Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

IRIDIUM DICARBONYL β-DIKETONATES

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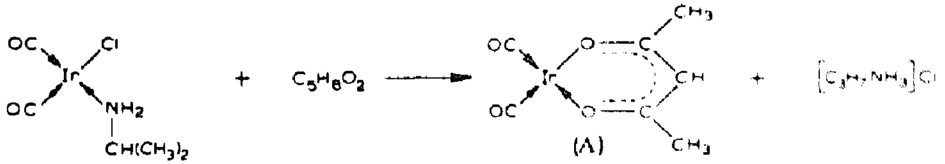
(Received July 14th, 1967)

When this work was undertaken[1], metal carbonyl compounds having chelating ligands such as β-diketones as substituent, were known only in the case of rhodium[2]. Previous attempts to isolate similar derivatives by the reaction of a metal carbonyl with an appropriate ligand, *e.g.* acetylacetone, had produced only the corresponding β-diketonate, with complete loss of carbon monoxide[3]. However, while our work was in progress, monovalent manganese carbonyl derivatives with hexafluoroacetylacetone were reported[4].

This paper deals with the preparation and the properties of stable dicarbonyl iridium β-diketonates.

SYNTHESIS

The preparation of iridium compounds of this class was more complex than that of the analogous rhodium compounds[2]. As the iridium analogue of $[Rh(CO)_2Cl]_2$ is as yet unknown, $Ir(CO)_3Br$ was tried as starting material. However, this compound (which can be prepared only in low yields) did not react with acetylacetone although a compound of formula $Ir(CO)_2(C_5H_7O_2)$ was obtained in low yield by reacting $Ir(CO)_3Br$ with thallium acetylacetonate. The same compound was obtained more easily by reacting iridium (I) derivatives[5] such as $Ir(CO)_2LCl$ (L = isopropylamine) with acetylacetone in the following manner:



This method of synthesis is not suitable, however, with other β-diketones which were found to react more easily with an impure compound of formula $Na_2[Ir_2(CO)_4Cl_{4.8}]$, which is obtained by carbonylation of Na_2IrCl_6[6]; in this manner we obtained many dicarbonyl derivatives in acceptable yields.

All the compounds obtained (Table 1) are air-stable crystalline solids which can be sublimed *in vacuo*. They are of various colours in the solid state—green—brown-violet—orange-yellow, but in $CHCl_3$ solution they are all yellow. Although the molecular weight determinations showed that they are monomeric in C_6H_6

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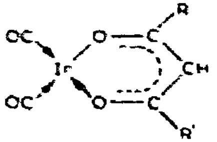
* For the Preliminary Note, see ref. 1.

TABLE 1

PROPERTIES OF COMPOUNDS OF FORMULA:

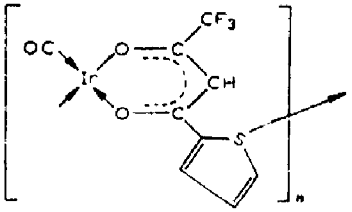


	R	*R'*	*Colour in solid state*	*Colour in $CHCl_3$ soln.*	*M.p. (°C)*	*Subl.*[a]	*Analyses*					
							C (%)		*H (%)*		*Mol.wt.*[b]	
							Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
I	CH_3	CH_3	violet-brown	yellow	160	80–85	24.20	23.87	2.02	2.38	388	362
II	CH_3	C_6H_5	green	yellow	126	90	35.60	35.91	2.18	2.28	410	405
III	C_6H_5	C_6H_5	orange-yellow	yellow	184	135	41.40	42.50	2.34	2.45	—	—
IV	CH_3	CF_3	green	yellow	148	60	21.80	21.91	1.00	1.12	402	415
V	CF_3	CF_3	deep-green	orange-yellow	92	40	18.42	18.29	0.22	0.15	456	500–550
VI	C_4H_4S	CF_3	green	yellow	160[c]	100	25.50	25.57	1.06	0.97	471	450

[a] Under a vacuum of ≤ 0.1 mm Hg. [b] Benzene soln. (osmometry). [c] Decomposition.

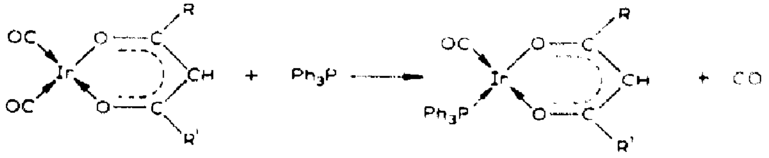
solution, there is some evidence for a small amount of association in dicarbonyl(hexafluoroacetylacetonato)iridium(I). Many of the green or brown compounds are dichroic.

