

Electrochemical Studies of the Reduction of $\text{Ru}_3(\text{CO})_{12}$

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Summary: The reduction of $\text{Ru}_3(\text{CO})_{12}$ and the oxidation of *triangulo*- $\text{Ru}_3(\text{CO})_{11}^{2-}$ in acetone solution were studied by polarography and cyclic voltammetry. The reaction scheme deduced from these experiments includes two-electron reduction and ring opening to give $\text{Ru}_3(\text{CO})_{12}^{2-}$ which undergoes CO loss followed by ring closure to give $\text{Ru}_3(\text{CO})_{11}^{2-}$. The key intermediates in the scheme are the linear anion $\text{Ru}_3(\text{CO})_{12}^{2-}$ and the triangulo anions $\text{Ru}_3(\text{CO})_{12}^{-}$ and $\text{Ru}_3(\text{CO})_{11}^{-}$.

Of the many group 8-10 clusters for which electron-transfer chain (ETC) catalyzed nucleophilic substitution reactions have been demonstrated,¹⁻⁵ few substrates afford better yields or higher product selectivity than $\text{Ru}_3(\text{CO})_{12}$.³ It has been assumed the radical anion stability is an essential feature of ETC reactions, but the $\text{Ru}_3(\text{CO})_{12}$ radical anion is apparently very unstable. Polarographic studies show a reduction step which is both chemically and electrochemically irreversible, even at low temperature.⁶ This behavior has led to the suggestion that fragments of higher and lower nuclearity participate in the nucleophilic substitution process.⁵ This suggestion is supported by the recent report⁷ that Ru_4 and Ru_6 cluster anions are formed in reactions of $\text{Ru}_3(\text{CO})_{12}$ with benzophenone ketyl and by kinetic studies⁸ of the thermal nucleophilic substitution of $\text{Ru}_3(\text{CO})_{12}$ by phosphines which suggest that fragmentation of $\text{Ru}_3(\text{CO})_{11}\text{L}$ and reaggregation of $\text{Ru}(\text{CO})_3\text{L}$ is responsible for the $\text{Ru}_3(\text{CO})_9\text{L}_3$ product obtained under synthetic conditions. On the other hand, the good yields and high selectivity obtained for the ETC reaction are difficult to rationalize if the mechanism involves a variety of fragments. Our studies of the $\text{Ru}_3(\text{CO})_{12}$ system are intended to resolve this apparent contradiction; we present here a preliminary report of our results.

The DC polarogram⁹ of $\text{Ru}_3(\text{CO})_{12}$ in acetone solution shows a well-defined wave with $E_{1/2} = -0.94$ V; the slope of a plot of E vs. $\log(i_d - i)/i$ is 35.5 mV and the diffu-

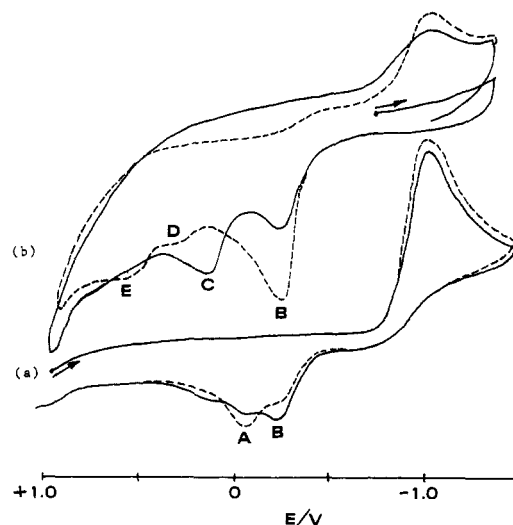


Figure 1. Cyclic voltammograms (600 mV s^{-1}) of (a) $\text{Ru}_3(\text{CO})_{12}$ and (b) $\text{K}_2\text{Ru}_3(\text{CO})_{11}$ in acetone under 1 atm of Ar (solid traces) and under 1 atm of CO (dashed traces); potentials are vs. Ag/AgCl in acetone.

