contaminated by product (XI).

(b) The preparation was attempted from $[Rh(CO)_2Cl]_2$ (0.36 g) and 2-phenyliminopenten-3-ol-4 (0.35 g) in benzene (20 ml). After one day's reflux, the solution was evaporated and the brown residue extracted with petroleum ether; the yellow solution gave, after evaporation, a brilliant red residue (0.21 g), which was crystallized from $EtOH-H_2O$ and analysed as follows: C, 39.3; H, 3.10; N, 2.70%; M, 315 (benzene), 303 (chloroform); *i.e.*, a 1 : 1 mixture of (XI) and (XIV).

Dicarbonyl(2-p-tolyliminopenten-3-olato-4)rhodium(I) (XIII)

(a) A benzene solution (30 ml) of dicarbonyl(*p*-toluidine)-chlororhodium(I) (0.7 g) and acetylacetone (2.0 ml) was refluxed for 6 h and allowed to stand for 4 days. A small amount of yellow precipitate was filtered off and the yellow solution evaporated; the oily residue was extracted with boiling petroleum (80 ml), the yellow extract evaporated, and the residue sublimed at *ca.* 0.1 Torr. Below 80° a small amount of dichroic red-green crystals were obtained: they were identified as dicarbonyl-(pentan-2,4-dionato)rhodium(I), (XIV), from the mixed m.p. and IR spectrum. Above 80°, yellow needles were obtained (155 mg), m.p. 133°, (XIII). It was possible to obtain yellow or red crystals or a mixture, according to the temperature at which the sublimation was carried out (see under b). The yellow precipitate was crystallized from benzene–chloroform (1:3) to yield $[p\text{-}CH_3C_6H_4NH_3]^+[(CO)_2RhCl_2]^-$, (XV), $Λ$, (10^{-3} *M* in nitrobenzene), 17.4 ohm^{-1} cm^2 mole^{-1}.

When a similar reaction was tried using 1,1,1,5,5,5-hexafluoropentan-2,4-dione instead of pentan-2,4-dione, the initial rhodium complex was recovered after a 28-h reflux.

(b) $[Rh(CO)_2Cl]_2$ (0.576 g) dissolved in petroleum ether (200 ml) and 2(*p*-tolylimino)penten-3-ol-4 (600 mg) were heated at 35–40° (internal temperature) for 19 h. A chlorine-containing precipitate (144 mg) was filtered off. This decomposed at *ca.* 126–30°; and on sublimation (120°/1 Torr, 6 h) gave yellow crystals (74 mg) which were identified as $[p\text{-}CH_3C_6H_4NH_3]^+[(CO)_2RhCl_2]^-$, (XV), by means of analyses, conductance and the IR spectrum. The yellow solution was evaporated, the residue (771 mg) washed with aqueous ethanol (1 : 1, 4 × 5 ml) and the dark-red residue dissolved in ether (20 ml). The solution was dried over $CaCl_2$, evaporated and the orange-yellow residue (279 mg) sublimed at *ca.* 0.01 Torr. At 50–60°, red and yellow crystals were collected (84.6 mg); at 60–80° only yellow crystals formed (37.8 mg) and no more sublimate was collected from a sample heated to 185°. When the red and yellow crystals were heated at *ca.* 100° they turned yellow; at *ca.* 122° they melted giving a red liquid; on cooling an orange-yellow solid formed; this melted again at *ca.* 125–127° giving the red liquid. The sublimed yellow crystals melted at 121°; after cooling, they melted at 127°; the colour was always yellow.

No successful method of purification was found for either the residue of the residue from evaporation of the $EtOH-H_2O$ washings, or for the sublimation residue.

(c) When $[Rh(CO)_2Cl]_2$ (330.4 mg) in petroleum ether–benzene (15+10 ml) was treated with a solution of 2(*p*-tolylimino)-penten-3-ol-4 (343 mg) in the same solvent (7+3 ml) (since its solubility in the aliphatic hydrocarbon is not good) a yellow precipitate was formed after a short time. The mixture was evaporated and the orange-yellow residue extracted with petroleum ether. The extract gave, on evaporation, a red chlorine-free residue, which on sublimation gave yellow crystals of (XIII); it showed the same chromatic behaviour. The residue from the extraction was crystallized from benzene-petroleum ether to yield a chlorine-containing compound, m.p. 141°, which analysed (C,H,N) as dicarbonyl(*p*-toluidine)rhodium(I) chloride, (XXIII), and had the same IR spectrum.

(d) Attempts to prepare the compound by reacting $[(CO)_2RhC_5H_7O_2]$ with *p*-toluidine in either benzene, acetone or xylene (always at reflux temperature) were unsuccessful. No reaction was evident when dicarbonyl(*p*-toluidine)chlororhodium(I) and 1,1,1,5,5,5-hexafluoropentan-2,4-dione were refluxed for 28 h in benzene. When $[Rh(CO)_2Cl]_2$ and 1,1,1,5,5,5-hexafluoro-2(n-propylimino)penten-3-ol-4 were reacted in boiling ligroin in the presence of $BaCO_3$, only a trace of unreacted rhodium compound was recovered; no other compound was sublimed away from the filtered and evaporated reaction mixture.

