Journal of Organometallic Chemistry, 451 (1993) 153–156

JOM 23456

Electrochemistry of $[\{Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)\}_2Hg]$ and $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)HgX]$ $\{X = Re(CO)_5$ or $MoCp(CO)_3\}$ *

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(Received October 5, 1992)

Abstract

The electrochemical reduction of $[\{Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)\}_2Hg]$ and $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)HgX]$ $\{X = Re(CO)_5$ or $MoCp(CO)_3\}$ has been investigated at both Pt and Hg electrodes in tetrahydrofuran (THF) at different temperatures by means of cyclic voltammetry and coulometry. All the compounds undergo chemically irreversible reduction followed by the formation of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]^-$ anion, mercury, and organometallic radical $X^{\cdot}$ at essentially the same potential. Despite the isolobal relationship between the proton in $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]$ and the HgX fragment, the reduction potentials of title compounds are significantly less negative (*ca.* 0.3 V) suggesting that the LUMO in these complexes is at lower energy than in the corresponding hydride, and has significant mercury character.

1. Introduction

In recent years there has been growing interest in mercury-containing transition metal clusters [1]. These investigations have verified the isolobal relationship between HgX^+ (X = halide) and H^+ [2]. In addition, mercury (formally Hg^{2+}) has been able to form μ_3-, μ_4-, and μ_6-bridges between a variety of transition metal cluster moieties [3]. We and others have put considerable effort into trying to understand how the electron deficient multicentre bonding in μ_n-mercury transition metal clusters ($n = 3$–6) differs in reactivity from the more traditional and well characterized electron precise mercury transition metal bonding in M–Hg–M′ and M–Hg–X systems (M or M′ = mononuclear transition metal moiety).

We report here a detailed study of the electrochemical reduction of three species containing electron deficient μ_4- and μ_3- mercury transition metal systems: $[\{Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)\}_2Hg]$ (**1**), $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)HgRe(CO)_5]$ (**2**), and $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)HgMo(CO)_3Cp]$ (**3**) (Fig. 1). Like their M–Hg–M′ analogues [4] which upon reduction generally eliminate of Hg, M^- and M'^- we observe formation of Hg and the well known $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]^-$ [5] in the case of **1**. However, by examining the electrochemical reduction at low temperature we were able to detect distinct differences in the behaviours of **2** and **3** and draw some definite conclusions about the pathways for reductive cleavage of the mercury-transition metal bonds in all three species. These studies have helped to shed some light on the previously reported photochemical and thermochemical behaviour of **1–3**.

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* Dedicated to Professor G.P. Chiusoli on the occasion of his 70th birthday.

0022-328X/93/$6.00

2. Results and discussion

2.1. Electrochemistry of [{$Ru_3(CO)_9(\mu_3$-η^2-C≡C^{t}Bu)}$_2$Hg] (1)

Two cathodic peaks (A and B respectively) are observed in the cyclic voltammetric (CV) response of compound **1** at room temperature at both Pt and Hg electrodes. They represent diffusion-controlled (i_p *vs.* $v^{1/2}$ is linear through the origin) and chemically irreversible (no associated reoxidation peaks) processes. Peak A corresponds to a two-electron reduction (as checked by comparison with the oxidation of ferrocene added as internal standard); peak B is twice as high and corresponds to an overall four-electron process. The stoichiometry is confirmed by controlled potential coulometry. At a Pt electrode, when the scan is reversed after peak A, an anodic, irreversible peak (P) appears. The potential of the cathodic peak B and the anodic peak P are equal to those found for [$Ru_3(CO)_9(\mu_3$-η^2-C≡C^{t}Bu)]$^-$, as measured in an independent experiment on an authentic sample [5] (Table 1). This anodic peak appears only when the potential sweep is reversed after peak B and corresponds to the oxidation of an unidentified fragment generated from [$Ru_3(CO)_9(\mu_3$-η^2-C≡C^{t}Bu)]$^-$. This peak is indeed observed in the CV response of the above mentioned anion. Thus, the reduction of **1** at room temperature proceeds with consumption of two electrons per molecule at the potential of peak A, followed by cleavage of Ru–Hg bonds and formation of two [$Ru_3(CO)_9(\mu_3$-η^2-C≡C^{t}Bu)]$^-$ anions which undergo further two electron reduction at the potential of peak B. Metallic mercury is produced and it coates the Pt electrode (see Experimental section). The overall reduction process for **1** can be described by the following scheme:

