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SYNTHESIS AND STABILITY OF MIXED SANDWICH CHELATE TRANSITION METAL COMPLEXES*

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SUMMARY

The reaction between salts of transition metal sandwich cations and β-diketones (HCh) has been investigated using allyl, cyclopentadienyl and arene derivatives of Fe, Pd, Cr, Ti as sandwich components, and with acetylacetone (HA), dibenzoylmethane (HD), thenoyltrifluoroacetone (HT), ferrocenoyltrifluoroacetone (Hϕ) as chelating components. The sequence of bond stabilities in bis-aromatic iron complexes has been established as Ch–Fe > Cp–Fe > Arene–Fe whilst in allyl complexes the corresponding sequence has been shown to be Ch–Fe > All–Fe > CO–Fe. Disproportionation products of mixed sandwich chelate complexes containing one hydrocarbon ligand have been isolated. The corresponding influence of hydrocarbon ligands and of the chelate in mixed complexes as indicated by IR and electronic spectra are discussed as are the possible changes in bond character which occur in these complexes.

INTRODUCTION

The formation of chelate salts by sandwich cations (for example, ferricenium carboxylates[1], $(Cp_2TiCh)^+An^-$[2], allyl–Pd–Ch[3], where Ch represents β-diketonate) has been previously described. In this paper the reaction of chelate salts of some sandwich cations with different β-diketones, $L_nM^{m+}Ch_m^-$ is described with particular emphasis on their stabilities and on the formation of products containing a smaller number of sandwich ligands from them. The structure, properties, stability and bond nature of the latter have been investigated.

In studying the stability of the chelate salts described in this paper special attention has been paid to the influence of (a) the covalent nature of the metal–ligand bond and (b) the electron shell structure of central metal atom upon the stability.

The degree of metal–ligand bond covalence is determined both by the initial chelated metal atom and the anion stability of the entering ligand (or alternatively by the base strength of the ligand anion). Ultimately, the covalent nature of the metal–

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ligand bond depends upon the effective charge produced on the metal atom by the initial ligands present in the complex and by the effect of this charge on the oxygen atoms of the entering ligand, the latter being regulated by the nature of the substituents in the β-diketone.

When the electronic structure of the central metal atom in the sandwich complex is filled through the utilization of the four electrons of the oxygen atoms of the chelating ligands and when the number of electrons in the outer shell exceeds 18 or 16 (the most characteristic number for some sandwhich complexes), then conditions leading to instability of the complex arise. Depending on the stability of the bonds associated with the initial ligands or the incoming ligand, either a variation in the degree of ligand bonding will occur or some of the ligands will be eliminated with the simultaneous formation of more stable complexes.

To investigate such processes the reactions of sandwich cations of the type $(Cp_2Fe)^+$, $(CpFeC_6H_6)^+$, $[AllFe(CO)_3]^+$, $(Arene_2Cr)^+$ (Arene=ethylbenzene, biphenyl), $(Cp_2Ti)^{2+}$, and $(AllPd)^+$, (usually as their salts or hydroxides) have been studied with the anions of β-diketones as the free diketone or sodium enolate chosen from the following acetylacetone (HA), dibenzoylmethane (HD), thenoyltrifluoroacetone (HT), ferrocenoyltrifluoroacetone (Hϕ).

EXPERIMENTAL

Reactions between ferricenium salts and β-diketones

Bis(acetylacetonato)cyclopentadienyliron. Ethanol solutions containing 0.02 mole of HA and 0.01 mole of the ferricenium salt (prepared by the oxidation of ferrocene by chloroanil in the presence of HNO_3) were heated at 60° for 3–4 h with constant stirring. On removing the solvent, the residue which contained $CpFeA_2$ and FeA_3, was washed with hot cyclohexane to remove ferrocene and chromatographed in benzene on deactivated Al_2O_3. Red crystals of $CpFeA_2$ were isolated by this process; yield 40–45%, m.p. 186–187° (decompn.) (Found: C, 56.46; H, 6.28; Fe, 17.45. $CpFeA_2$ calcd.: C, 56.42; H, 5.95; Fe, 17.57%.)