The compounds obtained are soluble in organic solvents, although they dissolve very slowly; the speed of dissolution is variable, being slower with sublimed than with crystallized samples. The derivative of thenoyltrifluoroacetone(VI) changes slowly, in the solid state, to a dark-violet, insoluble, non-volatile compound. This compound showed only one terminal carbonyl stretching band (2038 cm^{-1}, broad) and its carbon and hydrogen analyses were only slightly different from those of the original green compound. In view of the different IR spectrum we believe that it may be a polymer of type



SUBSTITUTION REACTIONS

The complexes reacted with triphenylphosphine in the following way:



$R = R' = CH_3$

$R = CH_3$; $R' = C_6H_5$

The compounds obtained were pale-yellow, dimagnetic, crystalline derivatives, monomeric in C_6H_6 solution. They did not show dichroism and were not very stable in air. No substitution of the carbonyl ligand was effected by the use of triphenylarsine or triphenylstibine. When the β-diketone was trifluoroacetylacetone(IV), a yellow penta-coordinated compound of formula $Ir(CO)(PPh_3)_2(C_5H_4O_2F_3)$ was isolated by reaction with PPh_3. Similar, and probably pentacoordinated compounds, were obtained by reacting the dicarbonyl derivatives with a chelating diphosphine such as $Ph_2P{-}CH_2{-}CH_2{-}PPh_2$(DPE). The yellow complex of formula, $(CO)(DPE)Ir(C_5H_7O_2)$, is not very stable and decomposes easily in air.

Compound (I) (solid) did not react with the diene, 1,5-cyclooctadiene, even under forcing conditions, although the expected reaction product is known to exist and to be stable: [diene $Ir(C_5H_7O_2)$] was obtained[7] from the chloride and thallium(I) acetylacetonate. Clearly, compound (I) must be considered as kinetically inert.

INFRARED SPECTRA

All the dicarbonyl derivatives showed in solution two strong infrared absorption bands in the region 2150–1900 cm^{-1} (Table 2). These bands can be attributed to the

TABLE 2

CARBONYL STRETCHING FREQUENCIES OF COMPOUNDS OF FORMULA (A)

Compound	*ν(CO) (cm^{-1} in nujol)*	*ν(CO) (cm^{-1} in hexane)*	*ν(CO) (cm^{-1} in CH_2Cl_2)*	*Δν*[a]
I	2078 (s) 2040 (w) 1997 (s) 1957 (w)	2082 (s) 2002 (s)		0
II	2055 (s) 1990 (s)	2063 (s) 1993 (s)	2069 (s) 1991 (s)	−14
III	2047 (s) 1993 (s)	2065 (s) 1994 (s)	2072 (s) 1992 (s)	−15
IV	2076 (s) 2006 (s)	2080 (s) 2010 (s)		+ 3
V	2007 (s) 2081 (w) 2023 (s) 2013 (w)	2095 (s) 2027 (s)		+19
VI	2028 (s) 2058 (s) 1992 (s)	2082 (s) 2007 (s)	2073 (s) 2005 (s)	+ 3

[a] Difference of the av. value of ν(CO) between a compound and (I) (cm^{-1}).

symmetrical and antisymmetrical stretchings of the two *cis* carbon monoxide ligands. When the two methyl groups on the chelated ring are replaced by two strongly electronegative substituents, less back-donation from the metal to the carbonyl groups is expected, with a consequent small raise of the carbonyl stretching frequencies. While this is the case for the hexafluoroacetylacetonate, the opposite is true for the benzoylacetonate and dibenzoylmethanate. In the last two cases, as well as in the corresponding rhodium derivatives[2,8], conjugation of the phenyl ring(s) with the chelated ring makes back-donation more difficult, thus eliminating the opposite contribution of the electronegative phenyl group.

In the two Figures, the average value of ν(CO) is reported against the sum of the appropriate σ, either σ_H, *i.e.*, Hammett constant (Table 1), or σ_T, Taft's σ polar constants[9] (Table 2). If $(CO)_2Ir(C_5H_7O_2)$ is ignored, a straight line can be drawn between all points related to iridium chelates and another similar line passes though all points related to all rhodium chelates. The slope of the line is substantially higher with iridium than with rhodium compounds. All the compounds showed absorption bands (Table 3) which can be attributed to ν(C=O) and ν(C=C) stretchings of a chelated β-diketonate[10]. The substitution compounds with PPh_3 showed one carbon monoxide stretching at lower frequencies (see experimental) as expected.

