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Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part XIII.[1] η^5-Oxocyclohexadienyl- and η^6-Phenol-Complexes.

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Summary

The acetone solvent complexes $[M(\eta^5\text{-}C_5Me_5)(Me_2CO)_3][PF_6]_2$, (M = Rh, Ir) prepared in situ from $[M(\eta^5\text{-}C_5Me_5)Cl_2]_2$ and $AgPF_6$ in acetone, reacted with phenol to give the hydrogen-bonded dimeric phenol complexes (II) $[\{M(\eta^5\text{-}C_5Me_5)\}_2\{\eta^6\text{-PhO-H}\cdots O(\eta^6\text{-})Ph\}][PF_6]_3$; these were easily deprotonated with base to the corresponding η^5-oxocyclohexadienyl complexes $[M(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_6H_5O)]PF_6$, which showed $\nu(C=O)$ at 1630 (Rh) and 1635 (Ir) cm^{-1}. An unstable η^6-phenol iridium complex, $[Ir(C_5Me_5)(PhOH)][PF_6]_2$, was obtained on protonation of (II, M = Ir).

Although a number of η^6-phenol complexes have been prepared [2-7] little of their chemistry has been reported. It is especially surprising that deprotonation reactions have not been more exploited in particular as a number of workers have noted that the acidity of phenol (and substituted phenols) is considerably enhanced on complexing to a transition metal [2,7].

In continuation of our work on the arene(pentamethylcyclopentadienyl)-rhodium and -iridium cations [1,8,9], we here report on cationic complexes of η^6-phenol and η^5-oxocyclohexadienyl (deprotonated phenol). The latter ligand does not appear to have been observed previously.

Note added in proof:

Since this paper was prepared we have noted that Cole-Hamilton et al. have also recently reported η^5-oxocyclohexadienyl complexes of Rh and Ru; the crystal structure of one of their complexes confirms the η^5-oxocyclohexadienyl formulation (D.J. Cole-Hamilton, R.J. Young, and G. Wilkinson, J.C.S. Dalton (1976) 1995.)

Phenol reacted with both the rhodium and iridium acetone solvent complexes (Ia and Ib) [10] to give the hydrogen-bonded dimer compounds (II), which are assigned the structure shown on the basis of analysis, NMR and particularly the IR spectra.

Complexes containing intermolecular hydrogen bonds show ν(OH) as a broad band in the region 1400-3000 cm^{-1} [11]; increase of the O-H···O bond strength is paralleled by a decrease in the frequency of the band and splitting is also observed. For example, the hydrogen-bonded adducts of 8-hydroxyquinoline with o-nitrophenolate complexes of Na, K, Rb and Cs showed two broad bands in the regions 1800-1900 and 2400-2600 cm^{-1} [12].

The iridium complex (IIb) showed similar broad bands at 1830 and 2360 cm^{-1}, the intensities of which were considerably decreased after exchange with D_2O, and which are assigned to (O-H···O) by analogy. For the rhodium complex (IIa) only the higher frequency vibration (at 2350 cm^{-1}) could be observed as a weak and very broad band; this band disappeared completely after exchange with D_2O.

Hydrogen-bonded complexes of this type have not been described previously, but Weiss and Hübel [13] noted the formation of H-bonded adducts between quinol and complexes the ligands of which contained a ketonic CO, e.g. cyclopentadienone- and tropone-(tricarbonyl)iron. They also noted that cyclopentadienone-(tricarbonyl)iron readily formed salts with acids, $[Fe(C_5H_4OH)(CO)_3]^+X^-$.

The rhodium hexafluorophosphate complex (IIa) was unstable in acetone and decomposed slowly (40% in 48h/20°C) to tris-μ-difluorophosphato-bis-(pentamethylcyclopentadienyl)dirhodium hexafluorophosphate, which we have previously shown to be generated from $[Rh(C_5Me_5)(Me_2CO)_3][PF_6]_2$, (Ia), on standing in acetone [10].

The complexes (IIa and IIb) reacted with base (Na_2CO_3-H_2O) to give the deprotonated compounds (III), the IR spectra of which now showed two new bands, a very strong one at 1630 cm^{-1} (Rh) [and 1635 (Ir)] together with one at 1595 cm^{-1} (Rh) [and 1610 (Ir)]. These we assign to coupled ν(C=O) and ν(C=C) vibrations [ν(C=C) at 1570 in (IIa) and 1552 cm^{-1} in (IIb) have now disappeared].

