The Chemical Activation of Iron, Ruthenium, and Osmium Carbonyl Cluster Anions using Oxidative Addition

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(The chemical activation of iron, ruthenium, and osmium carbonyl cluster anions has been achieved by investigating their oxidative electrochemistry and then matching the observed electrochemical oxidation potential with chemical reagents, by the use of oxidative addition in the presence of the required ligand; the dianionic clusters $[Fe_5C(CO)_{14}]^{2-}$, $[Ru_3(CO)_{11}]^{2-}$, $[Ru_5C(CO)_{14}]^{2-}$, $[Ru_6C(CO)_{16}]^{2-}$, $[Os_5(CO)_{15}]^{2-}$, $[Os_7(CO)_{20}]^{2-}$, and $[Os_{10}C(CO)_{24}]^{2-}$ have been found to react with multi-electron donor ligands in the presence of a suitable oxidant.

The approach employed in studying controlled synthesis in osmium and ruthenium carbonyl cluster chemistry has been the utilisation of stable intermediates that allow the displacement of ligand groups under mild conditions. The ready preparation of $[M_3(CO)_{11}NCMe]$ and $[M_3(CO)_{10}(NCMe)_2]$ (M = Ru or Os) by trimethylamine N-oxide oxidation of the carbonyl groups in acetonitrile has led to an extensive chemistry of these trinuclear clusters.[1] More recently this approach has been extended to $H_4Os_4(CO)_{12}$, $Os_5(CO)_{16}$, and $Os_6(CO)_{18}$ clusters.[2] Our attempts to extend this technique to iron, ruthenium and osmium cluster anions have so far proved unsuccessful, possibly because the trimethylamine N-oxide mediated reactions proceed *via* an anionic intermediate, involving nucleophilic attack of trimethylamine N-oxide at a metal carbonyl.[1]

However, our recent studies[3] on the redox chemistry of the deca-osmium carbido cluster $[Os_{10}C(CO)_{24}]^{2-}$ have shown that it can exist in five different oxidation states including the electron deficient cluster $[Os_{10}C(CO)_{24}]$, which was found to react with carbon monoxide in the presence of $AgBF_4$ to yield $[Os_{10}C(CO)_{25}]$ in moderate yield. This observation prompted us to investigate a series of iron, ruthenium, and osmium anionic clusters, namely, $[Fe_5C(CO)_{14}]^{2-}$, $[Ru_3(CO)_{11}]^{2-}$, $[Ru_5C(CO)_{14}]^{2-}$, $[Ru_6C(CO)_{16}]^{2-}$, $[Os_5(CO)_{15}]^{2-}$, $[Os_7(CO)_{20}]^{2-}$, and $[Os_{10}C(CO)_{24}]^{2-}$. We report here an alternative technique to activate iron, ruthenium, and osmium clusters by the use of either electrochemical or chemical oxidative addition.

The hexanuclear ruthenium cluster dianion $[Ru_6C(CO)_{16}]^{2-}$ shows an irreversible two electron oxidation wave in dichloromethane at $E_p = +0.48$ V *vs.* a Ag/AgCl reference electrode, and associated with this wave is a consequent reduction at $E_p = -0.47$ V, *i.e.* the reduction wave of the oxidised product. The controlled potential electrolysis of $[Ru_6C(CO)_{16}]^{2-}$ at a platinum gauze electrode under a steady stream of carbon monoxide or in the presence of a two electron donor ligand yields the desired product $[Ru_6C(CO)_{16}L]$ [L = CO, PPh_3, $P(OMe)_3$, *etc.*] in near quantitative yield. Thus an alternative method of synthesis using either chemical or electrochemical oxidation of iron, ruthenium, or osmium cluster dianions in the presence of the ligand is possible at room temperature.

Typically, a mixture of the cluster carbonyl anion and a slight excess of the ligand (1.1 equiv.) were dissolved in either dichloromethane or acetonitrile. The mixture was then treated dropwise under a nitrogen purge with a solution of the oxidant until reaction was found to be complete by i.r. monitoring, usually within five minutes. All of the reactions are essentially specific and high yield, so that work up is relatively straightforward. Table 1 summarises electrochemical data for the clusters examined (all oxidations were found to be irreversible) with E_p (oxidation) being the second

Table 1. Electrochemical data for the metal carbonyl cluster anions.

