59301-79-0; $Pt(dae)(SCN)_2$, 59301-78-9; $Pt(pae)(NCS)(SCN)$, 59301-85-8; $Pd(pae)(SCN)_2$, 59331-86-1; dithiocyanatobis(benzonitrile)platinum(II), 59301-80-3.

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γ-Carbon-Bonded 2,4-Pentanedionato Complexes of Trivalent Iridium

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Despite the thermal and oxidative stability of octahedral iridium(III)–carbon σ-bonded complexes, there are no well-characterized γ-C-bonded β-diketone complexes of iridium(III) analogous to the well-known derivatives of octahedral platinum(IV)[1] and of planar platinum(II)[1] and palladium(II).[2] Gibson[3] has reported that K_3IrCl_6 reacts with an excess of potassium acetylacetonate in aqueous solution to give, among other products, a complex tentatively formulated as $K_2Ir_2(acac)_7Cl\cdot H_2O$ which may contain γ-C-bonded acac groups.[4] In the course of an attempt to improve on the literature synthesis of $Ir(acac)_3$, **1**,[5] we have isolated some iridium(III) complexes which appear to contain both O- and C-bonded acac groups. The preparations and spectroscopic evidence for the formulations are reported in this note.

Experimental Section

Measurements. Ir spectra were recorded on a PE457 spectrophotometer using either KBr disks or 1-mm path length solution cells with KBr windows. Mass spectra were measured by Mr. G. Jordan (Queen's University) on an MS-902 instrument at 70 eV. ^1H NMR spectra (Table I) were run on a Varian HA-100 spectrometer by Mr. I. Jack and ^{13}C NMR spectra (Table II) on a Bruker WH90FT instrument by Dr. L. C. Waring (Queen's University). Microanalyses (Table III) were carried out in the departmental microanalytical laboratories by Miss Brenda Stevenson and Dr. Joyce Fildes and their associates (Australian National University) and by Messrs. B. McKnight and D. McClure (Queen's University).

Preparations. Bis(2,4-pentanedionato-*O,O*)(2,4-pentanedionato-C^3)pyridineiridium(III), 3. Hydrated iridium trichloride (1.05 g), 2,4-pentanedione (10 ml), and sodium bicarbonate (2 g) were heated under reflux in a nitrogen atmosphere for 40 h. The excess of diketone was removed in vacuo and the yellow residue was extracted with three 15-ml portions of dichloromethane. The extract was evaporated to ca. 5 ml and chromatographed on neutral alumina. The yellow band which eluted with benzene gave tris(2,4-pentanedionato-*O,O*)iridium(III), **1** (0.23 g, 18%),[5] identified by its ^1H NMR spectrum (Table I). The bright yellow solid (2.70 g) which remained after extraction with dichloromethane was heated under reflux with pyridine (40 ml) in a nitrogen atmosphere for 2 h. After filtration and evaporation to dryness, **3** was obtained as a lemon yellow solid (0.83 g, 49%) which was purified by recrystallization from dichloromethane–ether.

Bis(2,4-pentanedionato-*O,O*)(2,4-pentanedionato-C^3)(*p*-toluidine)iridium(III), 4. The dichloromethane-insoluble solid **2** obtained as described above from hydrated iridium trichloride (0.29 g) was stirred with excess *p*-toluidine (5 g) at 100 °C in a nitrogen atmosphere for 2 h. After cooling of the mixture to room temperature, ether (25 ml) was added, and the precipitated solid was dissolved in dichloromethane (5 ml). Chromatography on neutral alumina and elution with chloroform gave a yellow band, which, after evaporation of solvent and recrystallization of the residue from dichloromethane–ether, gave **4** as a lemon yellow solid (0.14 g, 29%).

Bis(μ-2,4-pentanedionato-*O,O,*C^3)-bis(2,4-pentanedionato-*O,O*)bis(2,4-pentanedionato-C^3)diiridium(III), 5. Solid **2** obtained from hydrated iridium trichloride (1.00 g) was boiled for 1 h with water (120 ml) to give an orange solution. This was evaporated to dryness in vacuo and the residue was extracted with two 50-ml portions of dichloromethane. Chromatography on neutral alumina, elution with chloroform, and crystallization from chloroform–ether gave **5** as an orange solid (0.62 g, 45%).

