Improved synthesis and reactivity of tris(acetylacetonato)ruthenium(III)

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[Ru(acac)]₃ has been prepared by a new method in high yield and found to be a precursor for the synthesis of [Ru(acac)₂L₂] (L = a neutral monodentate ligand viz., CH₃CN, py, 3Me-py, 4Me-py, dmpzH (3,5-dimethyl pyrazole), PPh₃ or AsPh₃; L₂ = a neutral bidentate ligand, viz., bipy(2,2'-bipyridine) or phen (1,10-phenanthroline). All the complexes are new except [Ru(acac)(CH₃CN)] and [Ru(acac)(PPh₃)], and are characterized by physical and electrochemical studies.

Our interest in the improved methods of synthesis of complexes of β-diketones originates from the observation that tris(acetylacetonato)ruthenium(III) is a homogeneous catalyst for the regiospecific tritiation of aromatic carboxylic acids. It has been used to synthesize the bis(acetylacetonato)ruthenium(II) complexes of the type [Ru(acac)₂(S-BINAP)] (S-BINAP = S-2,2'-bis(diphenylphosphino)-1,1-binaphthyl) which has been used as catalyst in enantioselective hydrogenation of 2-arylaacrylic acids and 2-arylacrynoic acids. A recent report by Knowles et al. describes various methods of preparations reported in the literature, along with percentage yield of the compound. The highest yield (76.3%) reported by Knowles et al. is based on the method of Earley et al.

Tris(acetylacetonato)ruthenium(III) is found to be much less reactive towards many of the monodentate and bidentate ligands. A report on the preparation of [Ru(acac)₂(CH₂CN)₂]ClO₄ by Kasahara et al. describes a reaction of [Ru(acac)]₃ with acetonitrile in the presence of the strong acids such as perchloric, sulphuric or hydrochloric acid. When Ru(III) in [Ru(acac)]₃ is reduced to Ru(II) using a suitable reducing agent and treated with a ligand, compounds of the type [Ru(acac)₂L₂] could be obtained. Ru(II) has higher tendency for π-backbonding and undergoes substitution much less rapidly. Thus synthesis of the complexes of the type [Ru(acac)₂L₂] (where L is a monodentate or L₂, a bidentate ligand) is interesting in its own right and if L happen to be weak donor ligand; it provides a convenient precursor.

The present work describes a convenient synthesis of [Ru(acac)]₃ using K₂[RuCl₃(H₂O)] or K[Ru(SO₄)₂(H₂O)]₂ as the starting material instead of RuCl₃·nH₂O. This method also gives an improved yield of [Ru(acac)]₃. Several Ru(II) compounds of the type [Ru(acac)₂L₂] (L = a monodentate or L₂, a bidentate ligand) have also been synthesized by the reduction of [Ru(acac)]₃ with zinc dust followed by a reaction with L or L₂.

Experimental
RuCl₃·H₂O was obtained from Arora-Mathey Limited, Calcutta. All the solvents were freshly distilled before use. K₂[RuCl₃(H₂O)] and K[Ru(SO₄)₂(H₂O)] were prepared by the previously reported procedures. C, H and N microanalyses were obtained from RSIC, CDRI, Lucknow. IR spectra were recorded as compressed KBr discs on a Perkin-Elmer Model 983 spectrophotometer in 4000-400 cm⁻¹ range. Electronic absorption spectra were recorded in chloroform on a Beckman DU-650 spectrophotometer in the range 800-200 nm. Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer EG and G PARC Model 155 at room temperature. 1H NMR spectra were recorded on a Bruker ACF-300, 300 MHz spectrometer, in chloroform-d or acetonitrile-d₃. Conductivity measurements were made on a Wayne-Kerr automatic precision bridge B 905 conductivity meter with millimolar solutions. Cyclic voltammetric studies were carried out on an EG and G PARC voltameter. The experiments were carried out in acetonitrile using TBAP as supporting electrolyte in a three electrode configuration using a Pt disc as the working electrode. All potentials are referenced to the SCE. Reported potentials are uncorrected for the junction contribution.