Cluster	E_p (oxidation)/V[a,b]	E_p (reduction)/V[a,c]	Oxidant
$[PPN]_2[Fe_5C(CO)_{14}]$[d]	+0.60[e]	−0.60[e]	$AgBF_4$
$[PPN]_2[Ru_3(CO)_{11}]$	+0.22[f]	−0.20[f]	$[C_7H_7]BF_4$
$[PPN]_2[Ru_5C(CO)_{14}]$	+0.15	−1.78	$[Ph_3C]BF_4$ or $[C_7H_7]BF_4$
$[PPN]_2[Ru_6C(CO)_{16}]$	+0.48	−0.47	$Fe(Cp)_2BF_4$ or $FeCl_3$
$[PPN]_2[Os_5(CO)_{15}]$	+0.47	−0.65	$Fe(Cp)_2BF_4$ or $FeCl_3$
$[PPN]_2[Os_7(CO)_{20}]$	+0.51	−0.10	$Fe(Cp)_2BF_4$ or $FeCl_3$
$[PPN]_2[Os_{10}C(CO)_{24}]$	+1.11	−1.30	$AgBF_4$

[a] Recorded at a Ag/AgCl reference electrode in CH_2Cl_2. All solutions 0.1 M in electrolyte (tetrabutylammonium tetrafluoroborate). Typical scan rates 100 or 200 mV s^{-1}. All potentials are uncorrected for solution resistance and junction potentials. [b] Controlled potential electrolysis performed using a platinum basket electrode. [c] E_p(reduction) is the reduction wave of the oxidised cluster. [d] PPN = $(Ph_3P)_2N$. [e] Ref. 4. [f] Ref. 5.

Table 2. Products obtained from the oxidative addition of the metal carbonyl cluster anions.

Cluster	Ligand	Product	Yield (%)	Reference
$[Fe_5C(CO)_{14}]^{2-}$	CO	$[Fe_5C(CO)_{15}]$	94	6
	PPh_3	$[Fe_5C(CO)_{14}PPh_3]$	61	7
	$P(OMe)_3$	$[Fe_5C(CO)_{14}P(OMe)_3]$	64	[a]
$[Ru_3(CO)_{11}]^{2-}$	CO	$[Ru_3(CO)_{12}]$	92	8
	$P(OPh)_3$	$[Ru_3(CO)_{11}P(OPh)_3]$	88	[a]
	PPh_3	$[Ru_3(CO)_9(PPh_3)_3]$	92	9
	dpam[b]	$[Ru_3(CO)_{10}dpam]$	67	10
$[Ru_5C(CO)_{14}]^{2-}$	CO	$[Ru_5C(CO)_{15}]$	95	11
	PPh_3	$[Ru_5C(CO)_{14}PPh_3]$	82	11
	PhCCPh	$[Ru_5C(CO)_{13}PhCCPh]$	76	[a]
$[Ru_6C(CO)_{16}]^{2-}$	CO	$[Ru_6C(CO)_{17}]$	96	12
	PPh_3	$[Ru_6C(CO)_{16}PPh_3]$	91	13
	dppe[c]	$[Ru_6C(CO)_{15}dppe]$	89	[a]
	$C_6H_5(CH_3)$	$[Ru_6C(CO)_{14}C_6H_5(CH_3)]$	57	14
$[Os_5(CO)_{15}]^{2-}$	CO	$[Os_5(CO)_{16}]$	77	15
	PPh_3	$[Os_5(CO)_{15}PPh_3]$	63	[a]
	$P(OPh)_3$	$[Os_5(CO)_{15}P(OPh)_3]$	68	[a]
$[Os_7(CO)_{20}]^{2-}$	CO	$[Os_7(CO)_{21}]$	73	15
	$P(OMe)_3$	$[Os_7(CO)_{20}P(OMe)_3]$	49	[a]
$[Os_{10}C(CO)_{24}]^{2-}$	CO	$[Os_{10}C(CO)_{25}]$	42	[a]

[a] All new compounds have satisfactory i.r., mass spectra, elemental analysis, i.r., and ^1H n.m.r. spectra; dpam = $CH_2(AsPh_2)_2$, dppe = $Ph_2P(CH_2)_2PPh_2$. [b] dpam = 1,2-bis(diphenylarsenido)methane. [c] dppe = 1,2-bis(diphenylphosphino)ethane.

oxidation wave (for Ru_6 and Os_7 clusters only one two-electron irreversible oxidation wave is observed) and E_p (reduction) being the reduction wave of the oxidised cluster. Table 2 summarises some selected reactions and products, and is explained in the following section. The chemical oxidation routes were generally preferred to the electrochemical oxidation as preparative methods, since isolation of the products from electrochemical solutions is complicated by the presence of an excess of base electrolyte.