$$\left[\{Ru_3(CO)_9(\mu\text{-C≡C}^tBu)\}_2Hg\right] \xrightarrow[(A)]{2e^-} 2\left[Ru_3(CO)_9(\mu\text{-C≡C}^tBu)\right]^- + Hg$$

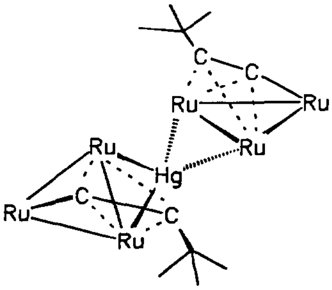
$$2\left[Ru_3(CO)_9(\mu\text{-C≡C}^tBu)\right]^- \xrightarrow[(B)]{4e^-} \text{products}$$

The initial 2e$^-$ reduction parallels the chemical reduction of **1** with sodium benzophenone ketyl (BPK) previously reported [6d].

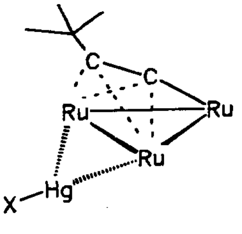
At temperatures below −70°C, the height of peak A corresponds to that typical of one-electron reduction

TABLE 1. Redox peak potentials of [{$Ru_3(CO)_9(\mu_3$-η^2C≡C^{t}Bu)}$_2$Hg] (**1**), [$Ru_3(CO)_9(\mu_3$-η^2-C≡C^{t}Bu)HgRe(CO)_5$] (**2**); [$Ru_3(CO)_9(\mu_3$-$\eta^2$-C≡C^{t}Bu)HgMo(CO)$_3$Cp] (**3**), along with those of [$Ru_3(CO)_9(\mu_3$-η^2-C≡C^{t}Bu)]$^-$, [{Re(CO)$_5$}$_2$] and [{Mo(CO)$_3$Cp}$_2$] in THF containing [Bu_4N][PF_6] (0.05 M), scan rate 200 mV s^{-1} (20°C)

Compound	Peak	Electrode	E_p (V *vs.* SCE)
1	A	Pt	−1.26
		Hg	−1.25
	B	Pt	−2.46
		Hg	−2.38
	P	Pt	+0.43
2	A	Pt	−1.31
		Hg	−1.28
	B	Pt	−2.46
		Hg	−2.38
	C	Pt	−2.03
		Hg	−1.90
	P	Pt	+0.43
3	A	Pt	−1.26
		Hg	−1.25
	B	Pt	−2.46
		Hg	−2.38
	P	Pt	+0.43
	Q	Pt	−0.24
[$Ru_3(CO)_9(\mu$-C≡C^{t}Bu)]$^-$	B	Pt	−2.46
	P	Pt	+0.44
[{Re(CO)$_5$}$_2$]	C	Pt	−2.03
		Hg	−1.87
[{Mo(CO)$_3$Cp}$_2$]		Pt	−1.06
		Hg	−0.95
	Q	Pt	−0.25



[1]



[2,3]

Fig. 1. Sketch of the structures of [{$Ru_3(CO)_9(\mu_3$-η^2-C≡C^{t}Bu)}$_2$Hg] (**1**), [$Ru_3(CO)_9(\mu_3$-η^2-C≡C^{t}Bu)HgX] [X = Re(CO)$_5$ (**2**); Mo(CO)$_3$Cp (**3**)]. Carbonyl groups are omitted for clarity.