Bis(2,4-pentanedionato-*O,O*)(2,4-pentanedionato-C^3)ammineiridium(III), 6. Compound **5** (0.103 g) was stirred with aqueous ammonia (0.880) (25 ml) for 2 h, the mixture being warmed gently. The mixture was worked up as described above for **5**, and the product was recrystallized from chloroform–ether to give a lemon yellow solid (0.060 g, 57% based on **5**).

Bis(2,4-pentanedionato-*O,O*)(2,4-pentanedionato-C^3)(*n*-propylamine)iridium(III), 7. Compound **5** (0.103 g) was heated under reflux with an excess of *n*-propylamine for 2 h. After removal of amine in vacuo the solid was purified as described for **5**. Compound **7** was obtained as a yellow-orange solid (0.059 g, 52% based on **5**) from dichloromethane–ether.

Results and Discussion

Tris(2,4-pentanedionato-*O,O*)iridium(III), **1**, was first prepared[5] in only 10% yield by heating freshly precipitated iridium(III) hydroxide with 2,4-pentanedione at pH 6 for 1 h. We tried to improve on this by adapting a method which has given good yields of tris(β-diketonato) complexes of ruthenium(III).[6] On heating chloroiridic acid or hydrated iridium trichloride with a large excess of neat 2,4-pentanedione and sodium bicarbonate, **1** is formed in 18% yield together with a yellow solid, **2**, which is insoluble in dichloromethane and other organic solvents. We have been unable to purify this solid or obtain reproducible analytical data for it, probably owing to the presence of sodium acetylacetonate and sodium chloride in addition to polymeric 2,4-pentanedionato complexes of iridium. However, **2** reacts with boiling pyridine to give a bright yellow, crystalline solid of empirical formula $Ir(acac)_3py$, **3**, which is soluble in chloroform and dichloromethane and is monomeric in the former solvent. The mass spectrum of **3** shows a parent ion. Compound **2** reacts with *p*-toluidine at 100 °C to give yellow $Ir(acac)_3(p\text{-}CH_3C_6H_4NH_2)$, **4**, and with boiling water to give a yellow complex **5** of empirical formula $Ir(acac)_3$ which is dimeric in chloroform. The yields in all three preparations are 30–50% based on iridium. Compound **5** reacts with pyridine to give **3** and with ammonia or *n*-propylamine to give yellow, crystalline derivatives of formula $Ir(acac)_3L$ ($L = NH_3$ (**6**) or $n\text{-}PrNH_2$ (**7**)). Similar adducts containing triphenylphosphine, dimethylphenylphosphine, *N*-methylaniline, or *N,N*-dimethylaniline could not be obtained.

The ir spectra of the O-bonded complexes $M(acac)_3$ (M = Rh or Ir) and of the adducts $Ir(acac)_3L$ (**3**, **4**, **6**, and **7**) show

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Table I. Ir and ^{1}H NMR Data[a]

		ν(C=O)		τ (no. of protons)	
Complex	Type of acac[b]	KBr	$CHCl_3$	CH_3	CH
1	O	1560, 1525	1555, 1520	7.98 (18)	4.52 (3)
$Rh(acac)_3$	O	1565, 1520	1535, 1520	7.85 (18)	4.52 (3)
3[c]	C	1670, 1640	1670, 1645	8.00 (6)	4.71 (1)
	O	1550, 1530	1550, 1520	8.04 (12)	4.68 (2)
4[d]	C	1660, 1640	1670, 1645	8.14 (6)	4.71 (1)
	O	1560, 1515	1550, 1520	8.13 (12)	4.68 (2)
6[e]	C	1670, 1660	1670, 1645	8.13 (6)	4.78 (1)
	O	1550, 1525	1555, 1525	8.03 (12)	4.53 (2)
7[f]	C	1670, 1660	1670, 1645	8.10 (6)	4.79 (1)
	O	1550, 1525	1555, 1525	8.01 (12)	4.52 (2)
5	C	1660	1670, 1650	8.07 (12)	4.91 (2)
	O	1560, 1525	1555, 1525	7.99 (12)	4.46 (2)
	B	1600	1600	8.02 (12)	4.91 (2)