With some compounds, particularly when R = R' and when the compounds are dichroic, two additional weak carbonyl stretchings appeared in the solid state (Table 2). This behaviour was found in other iridium(I) derivatives *e.g.*, $Ir(CO)_2LCl$ (L = amine) where evidence for a metal–metal interaction was found[11]. The appearance of these new bands can be attributed to the lowering of the molecular symmetry by

TABLE 3

INFRARED ABSORPTION BANDS IN THE REGION 1700–1500 cm^{-1} OF COMPOUNDS OF FORMULA (A)

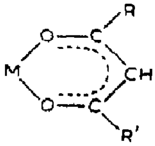
Compound	*Absorptions (cm^{-1})*
I	nujol: 1562m (br), 1540m (br)
II	CH_2Cl_2: 1580w, 1528m,sh; 1512m
III	CH_2Cl_2: 1598w, 1587w, 1535s; nujol: 1598w, 1591w, 1525s (br)
IV	nujol: 1603vs, 1528s
V	hexane: 1610m; nujol: 1672sh, 1660m, 1608m
VI	CH_2Cl_2: 1528s, 1548m, 1512w

metal–metal interaction in the crystal packing. However, it is strange that these bands appear in the compounds of higher molecular symmetry (when R = R′) which should pack more easily and with higher symmetry than in the compounds of lower molecular symmetry (when R ≠ R′). In any case, it is clear that the packing of these flat planar molecules must be quite different when R = R′ or R ≠ R′.

NMR SPECTRA

The dicarbonyl derivatives showed sharp ^{1}H NMR spectra (Table 4) which agree very well with their diamagnetic character.

TABLE 4

^{1}H NMR DATA ON  COMPOUNDS

Compound			Signals			Solvent	Ref.
R	R′	M	Methyl	H	Phenyl		
CH_3	CH_3	H	8.00	4.44	—	neat	15
CH_3	CH_3	$Rh(CO)_2$	7.89	4.48	—	CCl_4	2
CH_3	CH_3	$Ir(CO)_2$	8.42	4.85	—	C_6D_6	[a]
			7.90	4.26		CS_2	[a]
CF_3	CH_3	H	7.80	4.00	—	neat	15
CF_3	CH_3	$Rh(CO)_2$	7.75	3.98	—	CCl_4	2
CF_3	CH_3	$Ir(CO)_2$	7.70	3.78	—	$CDCl_3$	[a]
C_6H_5	CH_3	H	8.00	4.15	2.41–2.96	CCl_4	15
C_6H_5	CH_3	$Rh(CO)_2$	7.84	3.82	2.11–2.30; 2.58–2.71	CCl_4	2
C_6H_5	CH_3	$Ir(CO)_2$	7.78	3.60	*ca.* 1.9–2.8	$CDCl_3$	[a]
CF_3	CF_3	H	—	3.57	—	neat	15
CF_3	CF_3	$Rh(CO)_2$	—	3.52	—	CCl_4	2
CF_3	CF_3	$Ir(CO)_2$	—	3.36	—	$CDCl_3$	[a]
C_6H_5	C_6H_5	H	—	3.64	—	CCl_4	15
C_6H_5	C_6H_5	$Ir(CO)_2$	—	[b]	1.92–2.92	$CHCl_3$	[a]

[a] This work. [b] Not observed; see text.

^{19}F NMR spectra were recorded for compounds (IV) and (V). In the latter, the equivalence of the six fluorines was evident, only one peak, being observed.

^{1}H NMR spectra are reported in Table 4, together with those of the homologous rhodium compounds and those of the enol form of the parent diketone.

The remarkable difference in the chemical shift (*ca.* 0.5 τ) of both signals of compound (I) in deuterochloroform and in perdeuterobenzene is generally considered[12] as evidence for the presence of a delocalized electronic system on the chelated ring. The delocalized electronic system affords a pathway by which the effect of one substituent can be felt by another one on the same ring. The position of the CH_3-signal is lowered when another CH_3 is replaced by C_6H_5; a further lowering can be observed on replacement by the more electronegative CF_3-group. Both effects are greater with iridium than with rhodium derivatives.