(as monitored by the ferrocene standard) and the first process becomes chemically reversible. This indicates that the primary product of reduction of **1** is the corresponding anion radical $\mathbf{1}^{-\cdot}$, which is stable on the CV time scale only at temperatures as low as −70°C. The peak potential difference, $\Delta E_p = E_p{}^a - E_p{}^c$, 180 and 120 mV at Pt and Hg electrodes, respectively, is much larger than expected for an electrochemically reversible one-electron process ($\Delta E_p = 40$ mV) at −70°C. This indicates that the one-electron reduction of **1** is a quasi-reversible process, and is associated with a reversible but slow structural rearrangement.

However, once the second electron is transferred to $\mathbf{1}^{-\cdot}$ spontaneous degradation to two $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]^-$ anions and metallic mercury occurs. The persistence of the radical anion $\mathbf{1}^{-\cdot}$ on the CV time scale indicates that at low temperature the reduction of **1** is an EE process, while at more elevated temperature it is an overall ECE process. Again, this is consistent with chemical behaviour of **1** where up to one mole of BPK could be used to promote phosphine substitution with no degradation of **1**. When two moles of BPK are used, spontaneous reductive elimination of mercury is observed and only $[(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]$ is recovered after workup [6d]. This suggests that the LUMO for **1** contains considerable $Ru_2\text{–}\mu_4Hg\text{–}Ru_2$ character. Indeed phosphine substitution of **1** is very slow even in the presence if one mole of BPK (normally used in catalytic amounts) which is also consistent with considerable $Ru_2\text{–}Hg\text{–}Ru_2$ character in the LUMO as phosphine substitution is observed only on the apical Ru atom [6d].

The reduction potential of BPK in THF is about −2.1 V *vs.* SCE, consistent with the fact that only reduction to the $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]^-$ anions, and no further reduction of the anions themselves, is observed. It is difficult to say exactly why rapid two-electron reduction is observed electrochemically at room temperature whereas the chemical reduction seems to proceed slowly under the same conditions, but it is well known that kinetic pathways for electrochemical and chemical reduction can be quite different [7].

2.2. *Electrochemistry of* $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)HgRe(CO)_5]$ *(2)*

Three cathodic, diffusion-controlled, chemically irreversible peaks are observed in the CV response of **2** at room temperature, at Pt and Hg electrodes. Peaks A and B have potentials values very close to those observed in the CV response of **1** (Table 1). The only difference is that the height of peak A corresponds to a one-electron reduction, confirmed by controlled potential coulometry, while peak B corresponds to a two-electron process. Moreover, the potential of peak C is exactly that of irreversible two-electron reduction of $[\{Re(CO)_5\}_2]$ measured in an independent experiment (Table 1). The anodic part of CV response consists of a set of anodic peaks, one of them (P) corresponding to the oxidation of the electrogenerated anion $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]^-$. The other anodic peaks are observed in CV response of $[Re(CO)_5]_2$ recorded in the same experimental conditions. No peak assignable to the oxidation of $[Re(CO)_5]^-$ appears upon inversion of the potential sweep after peak A. Furthermore the lowering of the temperature to −90°C does not cause any reversibility of peak A. This indicates a lower stability of the electrogenerated radical anion $\mathbf{2}^{-\cdot}$ as compared with $\mathbf{1}^{-\cdot}$.

These electrochemical results show that the one-electron reduction of **2** (at the potential of peak A) is followed by the formation of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]^-$ and the $[Re(CO)_5]^\cdot$ radical, which undergoes fast dimerization to $[\{Re(CO)_5\}_2]$, and Hg. This dimer and the $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]^-$ anion are further reduced at potentials of the peaks C and B, respectively. Hence, the mechanism of electroreduction of **2** can be schematically represented as follows;

$$[Ru_3(CO)_9(\mu\text{-}C{\equiv}C^tBu)HgRe(CO)_5] \xrightarrow[(A)]{1\,e^-}$$

$$[Ru_3(CO)_9(\mu\text{-}C{\equiv}C^tBu)]^- + [Re(CO)_5] + Hg$$

$$2[Re(CO)_5]^\cdot \longrightarrow [\{Re(CO)_5\}_2]$$

$$[\{Re(CO)_5\}_2] \xrightarrow[(C)]{2\,e^-} 2[Re(CO)_5]^- + \text{products}$$

$$[Ru_3(CO)_9(\mu\text{-}C{\equiv}C^tBu)]^- \xrightarrow[(B)]{2\,e^-} \text{products}$$

