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Complexes of the Platinum Metals. 13.[1] β-Diketonato Derivatives of Ruthenium, Osmium, and Iridium

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Received June 6, 1977

β-Diketones react with platinum metal hydrides and with $[Ru(CO)_3(PPh_3)_2]$ in boiling 2-methoxyethanol or toluene to give β-diketonato derivatives of ruthenium, osmium, and iridium. Products obtained in this manner include the O,O′-coordinated acetylacetonato complexes $[M(acac)H(CO)(PPh_3)_2]$ and $[M(acac)_2(PPh_3)_2]$ (M = Ru or Os), $[Ru(acac)Cl(CO)(PPh_3)_2]$, $[Ir(acac)H_2(PPh_3)_2]$, and $[Ir(acac)ClH(PPh_3)_2]$, together with the corresponding trifluoroacetylacetonato (facac) and hexafluoroacetylacetonato (facfac) derivatives. Stereochemical assignments have been made on the basis of ^1H and ^{31}P NMR data.

The acidolysis of platinum metal hydrides (eq 1) has recently gained favor as an alternative to the classic halide metathesis reactions (eq 2) for the introduction of anionic ligands, R, into platinum metal phosphine complexes. The method can also be applied to selected zero oxidation state complexes (eq 3 and 4). Reactions of this type are now being commonly used to introduce a variety of anionic ligands into platinum metal complexes. Examples from our own laboratory involve the formation of carboxylato,[2,3] perfluorocarboxylato,[2,4] 1,3-diaryltriazenido,[5] and, as described in the present paper, β-diketonato derivatives. A similar reaction involving oxidative addition of acetylacetone to the molybdenum complex $[Mo(Ph_2PCH_2CH_2PPh_2)_2(C_2H_4)]$ has previously been reported.[6]

$$L_nM\text{-}H + HR \rightarrow L_nM\text{-}R + H_2 \quad (1)$$

$$L_nM\text{-}X + M'R \rightarrow L_nM\text{-}R + M'X \quad (2)$$

M' = Na, Ag, Tl^I, etc.

$$L_{n+1}M + HR \rightarrow L_nMHR + L \quad (3)$$

$$L_nMHR + HR \rightarrow L_nMR_2 + H_2 \quad (4)$$

Our interest in β-diketonato complexes derives in part from the variety of bonding modes displayed by β-diketonate anions when coordinated to transition metals in general and platinum metals in particular.[7] In the present work, introduction of β-diketonate ligands into crowded coordination environments containing three or four bulky triphenylphosphine ligands was intended to encourage monodentate O or C coordination to the metal. However, the conditions required to induce reaction proved sufficiently vigorous to cause phosphine displacement, and all metal complexes synthesized contain β-diketonate anions bound in conventional fashion as O,O′ donor chelates. Moreover, attempts to convert β-diketonate ligands from O,O′-bidentate coordination to γ-C-monodentate coordination by addition of triphenylphosphine or pyridine were unsuccessful.

Experimental Section

The complex $[IrCl_2H(PPh_3)_3]$ was prepared as described by Vaska,[8] and all other platinum metal complexes employed in this work were synthetized using the single-stage techniques developed in our laboratory.[9] The β-diketones were obtained from BDH and Fluorochem and were used without further purification. Reagent grade organic solvents were dried over molecular sieves and degassed before use. The light petroleum used had a boiling range of 60–80 °C. Reactions were performed under a nitrogen atmosphere, but products were worked up in air. Analyses, by the microanalytical laboratory, University College, London, and melting points, taken in sealed tubes under nitrogen, are given in Table I. Infrared spectra were run as Nujol mulls on a Perkin-Elmer 457 grating spectrometer. Proton and phosphorus NMR spectra were obtained at 90 and 36.43 MHz, respectively, using a Bruker HFX90 NMR spectrometer. Spectroscopic data are recorded in Table II or are given in the text (^{31}P NMR). ^{31}P NMR data are referenced to external H_3PO_4 and are reported in ppm with a positive value indicating a resonance at low field relative to the H_3PO_4.

(Acetylacetonato)carbonylhydridobis(triphenylphosphine)ruthenium(II), $[Ru(acac)H(CO)(PPh_3)_2]$. Method I. A mixture of carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.2 g), acetylacetone (0.05 g), and triethylamine (1 mL) in 2-methoxyethanol (15 mL) was heated under reflux for 15 min. After the resultant yellow solution was cooled overnight, the required product separated and was washed with methanol and light petroleum to yield yellow crystals (0.134 g, 85%).