Carbonyl(triphenylphosphine)(2-p-tolyliminopenten-3-olato-4)rhodium(I) (XVI)

Triphenylphosphine (100 mg) in petroleum ether was added to a saturated solution of (XIII) (100 mg) in the same solvent. Yellow crystals, (XVI), were collected by filtration after the reaction had proceeded for a short time.

(1,5-cyclooctadiene)(2-p-tolyliminopenten-3-olato-4)rhodium(I) (XVII)

Freshly-distilled 1,5-cyclooctadiene (0.5 ml) was added to a benzene solution of dicarbonyl(2-*p*-tolyliminopenten-3-olato-4)rhodium(I), (XIII), (81.0 mg). After the solution had been heated for 0.5 h on a water bath, it was evaporated to dryness and the residue crystallized from benzene/light petroleum to yield yellow (XVII): its IR spectrum did not show any band due to a carbonyl stretching or to a free double bond.

Dicarbonyl(2-n-propylimino-penten-3-ol-4)chloroiridium(I) (XVIII)

2(n-propylimino)penten-3-ol-4 (218.0 mg) in light petroleum was added dropwise to a solution of $[Rh(CO)_2Cl]_2$ (300.0 mg) in the same solvent (30 ml). A yellow precipitate (380 mg), (XVIII), was filtered off and washed with light petroleum. The compound was analysed immediately since it was unstable and decomposed completely in a couple of days. When the reaction was carried out using 2(isopropylimino)-penten-3-ol-4, a brown oil, which settled on the bottom of the flask, was formed. After standing overnight, the oil gave a small yield of (XIV) identified by mixed m.p. and IR spectrum.

Dicarbonyl(2-n-propylamino-penten-3-olate-4)rhodium(I) (XIX)

Compound (XVIII) was refluxed for 3 h in benzene solution in the presence of excess $BaCO_3$. After the filtered solution had been evaporated a tarry residue was obtained. This was extracted with boiling petroleum ether to yield an orange solution; the violet-reddish residue obtained on evaporation (550 mg) was carefully sublimed at *ca.* 70°/0.1 Torr to give chlorine-free reddish crystals.

Dicarbonyl(pentan-2,4-dionato)rhodium(I) (XIV)

(a) Isopropylamine was added to a cold solution of $[Rh(CO)_2Cl]_2$ (200 mg), in the same solvent. The greenish-brown precipitate of dicarbonyl(isopropylamine)-chlororhodium(I), (XX), was filtered with pentane. The product was then dissolved in benzene (25 ml), pentan-2,4-dione (1.5 ml) was added and the solution heated at 60° for 3 days. The orange-yellow solution was filtered, evaporated to dryness and extracted with petroleum ether to yield on concentration a small quantity of the compound, (XIV), identified by a mixed m.p. and IR spectrum. The residue from extraction was an intractable oil.

The same result was obtained when n-propylamine was used, through the intermediate, (XXII).

(b) 1 ml of a solution of 2,6-dimethylaniline (0.272 ml) in petroleum ether was added to a saturated solution of $[Rh(CO)_2Cl]_2$ (388 mg) in the same solvent. The solution was evaporated to dryness. The solid residue was very soluble in all organic solvents tried, and had two very strong CO bands in the IR spectrum. This compound (350 mg) was refluxed for 15 h in benzene with thallium(I)pentan-2,4-dionate (405 mg). The filtered solution was evaporated to yield the compound, (XIV), (226.5 mg), identified by the m.p. and IR spectrum.

(c) Crude dicarbonyl(2,6-dimethylaniline)rhodium(I) chloride (from 350 mg of $[Rh(CO)_2Cl]_2$, see under (b)) was dissolved in benzene, pentan-2,4-dione (1.0 ml) was added and the solution refluxed for 6 h. The now greenish-red solution was filtered from a black precipitate and concentrated to small volume; the addition of petroleum ether produced an orange-yellow precipitate, in which no rhodium or carbonyl group could be found. The mother-liquor was evaporated to dryness and the residue extracted with hot ligroin. The product, (XIV), was sublimed away from the evaporated yellow extract. It was identified by a mixed m.p. and IR spectrum.

(d) 2,6-dimethylaniline (10 ml), benzene (60 ml) and pentan-2,4-dione were heated under reflux for a short time; the solvent was then distilled off at atmospheric pressure. At 96°/*ca.* 0.1 Torr, liquid (2,6-dimethylphenyl)iminopenten-3-ol-4 was collected. The organic ligand (1.0 ml) and $[Rh(CO)_2Cl]_2$ in petroleum ether were refluxed for two days (no reaction took place at room temperature for 1 day). The solution was filtered while hot and cooled. Orange yellow crystals (415 mg) were collected; they were identified as dicarbonyl(2,6-dimethylaniline)rhodium(I) chloride, (XXI), by the IR spectrum. When the reaction was carried out in the complete absence of moisture, only an intractable oil was isolated.

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SUMMARY

Dicarbonyliridium(I)- and dicarbonylrhodium(I)-β-ketoiminates and their derivatives were synthesized starting from $[(CO)_2RhCl]_2$, $[(CO)_2(amine)RhCl]$, $[(CO)_2(amine)IrCl]$, $Na_2[Ir_2(CO)_4Cl_{4|8}]$ and acetylacetone or the appropriate Schiff base. Some of the compounds exist in two different crystalline forms. The course of the reactions and possible mechanisms are discussed.

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