[a] Frequencies in cm^{-1}; chemical shifts (τ) measured in $CDCl_3$ with internal TMS. All acac resonances were singlets. [b] Abbreviations: O, O-bonded acac; C, γ-C-bonded acac; B, bridging acac (see text). [c] Pyridine resonances: τ 1.67 (complex d, 2), 2.13 (complex t, 1), 2.59 (complex d, 2). [d] *p*-Toluidine resonances: τ 2.99 (unsym d, 2), 3.10 (unsym d, 2), 4.88 (br s, 2, NH_2), 7.72 (s, 3, CH_3). [e] Ammine resonance: τ 7.00 (br s, 3). [f] *n*-Propylamine resonances: τ 6.85 (m, 2), 7.52 (m, 2), 8.50 (m, 2, CH_2), 9.11 (t, 3, CH_3, J = 7 Hz).

Table II. ^{13}C NMR Data[a]

	O-acac			*C*-acac			Bridging acac		
Complex	CH_3	CH	C=O	CH_3	CH	C=O	CH_3	CH	C=O
1	26.45	102.10	186.20						
3[b]	27.41	102.84	185.14	31.76	40.20	213.51			
5	27.23	103.20	184.64	32.10	39.77	212.12	29.90	62.00	202.96

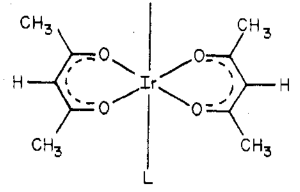
[a] Chemical shifts in ppm downfield of TMS, measured in $CDCl_3$. [b] Pyridine resonances appeared at 125.11, 138.51, and 149.73 ppm.

Table III. Analytical Data

	% C		% H		% N	
Complex	Calcd	Found	Calcd	Found	Calcd	Found
$Ir(acac)_3py$ (**3**)[a,b]	42.24	42.42 41.73[c]	4.61	4.56 4.64[c]	2.46	2.29 2.38[c]
$Ir(acac)_3(p\text{-}CH_3C_6H_4NH_2)$ (**4**)	44.28	44.23	5.07	4.98	2.25	2.23
$Ir_2(acac)_6$ (**5**)[d,e]	36.80	36.61	4.32	4.30		
$Ir(acac)_3(NH_3)$ (**6**)	35.57	35.44	4.78	4.79	2.77	2.66
$Ir(acac)_3(n\text{-}PrNH_2)$ (**7**)	39.41	39.87	5.51	5.43	2.55	2.50

[a] Molecular weight: calcd, 569; found, 556 (osmometry in $CHCl_3$), 569 (mass spectrometry). [b] Percent Cl: calcd, 0; found, 0.43. Presence of small amount of CH_2Cl_2 of crystallization confirmed by ^{1}H NMR in $CDCl_3$. [c] Analyses for duplicate sample of 3. Percent Cl: found, 0.0. [d] Molecular weight: calcd, 939; found, 948 (osmometry in $CHCl_3$). [e] Percent Cl: calcd, 0; found, 0.55. This is assumed to arise from a small amount of chloroform of crystallization.

a pair of ν(C=O)[7] bands in the 1520–1560-cm^{-1} region characteristic of bidentate O-bonded acac groups, but **3**, **4**, **6**, and **7** also show a pair of ν(C=O) bands in the 1640–1670-cm^{-1} region (Table I) characteristic of γ-C-bonded acac complexes.[1,2] Also the ^{1}H NMR spectra of **3**, **4**, **6**, and **7** (Table I) exhibit two methyl singlets and two methine singlets, each in a 2:1 ratio, corresponding to two β-diketone groups of one type and one of another. These data are accommodated by structure I, which contains two mutually trans, bidentate,