Method II. Acetylacetone (0.05 g) was added to a suspension of carbonyldihydridotris(triphenylphosphine)ruthenium (0.2 g) in 2-methoxyethanol (15 mL), and the mixture was heated under reflux for 30 min. The required product separated from the yellow solution on cooling and was purified as described above to yield yellow crystals (0.131 g, 80%).

Method III. A mixture of acetylacetone (0.05 g) and tricarbonylbis(triphenylphosphine)ruthenium (0.2 g) in 2-methoxyethanol (15 mL) was heated under reflux for 6 h. The resultant yellow solution was evaporated to dryness and the residue washed with methanol and then recrystallized from dichloromethane/methanol to yield the required product as yellow crystals (0.169 g, 80%).

Similarly prepared using any of the above methods were: **carbonylhydrido(trifluoroacetylacetonato)bis(triphenylphosphine)ruthenium(II)** as lime yellow crystals (ca. 85%) and **carbonyl(hexafluoroacetylacetonato)hydridobis(triphenylphosphine)ruthenium(II)** as yellow crystals (ca. 80%).

(Acetylacetonato)carbonylchlorobis(triphenylphosphine)ruthenium(II), $[Ru(acac)Cl(CO)(PPh_3)_2]$. A mixture of acetylacetone (0.05 mL) and carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.2 g) in 2-methoxyethanol (15 mL) was heated under reflux for 30 min and then cooled overnight. The resultant precipitate was

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Table I. Melting Point and Analytical Data for β-Diketonato Complexes

Complex	Mp, °C	Analytical data[a]		
		% C	% H	% P
$Ru(acac)Cl(CO)(PPh_3)_2$ (Ia)	257–259	63.97 (63.99)	4.85 (4.73)	
$Ru(facac)Cl(CO)(PPh_3)_2$ (Ib,c)	190–192	59.14 (59.64)	4.10 (4.05)	7.18 (7.32)
$Ru(facfac)Cl(CO)(PPh_3)_2$ (Id)	191–192	56.50 (56.29)	3.59 (3.46)	
$Ru(acac)H(CO)(PPh_3)_2$ (IIa)[b]	199–200	66.60 (66.91)	5.06 (5.08)	
$Ru(acac)H(CO)(PPh_3)_2$ (IIa)[b]	198–200	66.91 (66.91)	5.31 (5.08)	
$Ru(acac)H(CO)(PPh_3)_2$ (IIa)[b]	198–200	66.92 (66.91)	5.18 (5.08)	
$Ru(facac)H(CO)(PPh_3)_2$ (IIb,c)	187–188	61.43 (62.45)	4.29 (4.30)	7.51 (7.67)
$Ru(facfac)H(CO)(PPh_3)_2$ (IId)	222–224	57.92 (58.13)	3.68 (3.72)	7.20 (7.09)
$Ru(acac)_2(PPh_3)_2$ (IIIa)	195–196	67.29 (67.06)	5.91 (5.38)	
$Ru(facfac)_2(PPh_3)_2$ (IIIb)	>280 dec	59.52 (59.31)	4.25 (4.10)	
$Ru(facac)_2(PPh_3)_2$ (IIIc–e)	>280 dec	53.01 (53.14)	3.11 (3.10)	
$Os(acac)H(CO)(PPh_3)_2$ (IIa)	214–216	60.72 (59.85)	4.68 (4.54)	
$Os(facac)H(CO)(PPh_3)_2$ (IIb,c)	194–196	55.41 (56.25)	3.95 (3.93)	6.75 (6.91)
$Os(facfac)H(CO)(PPh_3)_2$ (IId)	197–198	54.02 (53.11)	3.53 (3.29)	
$Os(acac)_2(PPh_3)_2$ (IIIa)	168–169	60.21 (60.51)	4.79 (4.86)	
$Os(facfac)_2(PPh_3)_2$ (IIIb)	211–212	53.99 (54.11)	3.67 (3.73)	
$Os(facac)_2(PPh_3)_2$ (IIIc–e)	213–215	49.69 (49.39)	2.85 (2.86)	
$Ir(acac)ClH(PPh_3)_2$ (IV)	dec	57.04 (57.77)	4.25 (4.50)	

[a] Calculated figures given in parentheses. [b] Samples prepared by methods a–c, respectively (see Experimental Section).

