Synthesis and Properties of Dichloroacetylacetonateruthenium(III)

NICHOLAS FARRELL and SERGIO G. DE ALMEIDA

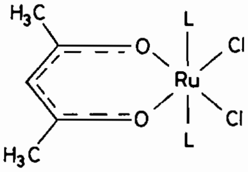
Departamento de Química, Universidade Federal de Minas Gerais, 30.000-Belo Horizonte, MG, Brazil

Received April 11, 1983

The usual preparation of metal–acetylacetonates consists of treatment of the metal chloride with acetylacetone in aqueous base, followed by extraction with organic solvents. In the course of synthesising [Ru(acac)$_3$] we found that evaporation of the aqueous layer remaining after separation of the tris-chelate and Soxhlet extraction of the solid obtained with CH_2Cl_2 gave a purple solid analysing as [Ru(acac)Cl_2] (*1*) in 10–15% yields based on $RuCl_3$, along with a CH_2Cl_2-insoluble maroon residue of variable composition. We have begun an investigation of the reactivity of this species and this paper reports our initial results.

Further studies showed that reaction of '$RuCl_3 \cdot xH_2O$' with acetylacetone in acid solution (HCl, pH = 1.2) for 3 hr gave a 50–60% yield of the dichloroacetonate after washing with ether, evaporation, extraction in CH_2Cl_2, drying and recrystallization from CH_2Cl_2/hexane. This is the preferred mode of preparation. The complex is soluble in water, sparingly soluble in chlorinated solvents, alcohol and acetone, and insoluble in benzene, hexane and ether.

The properties of the complex are given in Table I. The absence of bands due to carbonyl stretching above 1600 cm^{-1} in the infrared spectrum and the similarity of this spectrum with the known K[Pt(acac)Cl_2]$^-$ [1], indicates that the acetylacetonate is bound in the normal manner through both oxygen atoms. The molecular weight in water indicates a monomeric species, presumably with axial solvent ligands. The proposed structure is therefore:



(*I*)

Slight changes in visible maxima are observed in donor solvents such as DMSO, MeOH and CH_3CN due to formation of solvent adducts. The complex is a non-conductor in nitromethane and water.

Adduct formation with donor adducts such as phosphines is also observed. Diphenylphosphinoethane (dppe) reacts in CH_2Cl_2 (6 hr reflux) to give [Ru(acac)Cl_2(dppe)] as a red solid. Similar results are obtained with bipyridine giving a green product. The I.R. data indicate the acetylacetonate anion to be bound in the same manner as the starting material. Mixed halo–acetylacetonate complexes are not in fact very common; the analogous iron species is known [2] and similar adducts are obtained. More basic phosphines may reduce Ru(III) to Ru(II) and this aspect is under investigation. No reaction of *I* with CO is observed.

Electrophilic substitution of the central carbon atom in tris(acetylacetonate)metal complexes has been extensively studied [3, 4], and reactions such as halogenation can be easily achieved. Complex *1* reacts readily with N-bromosuccinimide or Br_2 to give deep blue solutions in chloroform. We have also noted similar reactions with [Ru(acac)$_3$]; attempts to iso-

TABLE I. Physical Properties of Dichloroacetylacetonateruthenium(III)^a.

Visible Spectra			I.R. cm^{-1} ^{b}		Mol. Wt.^{c}	Conductivity^d Ω^{-1} cm^2 mol^{-1}
λ_{max} nm	($\epsilon \times 10^{-3}$)	Solvent				
370(3.2)	505(2.1)	H_2O				
			1570, 1387	ν(CO)		
375(3.4)	525(2.1)	CH_2Cl_2				
			1210	$\delta(C_\gamma H)$	343	9
405(1.3)	510(0.8)	THF				
			820	$\pi(C_\gamma H)$		
390(1.4)	520(1.4)	CH_3CN				
			350	ν(Ru–Cl)		
385(1.9)	525(1.3)	CH_3OH				
395(1.5)	550(0.9)	DMSO				

^{a}Elemental analysis: C, 22.14; H, 2.58; Cl, 26.10%. Calcd. for $C_5H_7Cl_2ORu$: C, 22.68; H, 2.95; Cl. 25.35%. ^{b}In KBr discs. ^{c}In H_2O. Calcd. for Ru(acac)$Cl_2(H_2O)_2$ 307. ^{d}In $MeNO_2$.