The signal due to the proton in the central position on the ring is very sensitive to the nature of other substituents. The position of the signal is lowered by electronegative substituents on the ring. The lowering ($\Delta\tau$)(Table 5) is the same for the free ligand and rhodium and iridium derivatives, when one or two CF_3-groups are involved: *ca.* 0.47 and *ca.* 2 × 0.47, respectively. $\Delta\tau$ is the same (0.66) for the rhodium and iridium derivatives of benzoylacetone, but it is less than half this value in the free ligand; also, $\Delta\tau$ of dibenzoylmethane is greater than twice the $\Delta\tau$ observed for benzoylacetone. $\Delta\tau$ is always larger for a benzoylacetonate than for a trifluoroacetylacetonate, although the electronegativity alone would suggest the reverse order. The aromatic rings in dibenzoylmethane and benzoylacetone are unable to assume a position parallel to the *intra*molecular six-membered ring of the enol tautomer because of steric interaction with the carbon-bonded central hydrogen of the enol ring. When the hydrogen in the chelated ring is substituted by rhodium or iridium, the O–M–O angle becomes smaller and the other internal angles of the ring, bigger. In particular, a larger C–C–C angle in the ring means a greater distance between R and R'. For a sufficient distance, the aromatic rings can assume a position parallel to that of the chelated ring and extension of the conjugated system is possible (the presence of an extended conjugated system is supported by considerations of the IR spectrum reported above). As a result, the contribution to $\Delta\tau$ due to the long range shielding caused by the aromatic ring, is the same in both iridium and rhodium benzoylacetonates and is bigger than that observed in the unconjugated free ligand. This explains the observed order of $\Delta\tau$.

TABLE 5

$\Delta\tau$ FOR THE CENTRAL RING PROTON

R	*R'*	*M = H*	*M = (CO)$_2$Rh*	*M = (CO)$_2$Ir*	*Average*
		—[a]	—[b]	—[b]	
CH_3	CH_3	0.44	0.50	0.48	0.47 ± 0.03
C_6H_5	CH_3	0.29	0.66	0.66	—
CF_3	CF_3	0.87	0.96	0.90	0.92 ± 0.05
C_6H_5	C_6H_4	0.80	—	≥ 1.34	—

[a] The chemical shift of acetylacetone (enol form) was taken as zero (±0.02 $\Delta\tau$).
[b] The chemical shift of $M(C_5H_7O_2)$ was taken as zero.

The absence from the recorded spectrum of the signal due to the central hydrogen of the ring in iridium dicarbonyl dibenzoylmethanate (Table 4) can now be easily explained. $\Delta\tau$ for replacement of two methyl with two phenyl groups should be 1.32 ± 0.04 (*i.e.*, 0.66 × 2). Such a shift would then bring the signal below those due to the phenyl groups.

The $\Delta\tau$-values are always lower with iridium than with rhodium derivatives and it is possible that a more negative charge is present on the chelated ring in the former than in the latter.

ELECTRIC DIPOLE MOMENTS

The dipole moments of $(CO)_2Ir(\beta$-diketonato) compounds were determined in benzene solution, and are reported in Table 6 together with the results for two related rhodium compounds.

TABLE 6

ELECTRIC DIPOLE MOMENTS

Compound	$\omega_2 \cdot 10^{-3}$	$\Delta\varepsilon_{12} \cdot 10^{-3}$	α_0	$-\Delta v_{12} \cdot 10^3$	$-\beta$	P_M	P_E	μ_{20} (*Debye*)
I	11.02	52	4.72	—	—			
	17.44	80.3	4.61	5.44	0.31	387	38.9	4.08
II	4.68	25.1	5.35					
	6.17	32.9	5.33					
	10.90	—	—	3.5	0.32	508	58.6	4.62
III	9.67	43.8	4.53					
	13.92	59.5	4.28					
	4.76	21.3	4.48		0.30	505	78.3	4.48
IV	17.00	62.0	3.87					
	9.18	33.0	3.60					
	5.45	20.2	3.70		0.32	377	38.2	4.02
V	16.66	5.10	0.31		—	—	—	—
	10.31	1.98	0.19		—	—	—	
[a]	12.77	40.0	3.13					
	8.96	27.9	3.11		0.32	282	38.9	3.39
[b]	13.30	6.20	0.47					
	4.53	6.83	1.51					

[a] The compound is $(CO)_2Rh(C_5H_7O_2)$. [b] The compound is $(CO)_2Rh(C_5HF_6O_2)$.