Table II. Infrared[a] and Proton NMR[b] Data for β-Diketonato Complexes

Complex	τ_{Me}	τ_{CH}	τ_{MH}	^2J(PH), Hz	ν(MH), cm^{-1}	ν(CO), cm^{-1}	ν(dik), cm^{-1}
$Ru(acac)Cl(CO)(PPh_3)_2$ (Ia)	9.12	5.50				1940	1585
	8.58						1520
$Ru(facac)Cl(CO)(PPh_3)_2$ (Ib)	8.83	4.85 (b)				1965	1620
(Ic)	8.65						1525
$Ru(facfac)Cl(CO)(PPh_3)_2$ (Id)		4.56				1965	1630
							1555
$Ru(acac)H(CO)(PPh_3)_2$ (IIa)	8.89	5.64	23.91 (t)	19.85	1935	1910	1590
	8.66						1505
$Ru(facac)H(CO)(PPh_3)_2$ (IIb)	8.82	5.51 (b)	24.32 (t)	19.85	1970	1945	1620
(IIc)	8.66		24.09 (t)	19.6			1520
$Ru(facfac)H(CO)(PPh_3)_2$ (IId)		5.34	24.47 (t)	19.50	1980	1950	1630
							1545
$Ru(acac)_2(PPh_3)_2$ (IIIa)	8.53	5.10					1580
	8.30						1520
$Ru(facac)_2(PPh_3)_2$ (IIIc–e)	8.45	5.0					1605
	8.27	4.85					1530
$Ru(facfac)_2(PPh_3)_2$ (IIIb)		4.50					1610
							1550
$Os(acac)H(CO)(PPh_3)_2$ (IIa)	8.98	5.57	25.68 (t)	16.91	2040	1900	1585
	8.71						1515
$Os(facac)H(CO)(PPh_3)_2$ (IIb)	8.95	5.49	26.27 (t)	16.5	2120 (b)	1910 (b)	1615
(IIc)	8.75	5.44	26.00 (t)	16.86			1520
$Os(facfac)H(CO)(PPh_3)_2$ (IId)		5.29	26.49 (t)	16.18	2140	1930	1620
							1550
$Os(acac)_2(PPh_3)_2$ (IIIa)	8.72	5.05					1570
	8.30						1520
$Os(facac)_2(PPh_3)_2$ (IIIc–e)	8.65	4.85					1600
	8.35 (d)	4.10					1520
$Os(facfac)_2(PPh_3)_2$ (IIIb)		4.80					1570
							1550
$Ir(acac)H_2(PPh_3)_2$	8.82	5.46	35.35	17.10	2180		1590
					2155		1520
$Ir(facac)H_2(PPh_3)_2$	8.81	5.31	35.80	17.10	2210		1620
			36.25	17.10	2180		1520
$Ir(facfac)H_2(PPh_3)_2$		5.22	35.80	17.71	2220		1640
					2180		1590
$Ir(acac)ClH(PPh_3)_2$ (IV)	9.22	5.40	34.09	14.65	2200		1580
	8.69						1515

[a] Infrared spectra were taken using Nujol mulls. [b] NMR spectra were run in $CDCl_3$ using a deuterium lock and are referenced against internal Me_4S. d = doublet, t = triplet, b = broad.

washed successively with methanol and light petroleum to yield yellow crystals (0.139 g, 88%).

Similarly prepared were: **carbonylchloro(trifluoroacetylacetonato)bis(triphenylphosphine)ruthenium(II)** as lime yellow crystals (90%) and **carbonylchloro(hexafluoroacetylacetonato)bis(triphenylphosphine)ruthenium(II)** as orange crystals (82%).

cis-**Bis(acetylacetonato)bis(triphenylphosphine)ruthenium(II), [Ru(acac)$_2$(PPh$_3$)$_2$].** A mixture of acetylacetone (0.06 g), triethylamine (1 mL), and dihydridotetrakis(triphenylphosphine)ruthenium (0.3 g) was heated under reflux in 2-methoxyethanol (15 mL) for 1 h. The resultant red solution was evaporated to small volume under reduced pressure and then diluted with methanol to give a brown precipitate. Recrystallization from dichloromethane/methanol gave the required product as orange crystals (0.127 g, 76%).

Similarly prepared were: **bis(trifluoroacetylacetonato)bis(triphenylphosphine)ruthenium(II)** as orange crystals (70%) and **bis(hexafluoroacetylacetonato)bis(triphenylphosphine)ruthenium(II)** as orange crystals (68%).

(Acetylacetonato)carbonylhydridobis(triphenylphosphine)osmium(II), [Os(acac)H(CO)(PPh_3)$_2$]. Method I. A mixture of acetylacetone (0.05 g), carbonylchlorohydridotris(triphenylphosphine)osmium (0.25 g), and triethylamine (1 mL) in 2-methoxyethanol (15 mL) and benzene (2 mL) was heated under reflux for 45 min. The yellow solution was then evaporated to ca. 1 mL and diluted with methanol to precipitate a pale yellow solid. Recrystallization from dichloromethane/methanol gave the required product as pale yellow crystals (0.158 g, 77%).