The deprotonated complexes (IIIa and IIIb) may be formulated as containing either an η^6-phenolate (III') or an η^5-oxocyclohexadienyl (III) ligand. However, neither phenol, phenolate ion, nor complexes containing M-OPh show strong bands in the carbonyl region [14]. By contrast, a large number of complexed cyclic ligands containing α,β-α',β'-unsaturated ketones (-CR=CR-CO-CR=CR-) are known which show strong bands in the IR between 1550 and 1650 cm^{-1}. For example, a variety of substituted cyclopentadienone(tricarbonyl)iron complexes showed ν(CO) at 1605-1650 cm^{-1} [15], Ni(duroquinone)$_2$ has ν(CO) at 1577 cm^{-1} [16], [Rh(duroquinone)Cl]$_n$ has ν(CO) at 1608 cm^{-1} [17] (c.f. ν(CO) for uncomplexed cyclopentadienones is in the region of 1700 cm^{-1} and for free duroquinone is 1629 cm^{-1}).

We therefore conclude that the best representation for the deprotonated rhodium and iridium compounds is indeed the η^5-oxocyclopentadienyl form (IIIa) or (IIIb). Support for this suggestion also comes from the ^{1}H NMR spectra which show that in the complexes (III) the ortho-hydrogens are moved substantially more further upfield [ca. 0.6 ppm, by comparison with (IIa or b)] than are the m- and p-hydrogens [0.2 to 0.35 ppm]. Hydrogens attached to C(2) and C(6) in 2-6-η-cyclohexadienyl complexes are usually observed at high field [8,18]; the upfield shift in (III) is somewhat mitigated owing to the proximity of the carbonyl and also because of the positive charge on the complex.

The iridium complex (IIb) was protonated in hexafluorophosphoric acid to a complex which showed no ν(OH) in the IR spectrum attributable to hydrogen-bonding and only a medium-weak intensity band at 1565 cm^{-1}. This complex was difficult to purify and analyse and reverted to the hydrogen-bonded complex (IIb) when warmed in vacuo (5 min/54°C). It is formulated as the η^6-phenol complex (IV). Addition of HPF_6 to the rhodium complex (IIa) did not give a clean reaction and no product was isolated.

The interconversions are summarised in the Scheme.

