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Reaction of Pt^{IV} with β-diketones

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Using platinum(IV) hexahalogeno salts, a series of platinum(II)-β-diketone derivatives have been prepared. Infrared and n.m.r. spectroscopy together with their chemical reactions have shown these to be identical with the products obtained from the platinum(II) tetrahalogeno salts. The β-diketones, acetylacetone and the trifluoro analogue appear to behave as reducing agents. With $PtCl_4$ condensation of the acetylacetone occurs.

Introduction

The X-ray structural investigations of Mason[1] established the presence of a Pt–C unit in a series of platinum(II) β-diketone derivatives. Chemical studies by Lewis and coworkers[2,3] have shown that not only is this mode of attachment to platinum a common feature, but such complexes have an interesting and often unusual chemistry of their own.[4,5] For example, these complexes are often able to function as a ligand towards other metal ions and undergo some unexpected rearrangements in the presence of mineral acids.

This reactive nature of these Pt^{II} complexes is in contrast to that of the Pt^{IV} analogues, i.e. $(CH_3)_3Pt(dipy)(O_2C_5H_7)$ (where dipy = 2,2′-dipyridyl) which also contains a Pt–C unit. For the Pt^{IV} β-diketones there is a further dissimilarity from their Pt^{II} analogues, namely in the *trans* orientation of the carbonyl groupings. In the Pt^{II} complexes the carbonyl groupings are mutually *cis* and much of their reactivity requires this *cis* arrangement of these groups. Thus it seemed of interest to determine whether Pt^{IV} unidentate β-diketone complexes could be prepared which showed some of the reactions requiring a *cis* orientation of the carbonyl groups.

The present study reports two unusual products formed in the reaction of Pt^{IV} with β-diketone; (a) Reaction of $(PtX_6)^{2-}$, where X = Cl, Br, I, with acetylacetone and its trifluoro derivative result in reduction of the Pt^{IV} species; (b) Reaction of $PtCl_4$ with acetylacetone results in condensation of the organic entity.

Results and Discussion

β-diketones with $(PtX_6)^{2-}$ (X = Cl, Br, I)

Acetylacetone (acacH) and trifluoroacetylacetone (3FacacH) were the two β-diketones used in this work. Reaction of acetylacetone with the Pt^{IV} species $(PtX_6)^{2-}$, where X = Cl, Br, yielded yellow complexes whose analytical data (Table I) appeared to suggest the known Pt^{II} complexes $\{Pt(acac)_2X\}^-$. In an analogous manner $(PtI_6)^{2-}$ yielded a complex of apparent composition $[Pt(acac)_3]^-$. The reaction conditions used to prepare

TABLE I. Analytical Results.

	Found			Calc.		
	C	H	X	C	H	X
$KPt(acac)_2Cl$	25.5	3.1	–	25.7	3.0	–
$KPt(acac)_2Br$	23.4	2.9	15.9 (Br)	23.4	2.8	15.6
$KPt(acac)_3$	33.4	4.2	36.6 (Pt)	33.9	4.0	36.7
$KPt(3Facac)_2Cl \cdot 2H_2O$	20.0	1.9	5.9 (Cl)	19.6	2.0	5.8
$KPt(3Facac)_2Br \cdot 2H_2O$	18.6	1.8	12.2 (Br)	18.3	1.8	12.2
[a]$HPt(acac)_2Cl$	27.9	3.5	–	27.9	3.5	–
[a]$Cu(Pt(acac)_2Cl)_2$	26.0	3.1	–	26.1	3.1	–
$(C_{10}H_{13}O_2)_2PtCl_6$	32.5	3.6	28.0 (Cl)	32.5	3.5	28.7

[a] Prepared by literature methods.[4,5]

$[Pt(acac)_2X]^-$ were repeated using trifluoroacetylacetone. From each preparation, the corresponding yellow solid had empirical formula of a Pt^{II} species i.e. $[Pt(3Facac)_2X]^-$. Thus analytical data suggest that known Pt^{II} species are formed.

The infrared spectra, which are usually a useful diagnostic tool for providing structural information about the nature of β-diketone groupings, of these platinum derived species were then examined. In addition the presence of other ligands undetectable analytically, e.g. hydrogen, may well be demonstrated. These spectra were typical of both oxygen and carbon bonded β-diketone residues. In all cases the spectra were identical to the platinum(II) species suggested analytically. The recent normal coordinate analysis[6] of potassium chlorobis(acetylacetonate)platinum(II) has confirmed the earlier empirical methods of detecting a bidentate and unidentate β-diketone grouping. Thus it would appear that reduction of Pt^{IV} species has occurred.