The contribution of the atomic polarization (P_A) cannot be assessed, but it is not likely to be more than 15 ± 3 cc, if an average value of P_A is taken on the basis of the values reported[13] for several β-diketonates. The value of P_A will probably be the same for all compounds involved here, and any difference in P_A between our compounds is not likely to be of relevance.

The α_0-values for the two hexafluoroacetylacetonates are unsatisfactory, probably owing to variable association in benzene solution (see Table 1): the resulting dipole moments are not included in Table 6.

The other values of dipole moment indicate the existence of a more negative charge in the chelated ring of iridium than in that of rhodium acetylacetonate. No other conclusion can be drawn from the differences in the value of dipole moment of the β-diketonates. The structures of $(CO)_2Rh(C_5H_7O_2)$ and $(CO)_2Rh(C_5HF_6O_2)$[14] have shown that the molecule is not strictly planar, the acac ring being at a small angle with the $(CO)_2Rh$ plane in the solid state. There is no reason for assuming that in solution this angle will be the same for the acetylacetonates reported or discussed here.

CONCLUSIONS

The dichroism and the infrared spectra in the solid state suggest some weak metal–metal interaction. This is supported by the recent X-ray structural determinations on dicarbonyl acetylacetonate and hexafluoroacetylacetonate[13]. This is the first reported case of association of a β-diketonato complex *via* a metal–metal interaction, and not through tricoordinated oxygen. The compounds are the first examples of approximately square planar derivatives of acetylacetone without polymeric structure like divalent nickel acetylacetonate, or without a tendency to coordinate additional donor molecules like nickel (II) acetylacetonate and copper(II) β-diketonates. An electronic delocalization on the chelated ring appears to act on the electronic density of the metal. Variation of substituents on the ring affords quite remarkable variations, not only of the chemical shift of the NMR signal of the proton of the chelated ring, but also of the value of the stretchings of the carbonyl ligands which are far away from the substituents themselves.

