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Note

The use of photogenerated intermediates in the study of cluster build-up reactions: the generation of $Ru_6C(CO)_{17}$ from $Ru_3(CO)_{12}$

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Abstract

The use of photochemistry in the study of cluster build-up reactions involving transition-metal carbonyl complexes has been illustrated by an investigation into the generation of the hexanuclear carbido cluster $Ru_6C(CO)_{17}$ from the trinuclear precursor $Ru_3(CO)_{12}$.

Keywords: Photochemistry; Ruthenium complexes; Carbonyl complexes; Carbido complexes; Cluster complexes

1. Introduction

The advances in the field of transition-metal cluster chemistry in the past few years have been considerable; numerous novel compounds and bonding modes being reported every year [1,2]. However, synthetic routes to higher nuclearity clusters are largely of empirical origin and mechanistic insight is, in general, rather limited [3,4]. The majority of high-nuclearity transition-metal clusters are prepared from low-nuclearity precursors, this often requiring harsh reaction conditions such as thermolysis or pyrolysis [5]. Research in our group has focused on the selective synthesis of target ruthenium and osmium cluster complexes by photochemical generation of highly reactive mononuclear precursors and subsequent controlled reaction [6,7]. Photochemistry offers a simple route to organometallic compounds, overcoming large enthalpy barriers that would otherwise involve the use of high temperatures.

We report in this note how organometallic photochemistry can offer an insight into how the hexanuclear carbido cluster $Ru_6C(CO)_{17}$ (**1**) is formed from the trinuclear precursor $Ru_3(CO)_{12}$ (**2**).

2. Experimental

2.1. Materials

All reactions were conducted under an inert atmosphere of dry nitrogen using standard Schlenk techniques and solvents were distilled prior to use. All photochemical reactions were performed in a specially designed glass reaction vessel fitted with a gas bubbler, reflux condenser, solid carbon dioxide cooling finger and a stirrer to ensure that the temperature was even throughout the solution. A 250 W broad-band UV source was used as the light source and reflectors placed around the reaction vessel to maximise efficiency. Solution infrared (IR) spectra were recorded in hexane as solvent using a Perkin-Elmer PE 1710 Fourier-transform infrared spectrometer. Ruthenium trichloride was provided by Johnson Matthey. Literature methods were used to prepare $Ru_3(CO)_{12}$ [8], $Ru(CO)_4(C_2H_4)$ (**3**) [7] and $Ru(CO)_3(C_2H_4)_2$ (**4**) [9].

2.2. *Thermolysis of complexes 3 and 4*

A heptane solution of complex **3** (30 mg in 100 ml) was refluxed for 2 h. The solvent was subsequently removed in vacuo and the crude product separated by thin-layer chromatography (1:1 dichloromethane/hexane as eluent) giving complex **2** in 95% yield.

In the case of complex **4**, complexes **2** (40%) and **1** (25%) were formed on thermolysis together with some cluster carbonyl products, which are at present uncharacterised.

2.3. *Thermolysis of complexes 3 and 4 under an atmosphere of CO*

A heptane solution of complex **3** (30 mg in 100 ml) was refluxed for 2 h under an atmosphere of CO. Purification of

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the product mixture by thin-layer chromatography (1:1 dichloromethane/hexane as eluent) gave complex **2** (90%) together with some cluster carbonyl complexes which are at present uncharacterised.

In the case of complex **4**, again complex **2** (60%) was the only characterised product.

2.4. Thermolysis of a heptane solution of complex 4 in a sealed vessel

A heptane solution of complex **4** (10 mg in 20 ml) was heated cautiously to 50°C for 5 h in a sealed vessel within a bomb calorimeter. The solvent was then frozen and the gaseous reaction products collected and analysed. Evidence for the evolution of CO_2 during the reaction was obtained.

3. Results and discussion

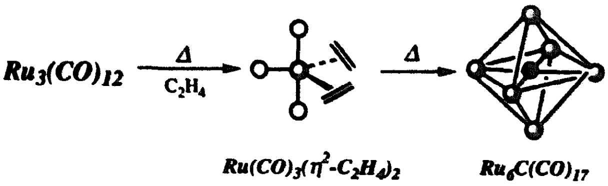
Conventionally, complex **1** was prepared by thermolysis [10,11] or pyrolysis [12] of complex **2**. More recently, reaction of a heptane solution of **2** with ethene under conditions of moderate temperature and pressure (150°C; 30 atm) has been shown to generate **1** in substantially higher yield [13].

Broad-band UV photolysis of $Ru_3(CO)_{12}$ (**2**) in hexane under an atmosphere of ethene leads to the quantitative generation of $Ru(CO)_4(\eta^2\text{-}C_2H_4)$ (**3**) and, after longer photolysis times, $Ru(CO)_3(\eta^2\text{-}C_2H_4)_2$ (**4**) (Eq. (1)) [7,9].

$$\mathrm{Ru_3(CO)_{12}} \xrightarrow[\mathrm{C_2H_4}]{h\nu} \underset{\mathbf{3}}{\mathrm{Ru(CO)_4(\eta-C_2H_4)}} \xrightarrow[\mathrm{C_2H_4}]{h\nu} \underset{\mathbf{4}}{\mathrm{(CO)_3(\eta-C_2H_4)_2}} \tag{1}$$

The olefin ligand is highly labile, complexes **3** and **4** acting as ready sources of '$Ru(CO)_4$' and '$Ru(CO)_3$' fragments, respectively. Heptane solutions of **3** and **4** were refluxed under a nitrogen atmosphere for 2 h and reactions monitored using infrared (IR) spectroscopy. In the case of **3**, the only product formed in the reflux was **2**. This result is expected since $Ru_3(CO)_{12}$ can be considered as consisting of three '$Ru(CO)_4$' units. In the case of **4**, the formation of **2** and $Ru_6C(CO)_{17}$ (**1**) was observed. Consequently, it is most likely that **1** is formed from **2** via the formation of '$Ru(CO)_3$' type mononuclear complexes, these then combining in a sequential manner to yield the hexanuclear product. Any concerted combination of six mononuclear fragments would, from a simple thermodynamic consideration, be highly unlikely.