Method II. A mixture of acetylacetone (0.05 g) and carbonyldihydridotris(triphenylphosphine)osmium (0.25 g) in 2-methoxyethanol (15 mL) was heated under reflux for 45 min. The yellow solution was then evaporated to ca. 1 mL and diluted with methanol to precipitate a pale yellow solid. Purification as described above gave yellow crystals (0.178 g, 85%).

Similarly prepared by either method were: **carbonylhydrido(trifluoroacetylacetonato)bis(triphenylphosphine)osmium(II)** as pale yellow microcrystals (ca. 80%) and **carbonyl(hexafluoroacetylacetonato)hydridobis(triphenylphosphine)osmium(II)** as yellow microcrystals (ca. 75%).

Bis(acetylacetonato)bis(triphenylphosphine)osmium(II), [Os(acac)$_2$(PPh_3)$_2$]. Acetylacetone (0.1 g) and tetrahydridotris(triphenylphosphine)osmium (0.25 g) were heated under reflux in toluene (15 mL) for 6 h. The resultant dark red solution was evaporated to ca. 2 mL and then diluted with methanol to give a dark red solid which, upon recrystallization from dichloromethane/methanol, afforded the required product as red crystals (0.169 g, 71%).

Similarly prepared were: **bis(trifluoroacetylacetonato)bis(triphenylphosphine)osmium(II)** as dark red crystals (68%) and **bis(hexafluoroacetylacetonato)bis(triphenylphosphine)osmium(II)** as dark red crystals (60%).

(Acetylacetonato)dihydridobis(triphenylphosphine)iridium(III), [Ir(acac)H$_2$(PPh_3)$_2$]. A mixture of acetylacetone (0.1 g), triethylamine (1 mL), and *mer*-trihydridotris(triphenylphosphine)iridium (0.2 g) was heated under reflux in 2-methoxyethanol (15 mL) for 30 min. The required product deposited from solution on cooling and, after filtering off, was washed with methanol and dried in vacuo to afford yellow needle crystals (0.133 g, 80%).

Similarly prepared were: **dihydrido(trifluoroacetylacetonato)bis(triphenylphosphine)iridium(III)** as yellow crystals (76%) and **(hexafluoroacetylacetonato)dihydridobis(triphenylphosphine)iridium(III)** as yellow crystals (74%).

(Acetylacetonato)chlorohydridobis(triphenylphosphine)iridium(III), [Ir(acac)ClH(PPh_3)$_2$]. A mixture of acetylacetone (0.06 g), triethylamine (0.06 g), and dichlorohydridotris(triphenylphosphine)iridium (0.2 g) was heated under reflux in 2-methoxyethanol for 1 h. The solution was evaporated under reduced pressure and then diluted with acetone and filtered to remove chlorodihydridotris(triphenylphosphine)iridium. The filtrate was evaporated to ca 1 mL under reduced pressure to yield a pale yellow solid. Recrystallization from acetone/methanol gave the required product as pale yellow crystals (0.120 g, 63%).

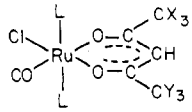
Treatment of (Acetylacetonato)carbonylhydridobis(triphenylphosphine)ruthenium(II) with Pyridine. (Acetylacetonato)carbonylhydridobis(triphenylphosphine)ruthenium (0.2 g) was heated in neat pyridine (10 mL) at ca. 100 °C for 3 h. The yellow solution was evaporated to dryness under reduced pressure and then treated with methanol (5 mL). The resultant precipitate was filtered off, washed with light petroleum, and identified as unchanged starting complex (80%) by comparison with an authentic specimen. Carbonylhydrido(hexafluoroacetylacetonato)bis(triphenylphosphine)ruthenium was also recovered unchanged after similar treatment.

Treatment of (Acetylacetonato)carbonylhydridobis(triphenylphosphine)ruthenium(II) with Triphenylphosphine. (Acetylacetonato)carbonylhydridobis(triphenylphosphine)ruthenium (0.2 g) and triphenylphosphine (0.07 g) were heated under reflux in 2-methoxyethanol (10 mL) for 4 h. The yellow solution was evaporated to dryness and then treated with methanol (5 mL). The resultant cream solid was filtered off, washed with light petroleum, and identified as unchanged starting material (80%) by comparison with an authentic sample. Carbonylhydrido(hexafluoroacetylacetonato)bis(triphenylphosphine)ruthenium was also recovered unchanged after similar treatment.