2.3. *Electrochemistry of* $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)HgMo(CO)_3Cp]$ *(3)*

Two cathodic, diffusion-controlled, chemically irreversible peaks, A and B, are observed in CV response of **3** at room temperature at both Pt and Hg electrodes. Their potentials are very close to those observed for **1**, and height of each of them corresponds to a two-electron reduction process. When the potential scan is reversed after peak A, two anodic irreversible peaks, P and Q, appear. The potential of peak P corresponds to that previously found for the oxidation of fragment generated from $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]^-$, and the potential of peak Q is exactly that found for oxidation of $[Mo(CO)_3Cp]^-$ (Table 1). Even at −90°C peak A does not exhibit any associated reoxidation peak, consistent with the low stability of the electrogenerated radical anion $\mathbf{3}^{-\cdot}$. The proposed two-electron reduction of **3**, followed by the formation of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}$

$C{\equiv}C^tBu)]^-$ and $[Mo(CO)_3Cp]^-$ anions is consistent with the fact that the reduction potential of an authentic sample of $[\{Mo(CO)_3Cp\}_2]$, in the same experimental conditions, (Table 1) is more positive than that of **3**. The above pathway is summarized in the following scheme:

$$[Ru_3(CO)_9(\mu\text{-}C{\equiv}C^tBu)HgMo(CO)_3Cp] \xrightarrow[(A)]{2e^-}$$

$$[Ru_3(CO)_9(\mu\text{-}C{\equiv}C^tBu)]^- + [Mo(CO)_3Cp]^- + Hg$$

$$[Ru_3(CO)_9(\mu\text{-}C{\equiv}C^tBu)]^- \xrightarrow[(B)]{2e^-} \text{products}$$

Only for **1** can we observe the separation of the initial two-electron process into one-electron processes at low temperature. For **2** and **3**, immediate degradation of the cluster with elimination of Hg is observed. This suggests a more delocalized and stable Ru_2–μ_4Hg–Ru_2 bond for **1** compared with the Ru_2–μ_2Hg–X [X = $Re(CO)_5$ or $MoCp(CO)_3$] bond in **2** and **3**. This is consistent with the fact that **1** is photochemically inactive as compared to **2** and is thermally more stable [8].

In all the title compounds the first reduction potential is similar and significantly less negative (*ca.* 0.3 V) than in $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]$ [9]. CNDO calculations [10] indicate that the LUMO in $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]$ involves the antibonding Ru–Ru orbital with little contribution from the bridging hydride. The involvement of the mercury-transition metal fragment in the LUMO of **1–3** to give a more delocalized orbital could explain the lowering of reduction potential.

Finally, the fate of the radical $\mathbf{X}^\cdot$ formed upon reduction depends on its reactivity and its redox potential: it can undergo fast dimerization to X–X (as **2**) or can be further reduced to X^- (as in **3**).

3. Experimental section

Compounds **1–3** were synthesized according to published procedures [6]. Their purity was checked by IR and ^{1}H-NMR spectroscopy. The apparatus and materials for electrochemical measurements have been previously described [11]. The Pt electrode is always coated with Hg during the electroreduction of all the title compounds. Therefore such an electrode was carefully polished with diamond paste, rinsed with acetone, and dried with tissue paper before each scan. All the potentials are relative to an aqueous saturated calomel electrode (SCE) and calibrated against the ferrocene (0/1 +) couple [12]. The coulometric measurements were caried out using Hg pool-electrode in a two-compartment cell separated by a high-porosity fritted glass.

Acknowledgments

We thank CNR, MURST, NATO (870705) and NSF (CHE-9016495) for financial support, Johnson Matthey Ltd. for a generous loan of $RuCl_3$, and P.A. Loveday (University Chemical Laboratory, Cambridge, UK) for high-pressure synthesis of $Ru_3(CO)_{12}$.

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