The IR-spectrum of this compound exhibited the following bands: 420, 490, 580, 595, 665, 695, 780, 795, 945, 1025–1033, 1200, 1280, 1300, 1379, 1425, 1530, 1590 cm^{-1}. Bromination of $CpFeA_2$ in CCl_4 yielded $(Cp_2Fe)^+(FeBr_4)^-$ (I) and then $C_5H_5Br_5$. Compound (I) contained: Fe, 20.8; Br, 56.9% and its electronic spectrum exhibited maxima at 250 and 618 mμ.

Bis(dibenzoylmethanato)cyclopentadienyliron ($CpFeD_2$) and bis(thenoyltrifluoroacetonato)cyclopentadienyliron ($CpFeT_2$) were prepared in a similar manner from HD and HT as fine dark-red crystalline powders, m.p. $CpFeD_2$ 265–270° (decompn.). (Found: C, 75.25; H, 5.31; Fe, 8.80; mol.wt. using Rast's method, 549. $CpFeD_2$ calcd.: C, 75.00; H, 4.82; Fe, 8.88%; mol.wt., 567.) The m.p. of $CpFeT_2$ was 143–145° (decompn.). (Found: C, 45.00; H, 2.74; Fe, 10.32. $CpFeT_2$ calcd.: C, 44.92; H, 2.31; Fe, 9.98%.)

The yield of $CpFeCh_2$ decreased and that of $FeCh_3$ increased when prolonged reaction times and/or elevated temperatures (>80°) were used during reactions of Cp_2Fe^+ with HCh. Cyclopentadiene was detected by means of a gas chromatographic technique amongst the products of the thermal decomposition of $CpFeCh_2$ in sealed tubes at 250–300°.

Reaction between benzenecyclopentadienyliron(II) cation and β-diketones

Reaction with acetylacetone. An aqueous solution (40 ml) of $(CpFeC_6H_6)^+$ (0.022 mole) and excess of HA (10 ml) were stirred for 3 h at 20°, the excess of HA extracted with hexane and the residue further extracted with benzene when $CpFeA_2$ was isolated, yield 49%, m.p. 187° (decompn.); $CpFeA_2$ is readily soluble in acetone, only sparingly soluble in hexane, and insoluble in water.

Reaction with dibenzoylmethane. On stirring a mixture consisting of 20 ml 0.022 *M* of an aqueous solution of $(CpFeC_6H_6)^+$ and an acetone solution of 0.187 g of HD for 3–4 h at 20°, $CpFeD_2$ was precipitated as a crystalline powder, yield 23%, m.p. 265° (decompn.). $CpFeD_2$ is moderately soluble in acetone and $CHCl_3$, sparingly soluble in ethanol and benzene and insoluble in water.

Reaction with thenoyltrifluoroacetone. On shaking an aqueous solution of the cation $(CpFeC_6H_6)^+$ with a hexane solution containing an equimolar quantity of HT a blue solid was formed at the phase boundary and the hexane layer was coloured bright red. The blue complex was very unstable, especially in solution, and converted readily to red $CpFeT_2$.

Hydrogen peroxide caused the instantaneous transformation of the blue complex into $CpFeT_2$ and $(CpFeC_6H_6)^+OH^-$. $CpFeT_2$ was also isolated from the red-coloured hexane layer mentioned above.

Reactions of allyltricarbonyliron iodide with β-diketones

The reactions of $AllFe(CO)_3I$ with HCh in benzene solution in the presence of diethylamine, in ethanol solution and with the sodium enolate of β-diketones at 60° were followed by CO evolution and by formation of $AllFeCh_2$ (the yield of CO was found to be about three moles per mole of $AllFeCh_2$ formed).

Bis(acetylacetonato)allyliron. 15–20% yield, red crystals, decomposed at 162°, readily soluble in alcohols, $CHCl_3$, CCl_4, and C_6H_6. (Found: C, 52.64; H, 6.70; Fe, 18.04; mol.wt. using Rast's method in cyclohexanol, 312. $AllFeA_2$ calcd.: C, 52.88; H, 6.40; Fe, 18.96%; mol.wt., 295.)