Additional proof of the reduction to known platinum(II) species was provided by two further observations. Proton magnetic resonance spectroscopy showed only the anticipated spectra of the platinum(II) β-diketone complexes, i.e. the absence of M–H bonds was confirmed. Secondly, the products of two characteristic reactions of carbon bonded β-diketonates of platinum(II) were obtained from the platinum(IV) derived species: viz. reaction with mineral acids and copper(II) (see Table I).

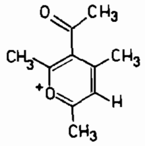
Thus the β-diketones acetylacetone and its trifluoro analogue behave as reducing agents to ionic monomeric platinum(IV) halide species. The reducing action of β-diketones has been observed previously in the preparation of $Re(acac)_3$,[7] where acetylacetone acts as a reducing agent for the reduction of Re^{IV} to Re^{III}.

AcacH with $PtCl_4$

Dissolution of platinum tetrachloride in freshly distilled acetylacetone resulted in yellow crystals of stoichiometry $Cl_6PtC_{20}H_{26}O_4$. As the molecular weight, determined by density measurement, was 730 ± 20 the most likely formulation was $(C_{10}H_{13}O_2)_2PtCl_6$, M. Wt. 737.

The infrared spectra of this yellow solid confirmed that the acetylacetone grouping had been destroyed as there were no absorptions in the 1520–1620 cm^{-1} regions. The spectra showed no evidence of absorptions which could be associated with the presence of an OH group, but a strong absorptions at 1712 cm^{-1} implied the presence of a free carbonyl grouping. The low frequency infrared and Raman spectra, with absorption bands at 160(R) cm^{-1}, 327(R+IR) cm^{-1} and 347(R) cm^{-1}, are consistent with the presence of a $(PtCl_6)^{2-}$ species. As it was not possible to collect solution data on this complex because of its highly insoluble nature the structure has been determined by single crystal diffraction analysis.

This analysis showed the complex to contain a $\{PtCl_6\}^{2-}$ anion and the condensation product of the acetylacetone to be a substituted pyrillium cation:



This remarkable compound will be the subject of a separate communication.[8]

The differing course of the reaction for these Pt^{IV} species with acetylacetone presumably arises from the differing structures of the platinum(IV) starting materials. As $(PtCl_6)^{2-}$ is a monomeric species with six terminal halogen atoms, in the presence of strong base the acetylacetone ion so formed may simple act as a halogen trap so facilitating the reduction of platinum(IV) to platinum(II). The polymeric structure of platinum tetrachloride[9] means that the halogen atoms are not so readily accessible for such reaction and hence a different reaction product is observed.

This is the first reported example of this type of condensation. β-diketones are known to condense with elimination of water to give unsaturated ligand systems.[10] Platinum tetrachloride is known to have a great affinity for water, for example, the condensation of acetone to give mesityl oxide occurs in the presence of $PtCl_4$.[11] Thus the mechanism of the rearrangement of acetylacetone to the pyryllium ion may have as its driving force the elimination of two water molecules. At the moment we have been unable to prepare any platinum(IV) β-diketone complexes where the ligand nature of the β-diketone is preserved.

Experimental

The platinum complexes were prepared as described below. Potassium halo-platinate in 5 ml of water was treated with 3 ml of aqueous potassium hydroxide solution (1:3 wt/wt) together with an excess of the β-diketone. After stirring for two hours at 55–60° in some instances a solid precipitated on cooling, alternatively the cool solution was stood over H_2SO_4 until crystals began to form. These were filtered and washed with water and ethanol to give the appropriate platinum(II) derivative (Yields ≃ 40–50% based on platinum content).

$(C_{10}H_{13}O_2)_2PtCl_6$

Fresh $PtCl_4$ was dissolved in the minimum of acetylacetone by warming on a steam bath. The resulting red solution was filtered from the small grey–black residue (presumably platinum black) and allowed to cool.

After 24 hours small yellow crystals began to form which were filtered and washed with ethanol and ether.

Infrared Spectra

Measurements were made on a Perkin–Elmer model 225 Spectrometer.

Raman Spectra

Raman spectra were recorded using a Cary 81 spectrometer.

Crystal Data

Measurements were made using a Small–Travers 3 circle diffractometer using Cu Kα radiation (λ = 1.5418 Å).

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