Results and Discussion

The products described in this paper are generally prepared by heating a metal hydride complex with the appropriate β-diketone under reflux in an alcoholic medium, usually 2-methoxyethanol. In some instances the addition of triethylamine led to replacement of chloride ligands by acetylacetonate. For reactions of [OsH_4(PPh_3)$_3$] with β-diketones the preferred solvent is toluene. All the new complexes show clear infrared evidence for the presence of O,O′-coordinated bidentate β-diketonate ligands (ν(acac) 1590–1570 and 1520–1505 cm^{-1}; ν(facac) 1620–1600 and 1530–1520 cm^{-1}; ν(facfac) 1640–1570 and 1555–1545 cm^{-1}).[7,10]

[Ru(diketonato)Cl(CO)(PPh_3)$_2$] Complexes (diketonato = acac, facac, or facfac). The ruthenium complex [RuClH(CO)(PPh_3)$_3$] reacts with β-diketones in boiling 2-methoxyethanol to afford the corresponding β-diketonato complexes [Ru(diketonato)Cl(CO)(PPh_3)$_2$] as yellow or orange air-stable crystalline solids. The corresponding osmium precursor [OsClH(CO)(PPh_3)$_3$] fails to react with β-diketones, presumably because of the greater stability and/or the inertness of the Os–H linkage relative to the Ru–H bond. We have therefore been unable to synthesize the osmium species [Os(diketonate)Cl(CO)(PPh_3)$_2$] by the acidolysis method. The infrared spectrum of the acetylacetonato complex [Ru(acac)Cl(CO)(PPh_3)$_2$] shows bands attributable to a chelate acac ligand (1585 and 1520 cm^{-1}) and a carbonyl group (1940 cm^{-1}). The ^{1}H NMR spectrum shows two methyl resonances of equal intensity at τ 8.6 and 9.1, indicative of chelate acac bound trans to an asymmetric ligand pair. The proton decoupled ^{31}P NMR spectrum comprises a singlet (δ 29.22). These data permit unequivocal assignment of stereochemistry Ia to the acetylacetonato complex.

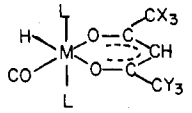


Ia, X = Y = H
b, X = F, Y = H
c, X = H, Y = F
d, X = Y = F
(L = PPh_3)

The corresponding trifluoroacetylacetonato complex, [Ru(facac)Cl(CO)(PPh_3)$_2$], shows infrared bands at 1620 and 1525 cm^{-1} (chelate facac ligand) and 1965 cm^{-1} (CO). The ^{1}H NMR spectrum contains two methyl resonances at τ 8.65 and 8.83 with relative intensities 1:2.5, and the proton-decoupled ^{31}P NMR spectrum comprises two singlets (δ 41.8 and 41.4) with a similar intensity ratio. These data point to the presence of two isomers of [Ru(facac)Cl(CO)(PPh_3)$_2$] (Ib and Ic). Since the spectroscopic data (ν(CO)) for the major isomer agree closely with the corresponding data for the facfac rather than the acac derivative, we conclude that this isomer is Ib with –C(=O)CF_3 trans to carbonyl rather than chloride. By analogy with the acac and facac derivatives, the facfac complex [Ru(facfac)Cl(CO)(PPh_3)$_2$] is assigned stereochemistry Id. This assignment is in accord with the available spectroscopic data (ν(CO) 1965 cm^{-1}; ^{31}P NMR, δ 48.41 (s)).

[M(diketonato)H(CO)(PPh_3)$_2$] Complexes (M = Ru or Os). The ruthenium complexes have been obtained by the reaction of the appropriate β-diketones with [RuH_2(CO)(PPh_3)$_3$], [$Ru(CO)_3$(PPh_3)$_2$], or [RuClH(CO)(PPh_3)$_3$]; in the last instance the presence of triethylamine is necessary for the formation of the hydrido product. The corresponding osmium complexes were prepared in an analogous manner from [OsH_2(CO)(PPh_3)$_3$] or [OsClH(CO)(PPh_3)$_3$] and NEt_3. The new complexes [M(diketonato)H(CO)(PPh_3)$_2$] are all air-stable yellow crystalline compounds soluble in chloroform or dichloromethane and sparingly soluble in benzene. The proton NMR spectra of the acetylacetonato derivatives [M(acac)H(CO)(PPh_3)$_2$] each contain a high-field triplet (M = Ru,

τ_{RuH} 23.91, $^2J(PH)_{cis}$ = 19.85 Hz; M = Os, τ_{OsH} 25.68, $^2J(PH)_{cis}$ = 16.91 Hz) and two methyl resonances of equal intensity (M = Ru, τ_{Me} 8.66 and 8.89; M = Os, τ_{Me} 8.71 and 8.98). The ^{31}P NMR spectrum of each compound comprises a singlet. These data are indicative of stereochemistry IIa.