Bis(dibenzoylmethanato)allyliron. 25% yield, red crystalline powder, m.p. 256° (decompn.), readily soluble in benzene, moderately soluble in alcohols. (Found: C, 73.94; H, 5.21; Fe, 9.81; mol.wt. using Rast's method, 545. $AllFeD_2$ calcd.: C, 73.34; H, 4.98; Fe, 10.32%; mol.wt., 567.)

Bis(thenoyltrifluoroacetonato)allyliron. 10% yield, m.p. 140–142° (decompn.). (Found: C, 41.62; H, 2.78; Fe, 9.90. $AllFeT_2$ calcd.: C, 41.81; H, 2.76; Fe, 10.20%.)

The IR spectrum of $AllFeCh_2$ exhibited bands corresponding to the Ch cycle, its substituents and to the All group: 1470 cm^{-1} $\nu_{as}(C{=}C)$; 1030–1040 cm^{-1} $\nu_s(C{=}C)$; 490–500 cm^{-1} $\delta(C{=}C{=}C)$. The chelate bands were found to be shifted slightly towards larger wave numbers in comparison with the spectrum of $FeCh_3$.

Thermal decomposition of $AllFeCh_2$ in sealed tubes yielded bi-allyl, metallic Fe (1 g-atom per mole of $AllFeCh_2$) and non-identifiable liquid products.

Reactions of allylpalladium chloride with sodium β-diketonates

The acetylacetonate and dibenzoylmethanate of allylpalladium were obtained as colourless crystals through the interaction of AllPdCl and NaA or NaD in alcoholic solution.

Recrystallization of these materials from petroleum ether yielded crystals which spontaneously decomposed in air, in vacuum and in an argon atmosphere at 20° after storage for 3–4 h. Metallic Pd was deposited from hexane solution on storage. Spectroscopic analysis indicated that $PdCh_2$ was one of the products of this decomposition.

(Ferrocenoyltrifluoroacetonato)allylpalladium. 0.70 g $(AllPdCl)_2$ and 0.40 g $(Na\phi)$ were reacted in ethanol at 40° for 2 h. Chromatography on Al_2O_3 led to the isolation of $AllPd\phi$ (0.25 g) in the form of red-brown crystals, m.p. 137–140°, yield 26%. (Found: C, 43.91; H, 3.71; Pd, 22.52. $AllPd\phi$ calcd.: C, 43.31; H, 3.18; Pd, 22.41%.) Thermal decomposition of $AllPd\phi$ at 250–300° yielded metallic palladium and biallyl.

Preparation of bis(arene)chromium(I) β-diketonates

Bis(biphenyl)chromium(I) dibenzoylmethanate. A solution consisting of 5 mmole of $(Ph_2)_2Cr^0$ in 150 ml of benzene was treated with a solution containing 5 mmole of HD in 30 ml of benzene with constant stirring and venting of O_2. $(Ph_2)_2CrD$ was gradually deposited as a yellow powder, 70% yield, m.p. 88° (decompn.). (Found: C, 76.00; H, 5.53; Cr, 8.60. $(Ph_2)_2CrD \cdot 1.5\ H_2O$ calcd.: C, 76.70; H, 5.57; Cr, 8.52%.)

It was found that bis(biphenyl)chromium(I) acetylacetonate and β-diketonates of bis(arene)chromium(I) cations derived from ethylbenzene exist as oils which were difficult to crystallize. These compounds decomposed to arene and $CrCh_3$ crystals.

All bis(arene)chromium(I) β-diketonates were readily soluble in $CHCl_3$ and alcohols, sparingly soluble in benzene and acetone, and insoluble in hexane and ether.

The IR and UV spectra of these complexes were identical with the superimposed spectra of the initial cation and anion.

Disproportionation of bis(biphenyl)chromium(I) dibenzoylmethanate

$$3\,(Ph_2)_2CrD \rightarrow 2\,(Ph_2)_2Cr^0 + CrD_3 + 2\,Ph_2$$

An ethanol solution of $(Ph_2)_2CrD$ was heated in a sealed tube at 95° for 12 h. Orange-golden crystals of $(Ph_2)_2Cr^0$ (yield 63% according to the above equation) and a red-brown crystalline powder of CrD_3 (yield 34%) were precipitated on cooling. After removal of the ethanol under reduced pressure biphenyl was extracted by treatment with ether followed by sublimation in vacuum (yield 65%).