$[PPN]_2[Fe_5C(CO)_{14}]$ [PPN = $(Ph_3P)_2N$] has been found to react with two electron donors under mild conditions (25 °C) in the presence of an oxidant such as $AgBF_4$ ($E_p > +1.25$ V *vs.* Ag/AgCl), to yield the monosubstituted products in excellent yields. This is in contrast to the thermal activation of $Fe_5C(CO)_{15}$ with two electron donors which resulted in many products in low yield.[7]

$[PPN]_2[Ru_3(CO)_{11}]$ reacts rapidly with either two or four electron donors in the presence of $[C_7H_7]BF_4$($E_p = +0.26$ V *vs* Ag/AgCl in CH_2Cl_2; see Tables 1 and 2), to give excellent yields of mono-, bis-, or tri-substituted products. This dianionic cluster is therefore favourable as an alternative in the activation of trinuclear ruthenium clusters with two- or four-electron donor ligands.

$[PPN]_2[Ru_5C(CO)_{14}]$ reacts rapidly with either two or four electron donors in the presence of $[Ph_3C]BF_4$ or $[C_7H_7]BF_4$ ($E_p = +0.29$ V *vs.* Ag/AgCl in CH_2Cl_2; see Tables 1 and 2), to give excellent yields of the monosubstituted products.

$[PPN]_2[Ru_6C(CO)_{16}]$ has been the most studied of the anionic metal carbonyl clusters and reacts rapidly in the presence of $[Fe(Cp)_2]BF_4$ (Cp = η^5-C_5H_5) ($E_p = +0.56$ V *vs.* Ag/AgCl in CH_2Cl_2) to give excellent yields of the monosubstituted products. The cluster has been found to react with two-, four-, five-, and even six-electron donors under mild conditions. This is in contrast to the thermal route to the arene substituted cluster $[Ru_6C(CO)_{14}C_6H_5(CH_3)]$ which was previously obtained in 10% yield as one of many products.[14]

$[PPN]_2[Os_5(CO)_{15}]$ reacts rapidly with two electron donor ligands to give the appropriate products using either $FeCl_3$ or $[Fe(Cp)_2]BF_4$ as the oxidant. Employing a lower temperature gives improved yields of these primary substitution products.

$[PPN]_2[Os_7(CO)_{20}]$ is slightly less reactive than the smaller iron, ruthenium, and osmium anionic clusters, nevertheless it reacts with two electron donor ligands in moderate yield under milder reaction conditions than previously used.

$[PPN]_2[Os_{10}C(CO)_{24}]$ is significantly less reactive than the other clusters studied. This could possibly be due to the increasing carbonyl saturation of the cluster surface. However, the lower temperature used resulted in a moderate yield of the neutral cluster $[Os_{10}C(CO)_{25}]$ using either electrochemical means or $AgBF_4$ ($E_p > +1.25$ V *vs.* Ag/AgCl in CH_2Cl_2) as the oxidant.

The redox reactions described above appear to be general for systems satisfying the following requirements. (i) The oxidation potential of the cluster anion is between -0.5 and $+1.5$ V *vs.* Ag/AgCl. (ii) The reduction potential of the oxidant is higher than the oxidation potential of the cluster to ensure that the redox reaction may occur. (iii) The oxidant does not react with the cluster anion. (iv) The metal carbonyl cluster bears at least a dinegative charge.

The mechanism that is proposed for these reactions is essentially one of electron transfer between the cluster anion and the oxidant, *e.g.* for $[Ru_6C(CO)_{16}]^{2-}$ the reactive species is presumably the electron deficient cluster '$[Ru_6C(CO)_{16}]$' which may lose or gain more carbonyl ligands as necessary. [See equations (1)—(4), where L is a two-electron donor and L–L is a four-electron donor].

$$[Ru_6C(CO)_{16}]^{2-} + Fe(Cp)_2^{+} \longrightarrow \text{`}[Ru_6C(CO)_{16}]\text{'} + Fe(Cp)_2 \quad (1)$$

$$\text{`}[Ru_6C(CO)_{16}]\text{'} + L \longrightarrow [Ru_6C(CO)_{16}L] \quad (2)$$

$$\text{`}[Ru_6C(CO)_{16}]\text{'} + L\text{–}L \longrightarrow \text{`}[Ru_6C(CO)_{16}L\text{–}L]\text{'}, \textit{etc.} \quad (3)$$

$$\text{`}[Ru_6C(CO)_{16}L\text{–}L]\text{'} \longrightarrow [Ru_6C(CO)_{15}L\text{–}L] + CO \quad (4)$$

From Table 2, it may be seen that this method affords many clusters in excellent yield, previously obtainable only by thermal routes in low yield. For anionic metal carbonyl clusters where the above conditions are favourable, the fast reaction time and mild reaction conditions should readily facilitate a vast expansion in their chemistry.

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