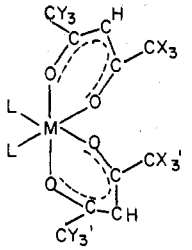


IIa, X = Y = H
b, X = H, Y = F
c, X = F, Y = H
d, X = Y = F
(L = PPh_3; M = Ru, Os)

The corresponding trifluoroacetylacetonato complexes [M(facac)H(CO)$(PPh_3)_2$] both exist in two isomeric forms. The isomers each contain two equivalent phosphorus nuclei (proton-decoupled ^{31}P NMR singlet) cis to the hydride ligand (^1H NMR high-field triplet) and are accordingly assigned stereochemistry IIb and IIc. On the basis of NMR integration data, the ratios of the ruthenium and osmium isomers are ca. 1:2 and 1:1.8, respectively. In each case the τ values of the hydride resonances in the NMR spectra of the major and minor isomers are close to those found for the corresponding facfac and acac complexes, respectively. We therefore conclude that the major isomers have stereochemistry IIb and the minor isomers have stereochemistry IIc. This assignment is in accord with the known strong σ-donor and strong π-acceptor properties of hydride and carbonyl ligands, respectively.

Finally, the hexafluoroacetylacetonato complexes [M(facfac)H(CO)$(PPh_3)_2$] have spectroscopic properties (τ_{RuH} 24.47 (t), $^2J(PH)_{cis}$ = 19.50 Hz; τ_{OsH} 26.49 (t), $^2J(PH)_{cis}$ = 16.18 Hz) indicative of stereochemistry IId.

[M(diketonato)$_2$(PPh_3)$_2$] Complexes (M = Ru or Os). The dark orange ruthenium complexes were prepared by heating [$RuH_2(PPh_3)_4$] and the appropriate β-diketone under reflux in 2-methoxyethanol in the presence of triethylamine. The dark-red osmium analogues were obtained by heating [$OsH_4(PPh_3)_3$] and the appropriate β-diketone under reflux in toluene solution. The acetylacetonato derivatives [M(acac)$_2$(PPh_3)$_2$] each display two methyl resonances of equal intensity and one γ-CH resonance, indicating the presence of two equivalent but asymmetrically bound acetylacetonate ligands in each complex. These data unequivocally establish stereochemistry IIIa. The ruthenium derivative [Ru(acac)$_2$(PPh_3)$_2$] has been prepared before from [$RuCl_2(PPh_3)_3$], acetylacetone, and triethylamine in boiling benzene and shown to crystallize in orange and green forms from methanol and benzene, respectively.[11] We have confirmed the occurrence of this reversible color change but are unable to provide any additional information concerning the origin of the phenomenon. The hexafluoroacetylacetonato complexes [M(facfac)$_2$(PPh_3)$_2$] are assigned the cis stereochemistry IIIb on the basis of their ^{19}F NMR spectra, each of which displays two CF_3 resonances of equal intensity, indicative of asymmetrically coordinated hexafluoroacetylacetonate ligands.

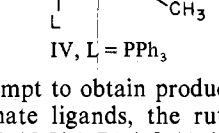


IIIa, X = X′ = Y = Y′ = H
b, X = X′ = Y = Y′ = F
c, X = X′ = H, Y = Y′ = F
d, X = X′ = F, Y = Y′ = H
e, X = Y′ = H, X′ = Y = F
(L = PPh_3; M = Ru, Os)

The corresponding trifluoroacetylacetonato complexes [M(facac)$_2$(PPh_3)$_2$] are capable of adopting five isomeric forms, two involving a trans pair of phosphine ligands and three (IIIc–e) containing a pair of cis phosphine ligands. Since the complexes [M(acac)$_2$(PPh_3)$_2$] and [M(facfac)$_2$(PPh_3)$_2$] were obtained only in the cis forms, it seems probably that the [M(facac)$_2$(PPh_3)$_2$] species adopt a similar geometry. The probable isomers are therefore IIIc–e. The proton NMR spectrum of each complex contains two methyl resonances of unequal intensity and thus suggests the presence of at least two of the three possible cis isomers.