Table

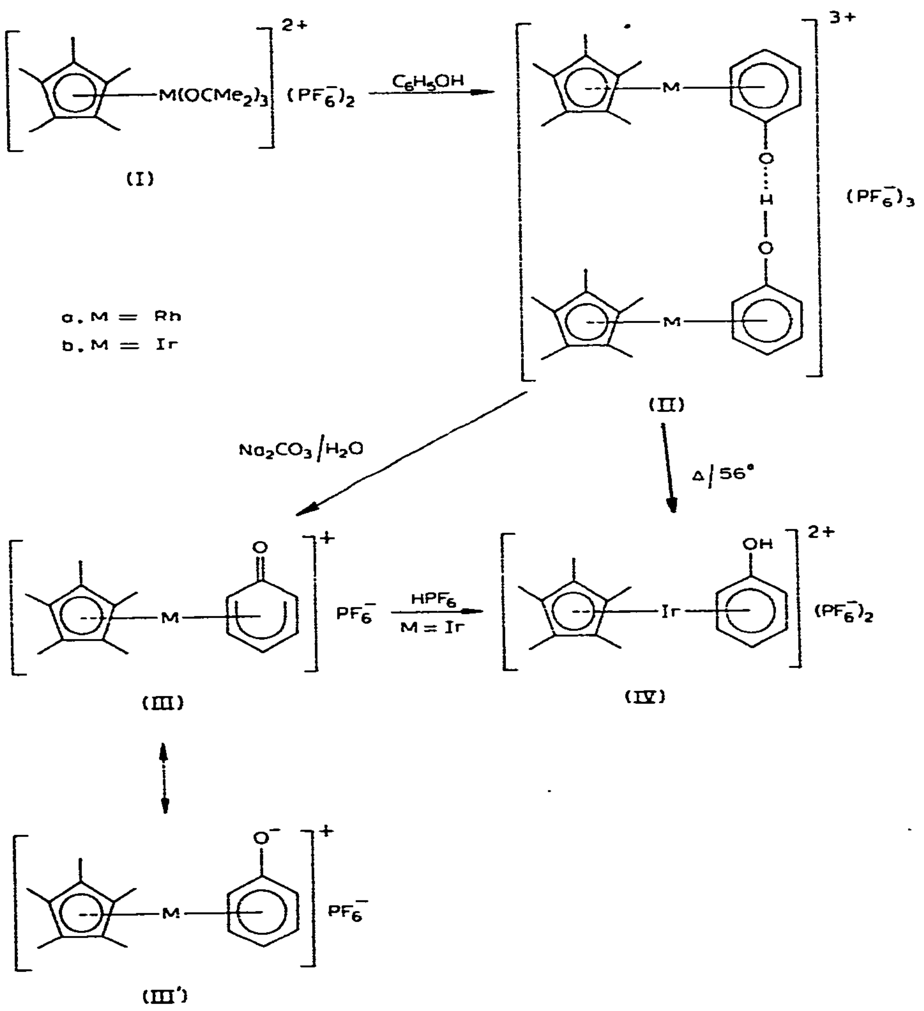
Analytical and spectroscopic data

Complex		Analyses (calculated figures in parentheses)		^{1}H n.m.r. (δ)[a]		Infrared[b] (cm^{-1})
		C	H	C_5Me_5	ring protons	
$[\{Rh(C_5Me_5)(C_6H_5O)\}_2H](PF_6)_3$	(IIa)	34.8	3.9	2.30(s)	o-H,6.32(m)	ν(O-H··O)2350(v.br)
		(35.0)	(3.8)		m-,p-H,7.05(m)	ν(C=C)1570(m)
$[\{Ir(C_5Me_5)(C_6H_5O)\}_2H](PF_6)_3$	(IIb)	30.1	3.1	2.42(s)	o-H,6.30(m)	ν(O-H··O)2360(br),1830(br)
		(30.4)	(3.2)		m-,p-H,6.80(m)	ν(C=C)1552(m),1512(w)
$[Rh(C_5Me_5)(C_6H_5O)]PF_6$	(IIIa)	40.2	4.4	2.22(s)	o-H,5.70d[*J*(H-H)=7]	ν(C=O,C=C)1630(vs),1595(s)
		(40.4)	(4.2)		m-H,p-H,6.62(m)	
$[Ir(C_5Me_5)(C_6H_5O)]PF_6$	(IIIb)	34.2	3.7	2.34(s)	o-H,5.76dd	ν(C=O)1635(vs),1610(s)
		(34.0)	(3.6)		[*J*(1-H-m-H)=7;	
					J(o-H-p-H)=2Hz]	
					m-H,p-H,6.60(m)	
$[Ir(C_5Me_5)(C_6H_5OH)](PF_6)_2$	(IV)	2.87[c]	3.1	2.48(s)	o-H,6.54(m)	ν(C=C)1565(m)
		(27.0)	(3.0)		m-H,p-H,7.07(m)	

[a] In acetone-d_6.

[b] As Nujol mulls.

[c] Readily deprotonated *in vacuo*.



EXPERIMENTAL

All reactions were carried out under nitrogen; analytical and spectroscopic data are collected in the Table. All the complexes showed ν(P-F) as a very strong band at 840 cm^{-1}.

$[\{Ir(C_5Me_5)\}_2\{(PhO)_2H\}][PF_6]_3$ (IIb)

$[Ir(C_5Me_5)Cl_2]$ (0.2g, 0.25 mmole) and $AgPF_6$ (0.25, 1.0 mmole) were stirred together in acetone (10 ml) for 10 min; the precipitated silver chloride was then filtered off to give a solution of the tris(acetone) complex,

$[Ir(C_5Me_5)(Me_2CO)_3][PF_6]_2$. Phenol (0.05 g, 0.53 mmole) was added to this solution and the mixture stirred for a further 10 min. The solvent was removed in vacuo to give an off-white solid which was washed with chloroform and ether, and then crystallized from acetone and ether to give pure white crystals of (IIb) (0.25 g, 78%).

The white rhodium analogue, $[\{Rh(C_5Me_5)\}_2\{(PhO)_2H\}][PF_6]_3$ (IIa), was prepared in 83% yield using the procedure described above.

$[Ir(C_5Me_5)(C_6H_5O)]PF_6$ (IIIb)

The hydrogen-bonded phenol complex (IIb) (0.2 g, 0.15 mmol) dissolved in acetone (20 ml) containing water (0.1 ml) was stirred with sodium carbonate (0.2 g for 30 min. The solvent was removed in vacuo to leave a yellow solid which was crystallised from acetone-ether to give $[Ir(C_5Me_5)(C_6H_5O)]PF_6$ (0.15 g, 85%).

$[Rh(C_5Me_5)(C_6H_5O)]PF_6$ (IIIa)

The yellow rhodium complex (IIIa) was obtained in 80% yield from (IIa) in an analogous manner. The ^{13}C $\{^1H\}$ NMR spectrum (in acetone-d_6) showed resonances at δ 9.5 (s,$C_5\underline{Me}_5$), 92.9 [d,$\underline{C}_5Me_5$,$\underline{J}$(C-Rh)=4Hz], 89.3 [d,p-C in C_6H_5O,$\underline{J}$=5Hz], 104.6 [d,o-C in C_6H_5O, $\underline{J}$=6Hz], and 106.3 [d,m-C in C_6H_5O, $\underline{J}$=6Hz]; C(1) in C_6H_5O could not be observed.

$[Ir(C_5Me_5)(PhOH)][PF_6]_2$ (IV)

A solution of the hydrogen-bonded iridium phenol complex (IIb) (0.1 g, 0.08 mmol) in acetone (10 ml) was treated with hexafluorophosphoric acid (0.3 ml). The solution was stirred for 5 min. and then ether was added until a white precipitate of $[Ir(C_5Me_5)(PhOH)][PF_6]_2$, (IV), appeared. The precipitate was filtered off, washed with ether and briefly dried. Yield, 0.05 g, 50%; attempts to purify this material further failed owing to the ease with which it decomposed to regenerate (IIb).

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