Reaction of Cp_2TiCl_2 with β-diketonates

Acetylacetonate and dibenzoylmethanate anions on reaction with Cp_2TiCl_2 form $(Cp_2TiCh)^+An^{-2}$. Sodium ferrocenoyltrifluoroacetonate causes extensive decomposition of Cp_2TiCl_2, which is accompanied by the generation of an intense red-violet colouration of the system. Chromatographic separation of the reaction products on Al_2O_3 yielded dark-violet coloured materials whose composition corresponded to $CpTi\phi_2Cl$; m.p. 140°. (Found: C, 49.20; H, 3.23; Cl+F, 17.90. $CpTi\phi_2Cl$ calcd.: C, 49.70; H, 3.15; Cl+F, 18.50%.) The product was found to be very unstable both in solution and in the solid state.

DISCUSSION

It has been found that in most cases during the formation of chelate salts of sandwich cations compounds corresponding to the displacement of arene or hydrocarbon radicals by the chelate cycle, as well as reduction products are formed. Thus, in the reaction of a ferricenium cation and a β-diketonate anion bis(β-diketenato)-cyclopentadienyliron and ferrocene are formed; bis(biphenyl)chromium(I) dibenzoylmethanate gives bis(biphenyl)chromium(0), tris(dibenzoylmethanato)chromium(III) and biphenyl on heating in ethanol, and metal palladium, biallyl and bis(β-diketonato)palladium are formed during the spontaneous decomposition of (β-diketonato)-allylpalladium.

The formation of these reaction products confirms the suggestion that chelate salts of sandwich cations undergo disporportionation reactions. Similar reactions occur with transition metal carbonyls[5]. In alkaline medium disproportionation reactions have been used for the synthesis of uncharged bis(arene)metal(0) complexes[6], and bis(arene)chromium hydroxide, iodide and acetate have been described as disproportionating to bis(arene)chromium(0)[7]. The ferricenium cation disproportionates in alkaline medium to yield ferrocene and $Fe(OH)_2$[8], and the disproportionation of (acetylacetonato)allylnickel has been quoted as an example of the behaviour of β-diketonates[9].

The reactions of the sandwich cations with β-diketonate anions described in the experimental section of this paper may be represented by the following disproportionation schemes:

$$2\,(\mathrm{Cp_2Fe})^+\mathrm{Ch}^- \rightarrow \mathrm{CpFeCh_2}+\mathrm{Cp_2Fe}+\tfrac{1}{2}\,\mathrm{C_{10}H_{10}} \qquad (1)$$

$$2\,(\mathrm{CpFeArene})^+\mathrm{Ch}^- \rightarrow \mathrm{CpFeCh_2}+\mathrm{CpFe^IArene}+\mathrm{Arene} \xrightarrow[\mathrm{H_2O}]{(\mathrm{O})} (\mathrm{CpFeArene})^+\mathrm{OH}^- \qquad (2)$$

$$2\,[\mathrm{AllFe(CO)_3}]^+\mathrm{Ch}^- \rightarrow \mathrm{AllFeCh_2}+3\,\mathrm{CO}+\tfrac{1}{2}[\mathrm{AllFe(CO)_3}]_2 \qquad (3)$$

$$2\,\mathrm{AllPdCh} \rightarrow \mathrm{Ch_2Pd}+\mathrm{All_2Pd} \rightarrow \mathrm{Pd}+\mathrm{All_2} \qquad (4)$$

$$2\,(\mathrm{Cp_2TiCl})^+\mathrm{Ch}^- \rightarrow \mathrm{CpTiCh_2Cl}+\mathrm{Cp_2TiCl}+\tfrac{1}{2}\,\mathrm{C_{10}H_{10}} \qquad (5)$$

$$\begin{array}{lr}
2\,\mathrm{Arene_2Cr^ICh} \rightarrow \mathrm{Arene_2Cr^0}+\mathrm{AreneCr^{II}Ch_2}+\mathrm{Arene} & (6)\\
\mathrm{AreneCr^{II}Ch_2}+\mathrm{Arene_2Cr^ICh} \rightarrow \mathrm{Arene_2Cr^0}+\mathrm{Cr^{III}Ch_3}+\mathrm{Arene} & (7)\\
\hline
3\,\mathrm{Arene_2Cr^ICh} \rightarrow 2\,\mathrm{Arene_2Cr^0}+\mathrm{Cr^{III}Ch_3}+2\,\mathrm{Arene} & (8)
\end{array}$$

The formation of mixed sandwich chelate compounds of zirconium and hafnium has been described by Brainina[10,11], and the synthesis of CpCrABr has been reported by Thomas[12].

