Journal of Organometallic Chemistry, 420 (1991) C21–C23
Elsevier Sequoia S.A., Lausanne
JOM 22282PC

Preliminary communication

The cleavage of a cluster carbonyl C–O bond by trifluoromethanesulphonic anhydride

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(Received August 1st, 1991)

Abstract

The reaction of the octahedral dianion $[Ru_6(CO)_{18}]^{2-}$ with trifluoromethanesulphonic (triflic) anhydride $[(CF_3SO_2)_2O]$ quantitatively yields the neutral carbido-cluster $[Ru_6C(CO)_{17}]$ as a result of the cleavage of a coordinated carbonyl ligand.

Whilst the majority of the carbido-clusters of the cobalt subgroup metals have been synthesised by use of halomethanes as the source of carbon [1], those of the iron subgroup have invariably been derived by the thermally induced cleavage of coordinated carbon monoxide. Carbon dioxide has been detected as a byproduct in several such reactions, implying the occurrance of the disproportionation shown in eq. 1 [2–4]. The central example of such a reaction in ruthenium chemistry is the

$$2\ CO \rightarrow C + CO_2 \qquad (1)$$

virtually quantitative conversion of the dianion $[Ru_6(CO)_{18}]^{2-}$ (**1**) into its carbido-analogue, $[Ru_6C(CO)_{16}]^{2-}$, which occurs on thermolysis of **1** at 162 °C in diglyme (eq. 2) [4]. The mechanism of this reaction remains unclear, but it may parallel that found to operate in the synthesis of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$, which involves the intermediacy of a structure containing η^2-coordinated carbonyl ligands [3].

$$[Ru_6(CO)_{18}]^{2-} \xrightarrow{\Delta/162\,^\circ C/\text{Diglyme}} [Ru_6C(CO)_{16}]^{2-} + CO_2 \qquad (2)$$

Alternative routes to CO-derived carbides involving the chemical activation of a coordinated carbonyl under mild conditions have also been developed [5–7]. The most successful of these utilises the oxygen nucleophilicity of μ_2- and μ_3-CO ligands attached to anionic cluster species by the electrophilic addition of the acylium cation $\{[CH_3CO]^+\}$, derived from acyl chloride, to this centre. The metalloester thus generated may be regarded as containing an incipient carbide coordinated to acetate. The reductive cleavage of such intermediates derived from $[M_3(CO)_{11}]^{2-}$ (M = Fe, Ru, Os) has yielded the ketenylidene clusters $[M_3(CO)_9(CCO)]^{2-}$ [6], whilst $[Fe_4(CO)_{12}\{COC(O)CH_3\}]^-$ yields $[Fe_4C(CO)_{12}]^{2-}$ on similar treatment or $[HFe_4(CO)_{12}(CH)]$ with acid [7]. The limitations of this

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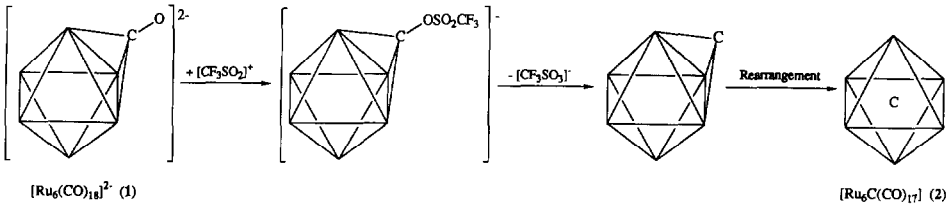

Scheme 1. The proposed mechanism for the cleavage of a carbonyl C–O bond by trifluoromethanesulphonic anhydride.

method are, first, the requirement for a cluster substrate in which a considerable amount of charge is delocallised on to the carbonyl ligands in order to overcome the limited electrophilicity of the acyl chloride reagent, and second, the relatively poor ability of acetate as a leaving group. In an attempt to avoid these limitations, an alternative reagent was sort, and reported here are preliminary results for the application of triflic anhydride $[(CF_3SO_2)_2O]$.

The chosen cluster substrate for this study was $[Ru_6(CO)_{18}]^{2-}$ (**1**), since the expected product, $[Ru_6C(CO)_{17}]$ (**2**), is a well known and easily identified material, and also its formation by this route would provide an interesting counterpart to the thermal generation of its dianionic analogue, $[Ru_6C(CO)_{16}]^{2-}$, from **1**, *vide supra*. Initial problems were encountered in that treatment of the $[PPN]^+$ salt of **1** in CH_2Cl_2 with 1.1 molar equivalents of $(CF_3SO_2)_2O$ gave only the protonation product $[HRu_6(CO)_{18}]^-$ (**3**), clearly the result of the presence of adventitious water. Even under extremely rigorous conditions for the exclusion of moisture the major product was **3**, but small amounts of **2** could also be identified from the IR spectrum of the reaction mixture. This problem was overcome by the addition of an excess of the base DBU * to the solution of **1** prior to the addition of the $(CF_3SO_2)_2O$, and in this case **1** was quantitatively converted into **2** on addition of ca. 1.5 molar equivalents of the reagent, and separated from the CH_2Cl_2 solution as red microcrystals. The product was identified by comparison of its IR and mass spectra with published data [8].

The probable mechanism for this reaction (Scheme 1) involves the addition of the strongly electrophilic trifluoromethanesulphonium cation to the oxygen of a μ_3-carbonyl ligand attached to **1**, which contains two such ligands [9], yielding a monoanionic intermediate which may be regarded as a triflate coordinated cluster carbide. The excellent leaving ability of triflate as an anion results in the spontaneous cleavage of the C–O bond to give the neutral $[Ru_6C(CO)_{17}]$. This species therefore possesses a tricoordinate surface carbide which is expected to be unstable with respect to the interstitial species, and consequently the structure undergoes a core rearrangement such that the newly formed carbide is encapsulated within the octahedron of ruthenium atoms to give the known cluster carbide **2**.

This appears to be the first example of the spontaneous fission of a carbonyl C–O bond under ambient conditions in ruthenium cluster chemistry, and work is in progress to evaluate the generality of this route, which should lead to a number of new carbido-cluster species.

* DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

Acknowledgements. The author would like to thank Professors Lord Lewis and B.F.G. Johnson for helpful discussions and comments.

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