The linearity of the correlations for rhodium and iridium compounds (Figs. 1

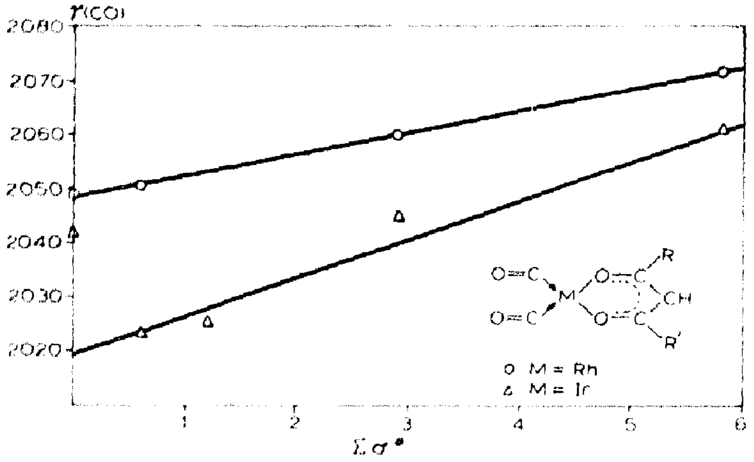


Fig. 1

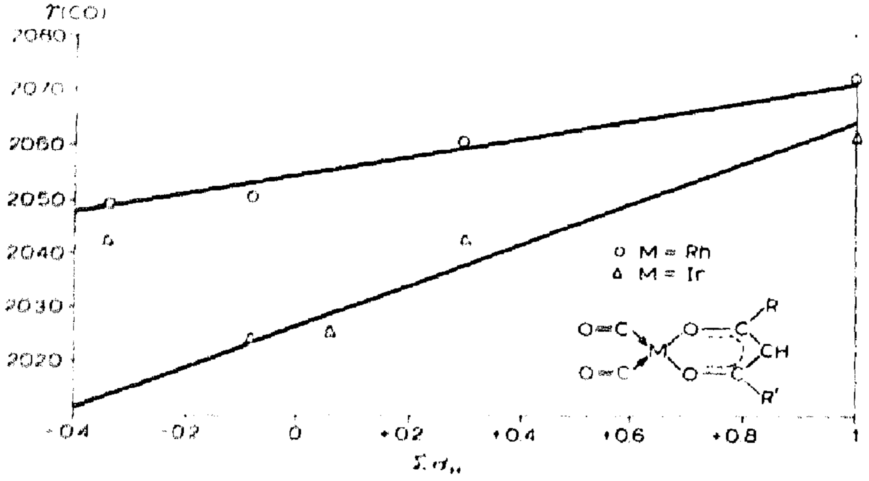


Fig. 2

and 2) [with the exception of compound(I)] suggest that the substituents act on the electronic density of the metal by changing the energy levels of the π-system of the chelated ring, and by allowing the first π-antibonding orbital of the ligand to interact with the non-bonding orbital of the metal. NMR, infrared and dipole moment data are in favour of a greater negative charge on the chelated ring in iridium than in rhodium chelates.

EXPERIMENTAL

All the initial reactions were carried out under nitrogen, but the products were isolated and purified under atmospheric conditions. Melting points (Table 1) were determined in air and are uncorrected. Molecular weights were determined on a Mechrolab osmometer and are reported in Table 1, together with the analytical data. Tables 2 and 3 record the relevant infrared data obtained with Perkin-Elmer 237 instrument. Proton NMR spectra (Table 4) were recorded with a Perkin-Elmer R-10 instrument, operating at 60 Mc using tetramethylsilane as internal standard. Evaporation was always carried out under reduced pressure (10–50 mm Hg) unless otherwise stated. Dielectric constants were measured on a WTW Dipolmeter at 25°. Density was determined at 25° in a U-shaped pyknometer.

Preparation of starting materials

Crude brown "[Na $Ir_2(CO)_4Cl_{4.8}$]" was prepared[6] by heating sodium hexachloroiridate(III) at 120° under 200 atm of carbon monoxide in the presence of copper wire for 16 h. Commercially available β-diketones were distilled or crystallized.

Dicarbonyl(pentan-2,4-dionato)iridium(I). (a) The crude [$Na_2Ir_2(CO)_4Cl_{4.8}$] (from 8 g Na_2IrCl_6), benzene (150 ml) and isopropylamine (2.0 g) were heated for 7 h on a bath at 75°. The decanted dirty-yellow solution was evaporated to dryness and the resulting brown residue extracted with petroleum ether (100 ml), an oily residue being discarded. On evaporating the solution, brownish-red crystals were obtained. These were dissolved in benzene (80 ml), pentan-2,4-dione (1.2 ml) was added, and the solution heated at 75° for 12 h. The filtered solution was evaporated to dryness and extracted with boiling petroleum ether: on cooling golden-brown crystals separated (I). By sublimation of the residue at 80°/1 mm, a further amount of product could be recovered.

(b) The crude "[$Na_2Ir_2(CO)_4Cl_{4.8}$]" (from 9 g Na_2IrCl_6) was suspended in benzene (250 ml); after the addition of pentan-2,4-dione (3.0 ml) and excess sodium bicarbonate, the mixture was refluxed for 6 h. The filtered solution and the benzene extracts (50 + 30 + 30 ml) of the residue, were evaporated to dryness (1.82 g). The product could be purified as above or by sublimation at 60–80°/0.3 mm (18 h)(yield 1.05 g).

(c) Tricarbonylbromoiridium(I) (52.0 mg) benzene (12 ml), pentan-2,4-dione (0.5 ml) and excess sodium bicarbonate were refluxed for 4 h. The product (52 mg) was isolated by sublimation from the filtered and evaporated solution.

(d) Tricarbonylbromoiridium(I) (54 mg), (pentan-2,4-dionato) thallium(I) and benzene (12 ml), were heated under reflux for 6 h. On sublimation the residue from the filtered and evaporated solution gave 7 mg of product. The identity of this and the other products was established through their infrared spectra.

Dicarbonyl(1-phenylbutan-1,3-dionato)iridium(I) (*II*). Crude "$[Na_2Ir_2(CO)_4Cl_{4.8}]$" (from 12 g Na_2IrCl_6), benzene (100 ml), 1-phenylbutan-1,3-dione (2.5 g) and excess sodium bicarbonate were heated under reflux for 4 h. The filtered solution and the benzene (50 ml) and petroleum ether (30 ml) extracts of the residue were combined and evaporated to dryness. The resulting oil was extracted with petroleum ether and the solution evaporated to dryness leaving a residue which became solid after standing in the refrigerator overnight (purification by chromatography was unsuccessful owing to decomposition). Careful sublimation of a sample of this residue (990 mg) at 0.2 mm gave 1-phenylbutan-1,3-dione (420 mg) at 60°, and the required product at *ca.* 90°; between 60° and 90° a mixture of the two compounds (45 mg) was collected. The residue was not investigated further. The product is brownish-green, but its concentrated benzene solution is red turning yellow on dilution.