0020-1693/83/$3.00

late pure solid have only given non-recrystallisable oils until now. The reactions are of interest however in that substitution occurs more readily for the monoacetylacetonate than the tris adduct, indicating a greater acidity of the γ-carbon-hydrogen atom in the former case.

A further interesting property of this complex is its behaviour in the presence of bases. In aqueous basic solution (CO_3^{2-}, OH^-) and at $pH > 7.8$, the blue-purple solution immediately turns green (< 1 min) with $\lambda_{max} = 670$ nm. Although reversible with acid, this solution is unstable and eventually turns yellow-brown ($t_{1/2} = 55$ min) independent of base concentration (Fig. 1). This behaviour is paralleled in non-aqueous solvents such as CH_2Cl_2 and CH_3OH in the presence of aliphatic amines such as piperidine and triethylamine ($K_b = 5.1$ and 2×10^{-3} respectively). The green complex *II* may be readily isolated from piperidine/CH_2Cl_2 by precipitation with hexane. The very hygroscopic complex has similar solubility properties to [Ru(acac)Cl_2] but is usually isolated as a piperidine solvate of variable stoichiometry. The reaction does not occur with pyridine, a simple adduct being isolated in this case.

The I.R. spectrum of *II* clearly shows the presence of piperidinium ion (3100, 2810, and 2714 cm^{-1}); no bands above 1600 cm^{-1} due to ν(C=O) are present and the bands at 1210 and 820 cm^{-1} in *I*, attributed to σ(C–H) and π(C–H) of the gamma-carbon [5] are absent. This evidence, combined with conductivity studies, is consistent with deprotonation ocurring at the central carbon of the acetylacetonate ring, the exact nature of the product being under investigation.

In summary, our studies of dichloroacetylacetonateruthenium(III) show the complex to have a range of interesting properties. In comparison to [Ru(acac)$_3$] the complex is stable in acid but reacts readily with base, whereas the opposite is true for the tris-chelate. Whether these differences reflect different reactivity of the acetylacetonate ring in both cases is being investigated and full results will be published on these aspects in due course.

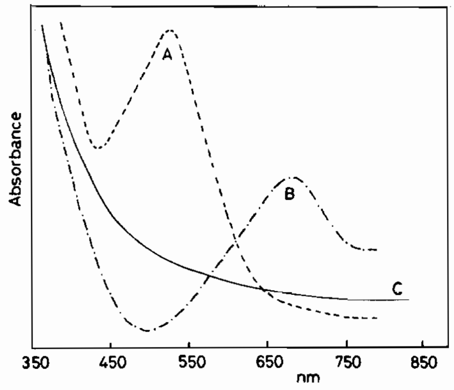


Fig. 1. Visible spectra of [Ru(acac)Cl_2] in aqueous solution: A, in distilled water; B, in basic solution (OH^-); C, decomposition of B.

Acknowledgements

We thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for award of a scholarship (to SGA). Johnson Matthey and Co. Ltd. is thanked for a loan of ruthenium trichloride. Maria de Lourdes Anastãcio is acknowledged for technical assistance.

References

1 G. T. Behnke and K. Nakamoto, *Inorg. Chem., 6*, 433 (1967).
2 K. Takeda, K. Isobe, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Japan, 49*, 1010 (1976).
3 J. P. Collman, *Angew. Chem. Int. Ed., 4*, 132 (1965).
4 J. P. Collman, *Adv. in Chem. Series, 37*, 78 (1963).
5 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York (1963), p. 216.