[Ir(diketonato)H$_2$(PPh_3)$_2$] Complexes. These complexes have previously been reported,[12] and the present syntheses differ from the original ones only in minor detail. Our spectroscopic data, given in Table II, are essentially in agreement with those reported by the earlier workers and support their stereochemical assignment (trans PPh_3 ligands).[12]

[Ir(diketonato)ClH(PPh_3)$_2$] Complexes. [$IrCl_2H(PPh_3)_3$] (trans chlorides) reacts with equimolar quantities of acetylacetone and base (triethylamine) in boiling 2-methoxyethanol to afford the cream air-stable [Ir(acac)ClH(PPh_3)$_2$]. In the presence of a slight excess of base, small amounts of [$IrClH_2(PPh_3)_3$] form, and if a large excess of base and acetylacetone is employed the major product is [Ir(acac)H_2(PPh_3)$_2$]. The latter product is identical with an authentic specimen prepared as described above. The NMR data (τ_{IrH} 34.09, $^2J(PH)_{cis}$ = 14.65; τ_{Me} 8.69 and 9.22; τ_{CH} 5.40) for the [Ir(acac)ClH(PPh_3)$_2$] complex are indicative of stereochemistry IV.



IV, L = PPh_3

In a further attempt to obtain products containing monodentate β-diketonate ligands, the ruthenium complexes [Ru(β-diketonate)H(CO)$(PPh_3)_2$] (β-diketonate = acac or facfac) were treated with triphenylphosphine or pyridine under various conditions. The palladium and platinum O,O′-chelated acetylacetonato complexes [M′(acac)$_2$] have recently been shown to react readily with these ligands to yield γ-C-bonded monodentate acetylacetonato derivatives [M′(acac)$_2$L] (L = PPh_3 or py) and [M′(acac)$_2$py$_2$].[13,14] However, no products containing monodentate β-diketonate ligands were obtained from our studies.

Finally, examination of the collected spectroscopic data (Table II) reveals a number of trends consistent with the greater inductive power of CF_3 relative to CH_3 groups. Thus, replacement of CH_3 by CF_3 groups in the β-diketonate ligands leads to a significant reduction of τ_{CH} and, where relevant, an increase in τ_{MH} for the trans hydride ligand. The same change also leads to an increase in the C–O stretching frequencies of the β-diketonate ligands concerned and an increase in ν(CO) and ν(MH) for the trans carbonyl and hydride ligands, respectively.

Acknowledgment. Maria A. M. Queirós wishes to thank the Universidade do Minho, Braga, Portugal, for leave of absence.

Registry No. Ru(acac)Cl(CO)$(PPh_3)_2$, 64567-29-9; Ru(facac)Cl(CO)$(PPh_3)_2$(Ib), 64625-04-3; Ru(facac)Cl(CO)$(PPh_3)_2$(Ic), 64567-28-8; Ru(facfac)Cl(CO)$(PPh_3)_2$, 64567-27-7; Ru(acac)H(CO)$(PPh_3)_2$, 61951-11-9; Ru(facac)H(CO)$(PPh_3)_2$(IIb), 64567-31-3;

Ru(facac)H(CO)$(PPh_3)_2$(IIc), 64625-62-3; Ru(facfac)H(CO)$(PPh_3)_2$, 64567-30-2; Ru(acac)$_2(PPh_3)_2$, 26455-78-7; Ru(facac)$_2(PPh_3)_2$, 64625-08-7; R(facfac)$_2(PPh_3)_2$, 64567-38-0; Os(acac)H(CO)$(PPh_3)_2$, 61950-99-0; Os(facac)H(CO)$(PPh_3)_2$(IIb), 64625-07-6; Os(facac)H(CO)$(PPh_3)_2$(IIc), 64567-37-9; Os(facfac)H(CO)$(PPh_3)_2$, 64567-36-8; Os(acac)$_2(PPh_3)_2$, 64567-35-7; Os(facac)$_2(PPh_3)_2$, 64567-34-6; Os(facfac)$_2(PPh_3)_2$, 64567-33-5; Ir(acac)ClH$(PPh_3)_2$, 64567-32-4; Ir(acac)$H_2(PPh_3)_2$, 64625-61-2; Ir(facac)$H_2(PPh_3)_2$, 64625-06-5; Ir(facac)$H_2(PPh_3)_2$, 64625-05-4; RuClH(CO)$(PPh_3)_3$, 16971-33-8; RuH_2(CO)$(PPh_3)_3$, 25360-32-1; Ru$(CO)_3(PPh_3)_2$, 14741-36-7; $RuH_2(PPh_3)_4$, 19529-00-1; OsClH(CO)$(PPh_3)_3$, 16971-31-6; OsH_2(CO)$(PPh_3)_3$, 12104-84-6; $OsH_4(PPh_3)_3$, 24228-59-9; *mer*-$IrH_3(PPh_3)_3$, 18660-46-3; $IrCl_2H(PPh_3)_3$, 16971-01-0.