Dicarbonyl(1,3-diphenylpropan-1,3-dionato)iridium(I) (*III*). Crude "$[Na_2Ir_2(CO)_4Cl_{4.8}]$" (from 4.7 g Na_2IrCl_6), benzene (80 ml), excess sodium bicarbonate and 1,3-diphenylpropan-1,3-dione (2.1 g) were heated under reflux for 4 h. The filtered solution and the benzene extract (3 × 30 ml) of the residue were combined and evaporated to dryness. On sublimation (125–135°/0.3 mm), product III was obtained (512 mg), and purified by resublimation.

Dicarbonyl(1,1,1-trifluoropentan-2,4-dionato)iridium(I) (*IV*). Crude "$[Na_2Ir_2(CO)_4Cl_{4.8}]$" (from 15 g Na_2IrCl_6), benzene (80 ml) excess sodium bicarbonate and 1,1,1-trifluoropentan-2,4-dione (3 ml) were heated under reflux for 1 h. The filtered solution and the benzene extracts (50 + 30 + 30, hot) of the residue were combined and evaporated to dryness to yield a green residue (2.856 g). On sublimation of a sample (634 mg) at 60°/0.3–0.4 mm, green, needle-like prisms (436 mg) of the required product were obtained. A concentrated benzene solution of this compound is reddish turning orange on dilution.

Dicarbonyl(1,1,1,5,5,5-hexafluoropentan-2,4-dionato)iridium(I)(*V*). Crude "$[Na_2Ir_2(CO)_4Cl_{4.8}]$" (from 11 g Na_2IrCl_6), benzene (100 ml), excess sodium bicarbonate, and 1,1,1,5,5,5-hexafluoropentan-2,4-dione (2.0 ml) were allowed to stand for 0.5 h and then heated at 60° for 15 min. The filtered dark-yellow solution and the benzene extracts (4 × 50 ml) of the residue, were combined and evaporated to dryness to yield handsome green needles of the required product (1.9 g), purified by sublimation (30–40°/0.2 mm). This compound is very volatile and covers the walls of storage flasks.

Dicarbonyl-1(2-thenoyl)-4,4,4-trifluorobutan-1,3-dionato)iridium(I)(*VI*). Crude "$[Na_2Ir_2(CO)_4Cl_{4.8}]$" (from 6.5 g Na_2IrCl_6), benzene (100 ml), excess sodium bicarbonate, and 1(2-thenoyl)-4,4,4-trifluorobutan-1,3-dione (0.716 g) were heated under reflux for 4 h. The filtered dark-red solution and the benzene extracts (50 + 40 + 40 ml) of the residue, were combined and evaporated to dryness (1.150 g). After sublimation (80–100°/0.2 mm; 16 h) green needles of the required product were obtained (650 mg). This compound is unstable on keeping. It becomes dark-violet and insoluble in benzene and methylene chloride (even hot) and cannot be sublimed.

Carbonyl(triphenylphosphine)(pentan-2,4-dionato)iridium(I) (*VII*). A saturated solution of triphenylphosphine (122 mg) in petroleum ether was added to an analogous solution of dicarbonyl (pentan-2,4-dionato)iridium(I): gas was evolved. The clear precipitate was crystallized from petroleum ether, to yield the required compound (64 mg), soluble in benzene and methylene chloride, m.p. 181. (Found: C, 49.79;

H, 4.03; mol.wt. (osmometric in $CHCl_3$), 555. $C_{24}H_{22}IrO_3P$ calcd.: C, 49.6; H, 3.78%; mol.wt. 581). IR spectrum (CO)(CH_2Cl_2)(nujol): 1969s, 1959m, 1934s. The compound is slowly decomposed in air.

Carbonyl[1,2-bis(diphenylphosphino)ethane](pentan-2,4-dionato)iridium(I). Prepared as (VII), but crystallized from benzene, m.p. 218. (Found: C, 54.09; H, 4.38; mol.wt. ($CHCl_3$), 762. $C_{32}H_{31}IrO_3P_2$ calcd.: C, 53.5; H, 4.32%; mol.wt. 718). IR spectrum (CO) (nujol): 1938s, 1927sh.