The disproportionation of chelate salts of sandwich cations is enhanced if the possibility of intermediate dimer formation occurs in the system, *i.e.*,

$$(\mathrm{Cp_2Fe})^+(\mathrm{FeX_4})^- \rightarrow (\mathrm{CpFeX_2})_2 \quad \text{(ref. 13) or}$$

$$[\mathrm{CpFe(CO)_2}]_2 \rightarrow \mathrm{Cp_2Fe}+\mathrm{Fe}+4\,\mathrm{CO} \quad \text{(ref.14)}$$

The position of the reaction equilibrium may be displaced towards the final disproportionation products through the removal of one of the products by oxidation or decomposition. For example, reaction (2) listed above is facilitated by the presence of hydrogen peroxide when it proceeds at room temperature; disproportionation of $[\mathrm{AllFe(CO)_3}]^+\mathrm{Ch}^-$ is facilitated by the evolution of CO, that of $\mathrm{Arene_2CrCh}$ by the loss of arene and that of AllPdCh through the decomposition of $\mathrm{All_2Pd}$.

TABLE 1

ELECTRONIC SPECTRA OF SANDWICH-CHELATE COMPLEXES

Compound	λ(nm)	$\varepsilon \times 10^{-3}$	λ(nm)	$\varepsilon \times 10^{-3}$	λ(nm)	$\varepsilon \times 10^{-3}$
A_3Fe	275	32.6	354	3.46	438	3.36
A_2FeCp	288	24.0	350	3.20	430	0.30
A_2FeAll	278	22.7	354	2.04	440	1.92
A_2Pd	290					
APdAll	303	10.7				
D_3Fe	257	45.0	335	60.0	415	14.0
D_2FeCp	255	43.0	345	90.0	410	6.30
D_2Pd			340			
DPdAll	253		353			
T_3Fe	275	20.6	347	66.0	385	22.9
T_2FeCp	280	20.6	347	50.0	430	2.4
T_2FeAll	264	33.5	335	35.7	390	
ϕ_2Pd			320	18.5	510	3.7
ϕPdAll	245	15.0	334	10.9	505	2.0
$\phi_2TiCpCl$			317		507	
					510	

Products containing one hydrocarbon ligand $LMCh_2$, which may be formed in disproportionation reactions of chelate salts of sandwich cations, are also capable of entering into the disproportionation reactions if the systems are stored for long periods of time or heated. From such reactions metal chelates from which hydrocarbon ligands are absent are isolated. For example, in the present work $FeCh_3$ was obtained from all of the sandwich chelate compounds of iron investigated ($CrCh_3$ from $Arene_2CrCh$):

$$2\,CpFeCh_2 \rightarrow Cp_2FeCh + FeCh_3$$

$$2\,AreneCr^{II}Ch_2 \rightarrow Arene_2Cr^{I}Ch + Cr^{III}Ch_3$$

Experimental evidence shows that the ease with which bis(aromate) chelate complexes enter into disproportionation reactions depend upon the nature of the β-diketone. Disproportionation products are most readily produced by ferrocenoyltrifluoroacetonates and dibenzoylmethanates followed by acetylacetonates and then by thenoyltrifluoroacetonates. This order is identical to the order in which the pK_a-values of the corresponding β-diketones decrease[15]*. As the pK_a-values for the β-diketones decrease an increase in the stability of the corresponding β-diketone anion occurs, resulting in an increase in the ionic character of the metal–ligand bond in the resulting chelate.