Thermolysis of complexes **3** and **4** under an atmosphere of CO resulted in the formation of complex **2** as the major product in both cases. This is not unexpected since the labile ethene ligands are readily displaced and CO, being both in higher concentration and a better coordinating ligand than ethene, reacts to yield **3** and $Ru(CO)_5$ both of which then trimerise readily to form **2**. Significantly, little **1** is formed on thermolysis of **4** in the presence of added CO [14].



Scheme 1.

Thermolysis of a heptane solution of complex **4** was also undertaken in a sealed vessel. Analysis of the gaseous products showed the presence of free CO_2. This concurs with previous reports that the carbide atom originates from a coordinated carbonyl ligand, this being the result of a metal-mediated disproportionation [12,14]. This contrasts to the case of rhodium carbonyl carbido clusters where the carbide is thought to originate from the solvent [15].

Of interest is that the carbide carbon does not originate from the ethene in complex **4**. As a consequence, it is suggested that, in the high yield thermolytic route to **1** performed under an atmosphere of ethene, the olefin acts simply as a stabiliser for the coordinatively unsaturated intermediates formed in the reaction. This explains also why yields of **1** were so very low in the original pyrolysis (~5%) and thermolysis (~30%) routes. The '$Ru(CO)_3$' fragments requisite for the formation of **1** are hard to form in the absence of added stabilising ligands. In addition, the fragments themselves are highly unstable reacting indiscriminately and yielding a number of high-nuclearity carbonyl clusters as well as **1**.

The plausible mechanism for the thermal generation of **1** from **2** under an atmosphere of ethene is shown in Scheme 1.

The formation of complex **1** by reduction of a coordinated carbonyl group suggests that the carbide atoms in polynuclear iron clusters such as $[Fe_5C(CO)_{15}]$ and $[Fe_6C(CO)_{16}]^{2-}$ may possibly be produced in a similar manner [16,17]. Work is currently under way to investigate this.

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References

[1] D.F. Shriver, Herbert D. Kaesz, Richard D. Adams (eds.), The Chemistry of Metal Cluster Complexes, VCH, New York, 1990.
[2] E.W. Abel, F.G.A. Stone, G. Wilkinson (eds.), Comprehensive Organometallic Chemistry, Elsevier, Oxford, 1995.
[3] M.D. Vargas, J.N. Nicholls, Adv. Inorg. Radiochem. 30 (1986) 123.

[4] B.F.G. Johnson, J. Lewis, Adv. Inorg. Radiochem. 24 (1981) 225.
[5] F. Calderazzo, R. Ercoli, G. Natta, in: I. Wender, P. Pino (eds.), Organic syntheses via metal carbonyls, Vol. 1, Wiley, New York, 1968.
[6] N.E. Leadbeater, J. Chem. Soc., Dalton Trans. (1995) 2923.
[7] A.J. Edwards, N.E. Leadbeater, J. Lewis, P.R. Raithby, J. Organomet. Chem. 512 (1995) 15.
[8] C.R. Eady, P.F. Jackson, B.F.G. Johnson, J. Lewis, M.C. Malatesta, M. McPartlin, W.J.H. Nelson, J. Chem. Soc., Dalton Trans. (1980) 383.
[9] Y.-M. Wuu, J.G. Bentsen, C.G. Brinkley, M.S. Wrighton, Inorg. Chem. 26 (1987) 530.
[10] B.F.G. Johnson, R.D. Johnston, J. Lewis, J. Chem. Soc. A (1968) 2865.
[11] B.F.G. Johnson, J. Lewis, I.G. Williams, J. Chem. Soc. A (1970) 901.
[12] C.R. Eady, B.F.G. Johnson, J. Lewis, J. Chem. Soc., Dalton Trans. (1975) 2606.
[13] B.F.G. Johnson, J. Lewis, S.W. Sankey, K. Wong, M. McPartlin, W.J.H. Nelson, J. Organomet. Chem. 191 (1980) C3.
[14] P.J. Bailey, M.J. Duer, B.F.G. Johnson, J. Lewis, G. Conole, M. McPartlin, H.R. Powell, C.E. Anson, J. Organomet. Chem. 383 (1990) 441.
[15] V.G. Albano, M. Sansoni, P. Chini, S. Martinengo, J. Chem. Soc., Dalton Trans. (1973) 651.
[16] E.H. Braye, L.F. Dahl, W. Hubel, D.L. Whamphler, J. Am. Chem. Soc. 84 (1962) 4633.
[17] M.R. Churchill, J. Wormald, J. Chem. Soc., Dalton Trans. (1974) 2410.