Carbonylbis(triphenylphosphine)(1,1,1-trifluoropentan-2,4-dionato)iridium(I). Prepared and purified as (VII), m.p. 176°. (Found: C, 55.27; H, 3.54; mol.wt. ($CHCl_3$) 898. $C_{42}H_{34}F_3IrO_3P_2$ calcd.: C, 55.2; H, 3.78; mol.wt. 843). IR spectrum (CO)(nujol): 1955s.

Carbonyl(triphenylphosphine)(1-phenylbutan-1,3-dionato)iridium(I). This compound (28 mg) was obtained by mixing a saturated solution of (II) (54 mg) and triphenylphosphine (54 mg) in petroleum ether–benzene (1 : 2), m.p. 126°. (Found: C, 54.6; H, 4.00. $C_{29}H_{24}IrO_3P$ calcd.: C, 54.2; H, 3.74). IR spectrum (CO)(nujol): 1954s.

Dipole moments

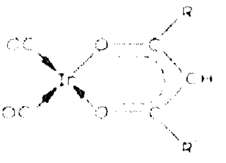
The dipole moments were calculated using the Halverstadt–Kumler formula[16]. The values of the electronic polarization (P_E) were calculated using data from the literature[17]. Since β was found to be practically the same for compounds (I) and (II), a similar value was assumed for the other compounds. All data are given in Table 6, including the resulting dipole moments calculated assuming $P_A = 0.20\ P_E$.

ACKNOWLEDGEMENTS

We wish to thank Consiglio Nazionale delle Ricerche for financial support, and Dr. S. BRADAMANTE for recording many NMR spectra.

SUMMARY

The preparation and the properties of compounds of general formula:



($R = R' = CH_3$
$R = R' = CF_3$
$R = R' = Ph$
$R = CH_3$; $R' = CF_3$
$R = CH_3$; $R' = Ph$
$R = CF_3$; $R' = C_4H_3S$)

are reported. The compounds, some of which have a weak metal–metal interaction in the solid state, are monomeric in solution. Substitution reactions of the carbonyl ligand(s) with MPh_3 (M = P, As, Sb), $Ph_2CH_2CH_2PPh_2$(DPE) and diolefins were investigated.

Infrared and NMR spectra and dipole moments, in solution, are in agreement with an electronic delocalisation on the chelated ring. The electronic effects of substituents R or R' are shown to be stronger in the iridium derivatives than in the analogous rhodium derivatives.

REFERENCES

1 F. Bonati and R. Ugo, *Chim. Ind. (Milan)*, 46 (1964) 1435.
2 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, (1964) 3156.
3 J. P. Fackler, Jr., *Progress in Inorganic Chemistry*, Vol. 7 edited by F. A. Cotton, 1967, J. Wiley, New York, p. 367.
4 F. A. Hartman, M. Kilner and A. Wojcicki, *Inorg. Chem.*, 6 (1967) 34.
5 F. Bonati and R. Ugo, *J. Organometal. Chem.*, 7 (1967) 167.
6 L. Malatesta and M. Angoletta, *J. Inorg. Nucl. Chem.*, 8 (1958) 237. L. Malatesta, Report of 31-X-1958, Air Force Office of Scientific Research, U.S.A.F. European Office.
7 S. D. Robinson and B. L. Shaw, *Tetrahedron Letters*, (1964) 1301.
8 F. Bonati, *Organometal. Chem. Rev.*, 1 (1966) 379.
9 J. Hine, *Physical Organic Chemistry*, McGraw-Hill, New York, 1956, p. 69, 276.
10 G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 6 (1967) 433.
11 M. Angoletta, *Gazz. Chim. Ital.*, 89 (1959) 2359.
12 H. Suhr, *Anwendungen der Kernmagnetischen Resonanz in der Organischen Chemie*, Springer Verlag, Berlin, 1965, p. 143.
13 J. W. Smith, *Electric Dipole Moments*, Butterworths, London, 1955, p. 278.
14 N. Bailey, F. Bonati, G. B. Robertson and R. Ugo, in press; C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collmann, J. C. Morrow, W. R. Roper and D. Ulku, *J. Am. Chem. Soc.*, 88 (1966) 4286.
15 J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, 86 (1964) 2105.
16 J. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, 64 (1942) 2988.
17 A. I. Vogel, *J. Chem. Soc.*, (1948) 1833