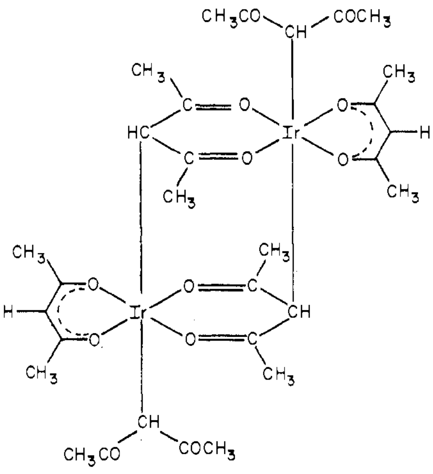


I

3, L = C_5H_5N **4**, L = $p\text{-}CH_3C_6H_4NH_2$
6, L = NH_3 **7**, L = $CH_3CH_2CH_2NH_2$

O-bonded acac rings and one γ-C-bonded acac group. In agreement with this formulation, the ^{13}C NMR spectra of **1** and **3** (Table II) show signals at ~27, ~103, and ~185 ppm which can be assigned respectively to the methyl, methine, and carbonyl carbon atoms of the bidentate O-bonded acac rings, and the spectrum of **3** shows in addition signals at ~32, ~40, and ~213 ppm arising from the γ-C-bonded acac group.

Complex **5**, $Ir_2(acac)_6$, shows three equally intense methyl singlets in its ^{1}H NMR spectrum (Table I), indicative of three different acac moieties. The corresponding methine signals appear in a 2:1 ratio, probably owing to accidental overlap of two of the resonances. In agreement, the ^{13}C NMR spectrum (Table II) shows the typical resonances arising from bidentate O-bonded acac and γ-C-bonded acac, but it also contains three signals which we assign to the methyl, methine, and carbonyl carbon atoms of a bridging, tridentate acac group in its keto form, bound through the γ-carbon atom to one iridium atom and O-bonded through two carbonyl oxygen atoms to the other iridium atom (structure II). As expected, the ^{13}C chemical shifts for the bridging ligand are intermediate between those of bidentate O-bonded delocalized acac and monodentate γ-C-bonded acac. This type of bridging acac has been identified by single-crystal x-ray study of the 4,6-nonanedionato complex $[(CH_3)_3Pt(C_3H_7COCHCOC_3H_7)]_2$[8] and of the allene dimer complex $Rh_2(acac)_2(C_3H_4)_2(PPh_3)_2$;[9] it is also thought to be present in the tetrafluoroethylene complex $[Rh(acac)(C_2F_4)(CH_3CN)]_2$.[10] It is noteworthy that the ir spectrum of **5** shows a ν(C=O) band at 1600 cm^{-1}, pre-



II

sumably arising from the bridging acac group, in addition to bands characteristic of O-bonded bidentate and γ-C-bonded acac groups (Table I). Gibson[11] reported that $[(CH_3)_3Pt(acac)]_2$ shows its ν(C=O) band at 1600 cm^{-1}, although other complexes believed to contain bridging acac groups, such as $[Rh(acac)(C_2F_4)(CH_3CN)]_2$ and $Co[PtCl(acac)_2]_2$, absorb in the 1640–1660-cm^{-1} region. Compound **5** is the first example of a complex which contains three different types of coordinated acac.

Attempts to convert O-bonded bidentate acac into γ-C-bonded acac on iridium(III) have not been successful; e.g., **1** is recovered almost quantitatively after heating in pyridine for 4 h, and there is no evidence for the formation of **3**. This is in marked contrast with the behavior of Pd^{II}–acac complexes; e.g., $Pd(acac)_2$, containing bidentate O-bonded acac, is converted almost quantitatively into $Pd(O\text{-acac})[CH(COCH_3)_2]py$ by treatment with pyridine at 80 °C.[2] The difference is undoubtedly due to the presence of a vacant coordination site on palladium(II), so that pyridine or other ligands can promote the change from O to C bonding. The reverse change does occur to a limited extent on iridium(III), since attempted sublimation of **5** at 270 °C (0.2 mm) gave an approximately 10% yield of **1**, in addition to unidentified decomposition products.

The low yield of $Ir(O\text{-acac})_3$ in this and previous preparations is due, at least in part, to the simultaneous formation of γ-C-bonded complexes. Iridium(III) clearly resembles isoelectronic platinum(IV) in binding strongly to the γ-carbon atom of 2,4-pentanedione to give octahedrally coordinated complexes.