From this it is possible to deduce that disproportionation of the bis(aromate) chelate complexes, $(Cp_2Fe)^+$, $(CpFeArene)^+$, $(Cp_2TiCl)^+$, and $(Arene_2Cr)^+$, is facilitated by the formation of more covalent, or lesser ionic, bonds between the metal and the β-diketonate.

With $AllPd^+$, however, the dependence of the stability of the complex towards disproportionation on the nature of the β-diketone was exactly the reverse of that

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* A pK_a value of 10.0 for ϕH was kindly determined by M.I. Gryasnova using an extraction method.

described above. Furthermore, ferrocenoyltrifluoroacetonates of allylpalladium disproportionate only after storage in light for at least a year or on thermal decomposition, while dibenzoylmethanate, and especially the acetylacetonate, of allylpalladium yield metallic Pd within hours of preparation.

These peculiarities regarding the stability of mixed sandwich chelate compounds are intelligible if it is assumed that the electron shell of central metal atom used in the donor–acceptor bonding of the complex accommodates four electrons from the two oxygen atoms of the β-diketonate anion.

For such a complex to be stable the number of electrons in the electronic shell of the metal atom should not exceed 18, and for metals which form 16-electron sandwich complexes this number should not exceed 16. If the electron shell involved in complex formation contains more than 18 or 16 electrons, then the stability of the sandwhich chelate will decrease through an increase in the covalent character of the metal–chelating agent bond as occurs for example in the series: $T > A > D \geqslant \phi$.

The following order of bond stability has been observed in the disproportionation reaction of bis(aromate) iron-containing sandwich cations: benzene < cyclopentadienyl < β-diketonate. For allyl–iron complexes the following order was observed: CO < All < Ch.

The peculiar behaviour of mixed allyl and cyclopentadienyl β-diketonate complexes of the transition metals is due to the interaction of the ligands not directly bound to each other being transmitted via the metal atom and thus being dependent on the nature of the metal–ligand bond. This mutual interaction of the ligands is exhibited in the UV and IR absorption spectra of these complexes.

Substitution of one chelate cycle in $FeCh_3$ by a Cp-group leads to a bathochromic shift of the long-wave absorption band of the chelate cycle in the UV spectrum by 10–13 nm. A small hypsochromic shift of the absorption band due to a transition in the iron atom is also observed, and the intensity of this band decreases considerably (2–10 times) in comparison with that of $FeCh_3$. The analogous band in the ferrocene spectrum at 440 nm has an insignificant intensity ($\sim$80 $mole^{-1} \cdot cm^{-1}$).

The decreasing intensity of the absorption band due to the metal and some shifts in the absorption band of the chelate to long wavelengths in the UV spectra indicate that some mutual interaction occurs between the ligands in $AllFeCh_2$ compounds.

A significant bathochromic shift of the chelate absorption band (by a value of 13–14 nm) occurs in AllPdCh in comparison with $PdCh_2$, an effect which is probably due to the influence of the donor allyl ligand. Distortion of the π-electron delocalization of the allyl ligand does not occur during the formation of allylpalladium β-diketonate from bis(allylpalladium chloride), the former being merely a π-allyl chelate of palladium. The characteristic shift of bands corresponding to the π-allyl ligand to a lower frequence region of the spectrum is observed in the IR spectra of allylpalladium ferrocenoyltrifluoroacetonate. This may be attributed to allyl stabilization brought about by the redistribution of the electron density of the palladium atom through the influence of the more polar β-diketonate ligand.

No significant shift of the characteristic bands of the π-allyl ligand occurs in either the IR spectrum of $AllFeCh_2$ or that of $AllFe(CO)_3I$ which indicates that the nature of the allyl bonds must be the same in both compounds.

The difference in the spectral behaviour of Cp- and All-groups bound to a transition metal atom in a chelate complex may probably be attributed to the differences in electron configurations attained in the two types of compound formed, Cp with for example Fe forming either the disadvantageous 19-electron complex or a 17-electron complex involving allyl-type distortion of the electron delocalization. The allyl ligand does not cause such distortions of the electron shell of the metal, and for this reason "allyl" $CpFeCh_2$ and $AllFeCh_2$ have a 17-electron configuration similar to that in tris(chelato)iron(III), $FeCh_3$.

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