sion-limited current corresponds to a two-electron reduction.¹⁰ Cyclic voltammograms of $\text{Ru}_3(\text{CO})_{12}$ at Pt or Hg electrodes show a chemically irreversible reduction step (peak potential, -1.01 V)¹¹ followed on the return scan by smaller oxidation peaks at -0.22 V (B) and -0.07 V (A) (see Figure 1a). At -30°C , only peak A is observed. As the temperature is increased, B increases at the expense of A. At room temperature, the A/B ratio increases with increasing scan rate and is larger under 1 atm of CO than under argon. Peak B can be identified as the oxidation of *triangulo*- $\text{Ru}_3(\text{CO})_{11}^{2-}$ (see below). Since this species is apparently a secondary product formed by a relatively slow process involving loss of CO, we identify A with the oxidation of $\text{Ru}_3(\text{CO})_{12}^{2-}$. This is a known species, reported to be stable under high CO pressure and thought to have an open-chain structure.¹²

Cyclic voltammograms of $\text{K}_2\text{Ru}_3(\text{CO})_{11}$, prepared as described by Shore,⁷ show oxidation peaks of approximately equal size at -0.22 (B) and $+0.20$ V (C) (Figure 1b). A small reduction peak at -1.0 V on the reverse cathodic scan suggests partial conversion to $\text{Ru}_3(\text{CO})_{12}$. Under 1 atm of CO, C is absent, B is approximately twice as large, and the $\text{Ru}_3(\text{CO})_{12}$ reduction peak is significantly larger.¹³ Apparently $\text{Ru}_3(\text{CO})_{11}^{2-}$ undergoes a one-electron oxidation to $\text{Ru}_3(\text{CO})_{11}^{-}$. In the absence of excess CO, this species (or a decomposition product) is oxidized at 0.2 V. Addition of CO produces *triangulo*- $\text{Ru}_3(\text{CO})_{12}^{2-}$ which is rapidly oxidized to $\text{Ru}_3(\text{CO})_{12}$ at -0.22 V, thus giving a two-electron oxidation overall.

Extended Hückel molecular orbital calculations¹⁴ on $\text{Ru}_3(\text{CO})_{12}$ have shown that the LUMO (the singly occupied MO in the initially formed radical anion) is strongly metal-metal antibonding and weakly metal-ligand anti-

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(9) Polarography and cyclic voltammetry experiments employed 0.1 mM solutions of substrates with 0.1 M tetra-*n*-butylammonium perchlorate supporting electrolyte; potentials are relative to a Ag/AgCl reference electrode in acetone.

(10) Controlled potential electrolytic reduction of $\text{Ru}_3(\text{CO})_{12}$ at -1.1 V consumed approximately one faraday per mole of substrate. The predominant product, identified by comparison with cyclic voltammograms of an authentic sample, prepared by the method of Shore,⁷ was $\text{Ru}_6(\text{CO})_{18}^{2-}$, apparently formed by reaction of $\text{Ru}_3(\text{CO})_{11}^{2-}$ with $\text{Ru}_3(\text{CO})_{12}$.

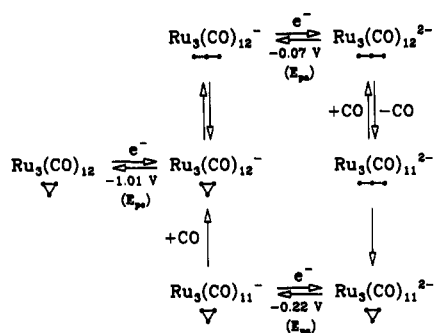
(11) Cyclic voltammetry peak potentials quoted here refer to scan rates of 600 mV s^{-1} .

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(13) Two other small oxidation peaks, D and E, are seen in this experiment; these features are characteristic of $\text{Ru}_6(\text{CO})_{18}^{2-}$, suggesting that formation of this species¹⁰ from $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{11}^{2-}$ is rapid.

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Scheme I



bonding. Thus the fate of the short-lived^{15,16} *triangulo*- $\text{Ru}_3(\text{CO})_{12}^{\bullet -}$ plausibly could be either ring opening to linear $\text{Ru}_3(\text{CO})_{12}^{\bullet -}$ or CO loss to form *triangulo*- $\text{Ru}_3(\text{CO})_{11}^{\bullet -}$. In either case, further reduction to a dianion is expected to be highly exoergic when the electrode potential is -1.01 V. The reverse of the CO loss pathway is responsible for the formation of $\text{Ru}_3(\text{CO})_{12}$ when $\text{Ru}_3(\text{CO})_{11}^{\bullet -}$ is oxidized in the presence of CO. However, since only the linear dianion is formed at low temperature and the product ratio dependence on scan rate suggests that *triangulo*- $\text{Ru}_3(\text{CO})_{11}^{\bullet -}$ is a secondary product, *triangulo*- $\text{Ru}_3(\text{CO})_{12}^{\bullet -}$ must decay via metal-metal bond cleavage with loss of CO subsequent to formation of the linear dianion. Since CO pressure significantly influences the dianion product ratio, CO loss is apparently reversible. On the other hand, the linear dianion is not formed from *triangulo*- $\text{Ru}_3(\text{CO})_{11}^{\bullet -}$ under 1 atm of CO pressure so that we are led to postulate a two-step process involving reversible loss of CO to form linear $\text{Ru}_3(\text{CO})_{11}^{\bullet -}$, followed by irreversible ring closure to give *triangulo*- $\text{Ru}_3(\text{CO})_{11}^{\bullet -}$. The various processes are summarized in Scheme I.