Registry No. **1**, 15635-87-7; **3**, 60195-60-0; **4**, 60209-65-6; **5**, 60184-33-0; **6**, 60195-61-1; **7**, 60195-62-2.

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Ground-State Geometries and Fluxional Behavior of Octakis(trifluorophosphine)dirhodium, Octakis(trifluorophosphine)diiridium, and Related Trifluorophosphine Complexes

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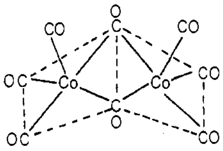
The reactions of dirhodium octakis(trifluorophosphine), $Rh_2(PF_3)_8$,[1,2] with hydrogen[2], group 4 hydrides[2], and acetylenes[3] (eq 1–3) are remarkably similar to the corresponding reactions of dicobalt octacarbonyl, $Co_2(CO)_8$.

$$Rh_2(PF_3)_8 + H_2 \rightarrow 2HRh(PF_3)_4 \tag{1}$$

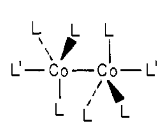
$$Rh_2(PF_3)_8 + (C_6H_5)_3MH \rightarrow HRh(PF_3)_4 + (C_6H_5)_3MRh(PF_3)_4 \tag{2}$$
(M = Si or Ge)

$$Rh_2(PF_3)_8 + ac \rightarrow Rh_2(PF_3)_6(\mu\text{-ac}) + 2PF_3 \tag{3}$$
(ac = HC_2H, $C_6H_5C_2H$, $C_6H_5C_2C_6H_5$, $CF_3C_2CF_3$, etc.)

However, there have been no published structural studies of $Rh_2(PF_3)_8$, and there are only two x-ray structural determinations on PF_3 complexes of the cobalt triad. The μ-diphenylacetylene complex $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)$[4] is structurally similar to $Co_2(CO)_6(C_6H_5C_2C_6H_5)$ and related bridging acetylene complexes derived from $Co_2(CO)_8$. The structure of $HCo(PF_3)_4$[5] can be described as a distorted trigonal bipyramid with the hydrogen atom occupying an axial position or as an essentially tetrahedral array of PF_3 groups with hydrogen in one of the tetrahedral faces.[6] The low-temperature limiting ^{19}F NMR spectra of $HM(PF_3)_4$ (M = Co, Rh, or Ir) show two sets of resonances in a 3:1 ratio,[6] indicating a structure with C_{3v} microsymmetry in solution. X-ray studies of many five-coordinate complexes of the type $YCo(CO)_4$, or ligand substitution products thereof, have shown the favored geometry to be trigonal bipyramidal with the anionic ligand Y in an axial position.[7] Dicobalt octacarbonyl itself has the CO-bridged structure I in the solid state[8], but in solution this is in equilibrium with an isomer containing no CO bridges, which is favored as the temperature is increased.[9,10] Although there has been disagreement about the structure of this isomer,[9,10] the most recent study[11] suggests structure IIa, consisting of two axially linked trigonal bipyramids (D_{3d} symmetry), as most likely, and this structure (IIb) is indeed adopted by $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$ in the solid state.[12] However, there is evidence for a small amount of a second "high-temperature" isomer of $Co_2(CO)_8$ which also contains no CO bridges.[11]



I



IIa, L = L' = CO
b, L = CO; L' = $P(n\text{-}C_4H_9)_3$
c, L = L' = $P(OCH_3)_3$

Analogies with $HCo(PF_3)_4$, with related nonbridged carbonyl complexes, and with the recently synthesized trimethyl phosphite complexes $M_2[P(OCH_3)_3]_8$ (M = Co[13] or Rh[14]) (IIc) would certainly suggest structure II as the most likely for $Rh_2(PF_3)_8$.[15] Our investigation shows that this expectation is not borne out, either for $Rh_2(PF_3)_8$ or for its iridium analogue.

Experimental Section

The complexes $Rh_2(PF_3)_8$ and $Ir_2(PF_3)_8$ were prepared as described previously.[2] The monomeric complexes $HRh(PF_3)_4$ and $IrCl(PF_3)_4$