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Synthesis and Circular Dichroism Studies of Isoelectronic Complexes: Tetracyanoferrate(II) and Tetracyanocobaltate(III) with (*R*)-1,2-Diaminopropane and (*R,R*)-*trans*-1,2-Diaminocyclohexane Chelates

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Received July 21, 1977

The preparation of diamagnetic isostructural and isoelectronic tetracyanoferrate(II) and tetracyanocobaltate(III) with optically active (*R*)-1,2-diaminopropane and (*R,R*)-*trans*-1,2-diaminocyclohexane is reported. Absorption, circular dichroism (CD), and ^{1}H NMR spectra are reported. The three visible components of the CD in the spectra of a Fe(II) complex have similar origins to the corresponding components of the Co(III) analogue.

Circular dichroism (CD) spectra have been measured for a variety of Co(III) complexes,[1] but there have been few reports on CD spectra of other d^6 metal complexes. In particular, no reports are available on diamagnetic Fe(II) complexes except those with certain conjugated ligands such as *o*-phenanthroline (phen) and 2,2′-bipyridyl (bpy). CD spectra of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ have been studied in terms of the exciton approach to deduce the absolute configuration.[2] These complexes have intense charge-transfer (CT) absorptions in the visible region which obscure d–d transitions.[2] The structural investigations of transition-metal complexes will be aided and expanded by investigation of CD spectra of isoelectronic and isostructural metal complexes. Since Fe(II) and Fe(III) ions are biologically important, a knowledge of the application of CD methods to model systems may someday allow CD techniques to be applied to the structural understanding of Fe complexes in biological systems. The first step in the elucidation of the CD spectra of Fe(II) complexes is a comparison of diamagnetic Fe(II) complexes with those of Co(III) complexes. Fe(II) complexes having an optically active diamine as the sole source of dissymmetry are especially suited to study because their CD spectra may be compared with those of Co(III) complexes for which a vast quantity of data has been accumulated. Tetracyanodiamineferrate(II) complexes have been shown to be diamagnetic[3] and isostructural with the corresponding cobalt(III) complexes.[4] Optically active derivatives of these complexes can be prepared with resolved diamines, (*R*)-1,2-diaminopropane (*R*-pn) and (*R,R*)-*trans*-1,2-diaminocyclohexane (*R*-chxn). The preparation and characterization of this type of new complexes are reported herein, and their CD spectra are reported in detail.

Experimental Section

Materials. Commercially available 1,2-diaminopropane, pn, was resolved into *R*-pn by the method of Dwyer;[5] $[\alpha]^{23}_D$ −33.6° (benzene). 1,2-Diaminocyclohexane (Tokyo Kasei) was resolved into the (*R,R*)-trans isomer, *R*-chxn, by the method of Jaeger and Bijkerk;[6] $[\alpha]^{23}_D$ −43.0° (free diamine, 3% methanol solution), lit.[7] $[\alpha]^{24}_D$ −44.1°. Ferrous perchlorate hexahydrate (Alfa) was used without further purification. Potassium bromopentacyanocobaltate(III) was prepared by the method of Adamson[8] from cobaltous acetate and 5 equiv of KCN followed by oxidation with bromine. The purity of this compound was found to be ca. 70% from optical absorbance at 395 nm, but it was used to prepare subsequent complexes without further purification because of lack of a method for recrystallization.[9]

Preparation of Tetracyano Complexes. Sodium Tetracyano(*R*-pn)ferrate(II)·0.5H_2O·0.5NaClO$_4$. A methanol solution (40 mL) of *R*-pn (14.5 g, 0.2 mol) was added to a methanol solution (200 mL) of ferrous perchlorate hexahydrate (35.2 g, 0.098 mol) with vigorous stirring under nitrogen at 0 °C, followed by the addition of aqueous sodium cyanide (19.1 g, 0.195 mol) in 80 mL of water. The resultant yellow-brown solution was concentrated to near dryness under reduced pressure below 40 °C. To the oily residue, ethanol (40 mL) was added, and a yellow precipitate was collected on a filter and washed with ethanol and ether; yield 29.4 g (87%). The crude product was recrystallized by dissolving it in 35 mL of water, followed by the addition of a 1:2 methanol ethanol mixture (180 mL) at 30 °C and letting the mixture stand overnight in a refrigerator. Anal. Calcd for $Na_2[Fe(C_3H_{10}N_2)(CN)_4]\cdot 0.5H_2O\cdot 0.5NaClO_4$: C, 24.90; H, 3.16; N, 24.25. Found: C, 24.00; H, 3.16; N, 23.99.[10]

Sodium Tetracyano(*R*-chxn)ferrate(II)·0.5H_2O·0.5NaClO$_4$. The same procedure was used as for the above preparation; yield 27.0 g

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