Preparation of [Ru(acac)]₃
K₂[RuCl₃(H₂O)] or K[Ru(SO₄)₂(H₂O)] (0.5 g) was dissolved in water (10 cm³) and acetylacetone (3 cm³) was added to the solution. The mixture was heated on a water bath for 10 min followed by the addition of a base, viz., KHCO₃ (0.3 g), KOH (0.1 g) or NEt₃ (1...
The mixture was further heated on a water bath for 2h and cooled to room temperature. The compound obtained was separated by centrifugation and washed twice with water (crop I). The mother liquor upon concentration (~2 cm³) yielded some more compound which was separated as above (crop II). Samples collected through the two crops were recrystallised from dichloromethane/hexane mixture.

Preparation of \([\text{Ru(acac)}_2 L_2]\) (where \(L = \text{py, 3Me-py, dmpzH; } L_2 = 2,2\text{-bipyridine or 1,10-phenanthroline}\))

To a solution of \([\text{Ru(acac)}_3]\) (0.2g) in ethanol (20 cm³), zinc dust (1g) was added and the solution was refluxed to boiling with constant stirring for 1h. Ligand (metal : ligand = 1:2 in case of monodentate ligands and 1:1 in case of bidentate ligands) was added to the mixture in hot condition and the mixture was further refluxed for 4h with continuous stirring when the colour of the solution changed from reddish brown to brown, yellow, green or violet depending on the ligand used. The solution was filtered in the hot condition to separate the zinc dust. The filtrate was concentrated to ~2 cm³ on a water bath, when crystals of the compounds separated out. The compound was separated by centrifugation and washed with ethanol and diethyl ether and dried in vacuo. Yields were between 60 and 70%.

Preparation of \([\text{Ru(acac)}_2 L_2]\) (where \(L = \text{PPh}_3\) or \(\text{AsPh}_3\))

A method similar to that described in the previous preparation was used. On filtration of the hot mother liquor, some compound remained with the zinc dust. Zinc dust was washed with dichloromethane to dissolve the compound, filtered and the solution was added to the mother liquor. Yellow coloured compounds were obtained, which were recrystallized from ethanol, washed with ether and dried in vacuo. Yield was between 60 and 70%.

Preparation of \([\text{Ru(acac)}_3(CH_3CN)]\)

The reaction was carried out in a similar way as in the previous preparation, except that CH₃CN was used as the solvent instead of ethanol. The mother liquor obtained after separating zinc dust was concentrated (~1 cm³), when the compound separated out. It was centrifuged, washed with dry ether and dried in vacuo; yield = 0.16g (84%).

Reactions of \([\text{Ru(acac)}_3(CH_3CN)]\) with py, 3Me-py, 4Me-py, dmpzH, PPh₃, AsPh₃, 2,2'-bipyridine or 1,10-phenanthroline

To a solution of \([\text{Ru(acac)}_3(CH_3CN)]\) in ethanol, \(L\) or \(L_2\) was added (metal : ligand = 1:2 for the monodentate ligand and 1:1 for the bidentate ligand) and the compound was refluxed on a water-bath for 2h. The reaction mixture was concentrated to a very small volume, when the compound separated out. It was separated by centrifugation, washed with ethanol and ether. It was dried in vacuo. The compounds isolated were of the general formula \([\text{Ru(acac)}_3 L_2]\) (where \(L = \text{py, 3Me-py, 4Me-py, dmpzH, PPh}_3, \text{AsPh}_3, 2,2\text{-bipyridine or 1,10-phenanthroline}\). Yield was between 60 and 70%.

Results and discussion

In a report by Knowles \textit{et al.}⁴ synthesis of tris(acetylacetonato)ruthenium(III) was reported in 76% yield by a modification of the method by Earley \textit{et al.}³, where a solution of ruthenium trichloride in acetylaceton was refluxed in presence of KHC0₃. In the present work, aqueous solution of K₃[RuCl₃(H₂O)] or K[Ru(SO₄)₂(H₂O)₂] and acetylacetone were treated with a base, viz., KHC0₃, KOH or NEt₃ and the mixture was refluxed for 2h on a water bath. \([\text{Ru(acac)}_3]\) was obtained in 70-87% yield. The
increase in the yield may be due to fact that the starting compounds used are pure Ru(III) complexes, whereas commercial RuCl₃·nH₂O contains impurities of higher oxidation state ruthenium compounds as well. The compound was characterized by the elemental analyses, magnetic measurement, IR, ¹H NMR and UV-visible spectral studies. The magnetic moment value, IR, ¹H NMR and UV-visible spectra matched well with those of the reported data.  