Unlike most other ETC processes involving transition-metal clusters, chemical and electrochemical initiation of Lewis base substitution on $\text{Ru}_3(\text{CO})_{12}$ do not give equivalent results. Electrochemical initiation results in much lower yields and poorer product specificity than when a catalytic amount of a chemical reducing agent is used. Although some nucleophilic substitution product is obtained, the current efficiency is low and the dominant products are $\text{Ru}_3(\text{CO})_{11}^{\bullet -}$ and $\text{Ru}_3(\text{CO})_{12}^{\bullet -}$. These results are consistent with the cyclic voltammetry studies discussed above and fit into the general scheme for competition between ETC catalysis and an ECE process presented by Saveant.¹⁷ The reason for the success of ETC catalysis as a synthetic method for Lewis base derivatives of $\text{Ru}(\text{CO})_{12}$ is apparently that reduction to the dianion

does not occur under the usual synthetic conditions.³ When a catalytic amount of benzophenone ketyl is used as an initiator, $\text{Ru}_3(\text{CO})_{12}^{\bullet -}$ reacts with nucleophile and completes the chain before another molecule of reducing agent is encountered. Studies are in progress on the electrochemistry of the $\text{Ru}_3(\text{CO})_{12}$ system in the presence of Lewis bases.

Preparation and Reaction Dynamics of $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{PPh}_3)_2\text{H}_3$. A Structurally Characterized η^4 -Cyclopentadiene Complex

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Summary: The complex $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{PPh}_3)_2\text{H}_3$ has been prepared by the reaction of $\text{Re}(\text{PPh}_3)_2\text{H}_7$ with cyclopentadiene at 25°C , isolated, and structurally characterized. Variable-temperature ^1H NMR shows at least two distinct fluxional processes. Spin-saturation NMR spectroscopy reveals a process in which the endo hydrogen exchanges with the hydride ligands.

The η^5 -cyclopentadienyl ligand is one of the most versatile and perhaps most important ligands in organometallic chemistry. While the ligand is observed to behave as a spectator group in many reactions, its variation in coordination number has led to many discoveries of the importance of reduced hapticity (η^1 or η^3) in substitution reactions involving $\eta^5\text{-C}_5\text{H}_5$ complexes.¹ Several reports of the related $\eta^4\text{-C}_5\text{H}_6$ complexes have appeared in the literature, either in the preparation of $\eta^5\text{-C}_5\text{H}_5$ complexes or as proposed reactive intermediates.²⁻⁵ Only a few substituted derivatives of the type $(\eta^4\text{-C}_5\text{H}_5\text{R})\text{M}$ have been

(15) Alkali-metal reduction of $\text{Ru}_3(\text{CO})_{12}$ in THF solution has been reported¹⁶ to produce an ESR-active radical species which was originally thought to be $\text{Ru}_3(\text{CO})_{12}^{\bullet -}$. We have found that when $\text{Ru}_3(\text{CO})_{12}$ in THF is exposed to a Na or K mirror at room temperature and then quickly cooled to dry ice-acetone temperature, a weak spectrum ($g = 1.986$) is observed which shows $^{99}\text{Ru}/^{101}\text{Ru}$ satellites ($a^{\text{Ru}} \approx 24$ Gauss) with amplitudes consistent with three equivalent Ru sites in the radical species, but whether this is due to $\text{Ru}_3(\text{CO})_{12}^{\bullet -}$, $\text{Ru}_3(\text{CO})_{11}^{\bullet -}$, or some other species is uncertain. When $\text{Ru}_3(\text{CO})_{12}$ was reduced at low temperature with Na, K or with an electrode or when $\text{Ru}_3(\text{CO})_{12}^{\bullet -}$ was oxidized electrochemically at low temperatures, no ESR spectrum could be detected. At present we have no explanation for these results.

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