Synthesis of ruthenium(II) compounds of the type [Ru(acac)₃L₂] (L = a monodentate ligand or L₂ = a bidentate ligand) were reported by the reduction of [Ru(acac)₃] or trans-Ph₃As[Ru(acac)Cl₂] using hydrogen gas, zinc-amalgam or activated zinc dust (d). In the present work, compounds of the type [Ru(acac)₃L₂] (where L = CH₃CN, py, 3Me-py, 4Me-py, dmmpzH, PPh₃, AsPh₃; L₂ = bipy or phen) are synthesized by two different methods: (i) by the reduction of ethanolic solution of [Ru(acac)₃] with zinc dust, followed by the addition of the ligand or (ii) by the substitution of CH₃CN molecules in [Ru(acac)₃(CH₃CN)] by the appropriate ligand. 

Except cis-[Ru(acac)₂(CH₃CN)] and [Ru(acac)₄(PPh₃)₂], all other compounds reported here, are new. The chemical compositions of the compounds have been confirmed with the help of analytical data (Table 1). The IR spectra of all the compounds showed two strong absorption bands around 1560 and 1505 cm⁻¹ which are characteristic of the chelated O-bonded acetylacetonato groups (d₁₅,1₅). Besides the above, characteristic bands due to the monodentate or bidentate ligands were also observed. The IR spectrum of [Ru(acac)₃(CH₃CN)] showed one sharp band of medium intensity at 2257 cm⁻¹, characteristic of ν(CN) of coordinated CH₃CN groups (d₁₅,1₅). All the compounds are diamagnetic at room temperature thereby confirming the presence of ruthenium(II) in low-spin d⁶ configuration. 

¹H NMR spectra of [Ru(acac)₂L₂] (where L = py, 3Me-py, dmmpzH, PPh₃, AsPh₃) in CDCI₃ exhibited two sharp singlets or one broad singlet in the region δ 1.41 to 1.84 which may be assigned to the methyl protons of the two cis-acetylacetonato groups. For a trans-isomer only one signal for all the methyl protons of the two acetylacetonates is expected, whereas a cis-isomer should give two singlets. Further, a singlet in the region δ 5.19 - δ 5.37 is observed, which may be assigned to the methine CH of the acetylacetonates. In the cases of pyridine, substituted pyridine, triphenylphosphine and triphenylarsine containing complexes, several signals were observed in the region δ 7.04 - δ 8.97, which may be assigned to the aromatic protons of the respective ligands. 

¹H NMR spectra of [Ru(acac)₂L₂] (where L₂ = bipy or phen) showed a sharp singlet at δ 1.65 and δ 1.82 respectively which may be assigned to the methyl protons of acetylacetonates. The spectrum of the 1,10-phenanthroline containing complex when recorded in CD₃CN showed a shift of this signal to a higher δ value (δ 2.18). Signals due to aromatic protons in 2,2'-bipyridine or 1,10-phenanthroline containing complexes recorded in CDCl₃ were observed in the region δ 6.91 - δ 8.58 which shifted to higher δ value when recorded in CD₃CN. 

The cyclic voltammetric studies of the complexes at room temperature in millimolar CH₃CN solution in presence of TBAP as supporting electrolyte showed that all the ruthenium(II) complexes [Ru(acac)₂L₂] undergo reversible oxidation (AEp = 60-100 mV) in the potential range -0.19 V to +0.27 V vs. SCE. This reversible oxidation is characteristic of one electron oxidation, viz., RuIII/RuII couple. Besides the metal oxidation couples, one irreversible one electron reduction in the region -0.75 V to -1.3 V is observed which may be assigned to the ligand reduction in these systems. 

The electronic absorption spectra of the complexes recorded in chloroform generally show two or three bands in the region 600-300 nm with ε (2 × 10³ to 22 × 10³). All these bands may be assigned to metal π(d)→ligand π* type of transitions. In some cases one band in the region 500-600 nm is observed having ε<10³. This band may have contribution from d-d transition of Ru(II), viz., ¹A₁g→¹T₁g or ¹T₃g besides having contribution from M→L CT transition. One or two absorption bands are observed below 300 nm, which may be assigned to the intraligand π→π* type of transitions. 

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