Comparison of the Ligand Substitution Rates of the 17-Electron Radicals (Arene)M(CO)₃⁺ (M = Cr, Mo, W)

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It is generally considered that ligand *substitution* in 17-electron organometallic radicals occurs by an associative mechanism, with a 19-electron radical being formed as an intermediate (or activated complex).[1] Nineteen-electron complexes are quite rare, although in a few cases it has been possible[2,3] to indirectly measure the thermodynamics of ligand *addition* to a 17-electron complex to generate a 19-electron product. Herein we present results that allow the direct comparison of the rate of associative ligand substitution at a 17-electron center as a function of the metal within a triad (Cr, Mo, W). As is well-known,[4] substitution rates at 18-electron centers are very dependent on the metal; usually the complex with the second row metal is by far the most reactive. As for 17-electron complexes, a recent study[5] of halide-induced disproportionation of the iron triad radicals M(CO)₃(PCy₃)₂⁺ was interpreted in terms of halide attack being rate determining, which led to the conclusion that the reactivity of these 17-electron complexes is not greatly dependent on the metal. The suggestion was made that periodic trends in 17-electron systems are generally attenuated in comparison to those for 18-electron analogues.

We recently showed[3] that the electrochemical oxidation of (mesitylene)W(CO)₃ (**1**) generates the 17-electron **1⁺**, which rapidly *adds* solvent (MeCN) or another ligand (P(OBu)₃) to give a 19-electron adduct that spontaneously oxidizes to (mesitylene)W(CO)₃L²⁺. In contrast, (mesitylene)Cr(CO)₃ (**2**) undergoes general decomposition upon oxidation in MeCN.[3,6] Although none of the radicals produced from **1** or **2** were *observable* in the sense of producing a chemically reversible voltammetric wave or an IR band, their existence was inferred from an analysis of the data and from digital simulations. The conclusion reached was that **1⁺** is more reactive than **2⁺** by a factor of about 10⁴ with respect to attack by MeCN.

We now report that suitable steric congestion at the arene in (arene)M(CO)₃ (M = Cr, Mo, W) inhibits associative attack so that all three metals may be oxidized in a chemically reversible 1-electron manner at a platinum electrode in CH₂Cl₂/0.10 M Bu₄NPF₆, thus permitting a *direct* comparison of the reactivities of the corresponding 17-electron radicals. The arene selected was C₆Et₆, which complexes to M(CO)₃ with the ethyls alternatively pointing toward and away from the metal side of the

$$(C_6Et_6)M(CO)_3{}^+ + P(OBu)_3 \longrightarrow$$
$$(C_6Et_6)M(CO)_2[P(OBu)_3]^+ + CO \quad (1)$$
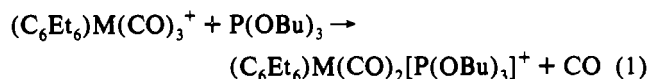
ring.[7,8] In contrast to the ligand *addition* reactions of **1⁺**, it was found that (C₆Et₆)M(CO)₃⁺ (M–3⁺, M = Cr, Mo, W) undergoes
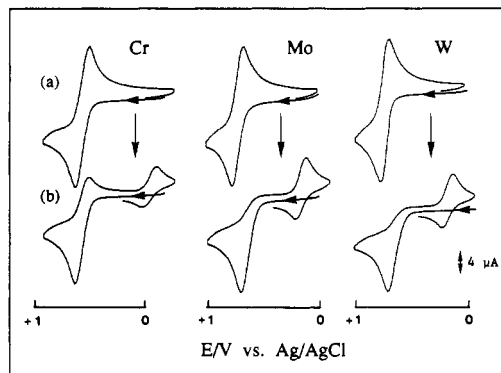

Figure 1. Cyclic voltammograms of 1.0 × 10⁻³ M (C₆Et₆)M(CO)₃ in CH₂Cl₂/0.10 M Bu₄NPF₆ with (a) no added P(OBu)₃ and (b) P(OBu)₃ present at 0.010 M (Cr and W) and 0.0020 M (Mo). The working electrode was a 1.6-mm-diameter platinum disk and the scan rate was 0.50 V/s. All potentials are relative to $E_{1/2}$(ferrocene) = 0.34 V.

clean CO *substitution* in the presence of P(OBu)₃ (eq 1). Figure 1 shows typical voltammograms; the reversible couple cathodic of the original oxidation is due to (C₆Et₆)M(CO)₂[P(OBu)₃]⁺/⁰. IR spectroelectrochemical experiments, along with our earlier work[9] with oxidatively induced CO substitutions in (arene)Cr(CO)₃, confirmed the validity of eq 1.

With Cr–3⁺, digital simulations[3,10] of cyclic voltammograms at various scan rates, P(OBu)₃ concentrations, and temperatures (+20 to –25 °C) established that the rate law is k[P(OBu)₃][Cr–3⁺], with k = (1.1 ± 0.2) × 10² M⁻¹ s⁻¹ at 20 °C. The activation parameters are as follows: $\Delta H^\ddagger$ = 22 ± 2 kJ; $\Delta S^\ddagger$ = –130 ± 20 J K⁻¹. As expected, these parameters point to an associative mechanism for eq 1. In contrast to the case with Cr–3, the cyclic voltammograms of Mo–3 and W–3 in the presence of excess P(OBu)₃ at 20 °C showed no chemical reversibility for the initial oxidation wave up to the maximum scan rate used (100 V/s), which indicated that the rate of eq 1 is much larger for Mo–3⁺ and W–3⁺ than for Cr–3⁺. It was possible to determine the rate constants for Mo–3⁺ and W–3⁺ by voltammetry in the presence of a deficiency of P(OBu)₃; this procedure, as described by Parker, et al.,[11] leads to a splitting of the oxidation wave into two peaks, provided the second-order rate constant exceeds 10⁶ M⁻¹ s⁻¹ under ordinary experimental conditions. Digital simulation of the experimental results produced the following rate constants for eq

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(8) Electrochemical experiments indicate that the steric protection of the metal provided by the three ethyl groups on the metal side of the ring in (C₆Et₆)W(CO)₃ is very nearly duplicated when the arene is 1,3,5-tri-*tert*-butylbenzene. The advantage of the latter complex (whose X-ray structure has been determined: Ryan, W. J.; Sweigart, D. A. To be published) is that the steric protection must be present regardless of the rotational orientation of the butyl groups.

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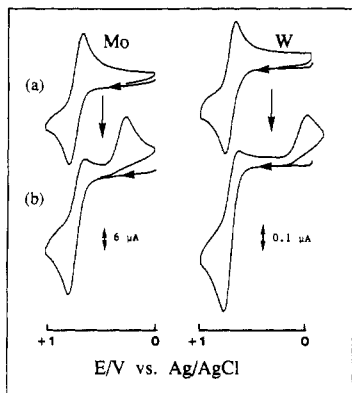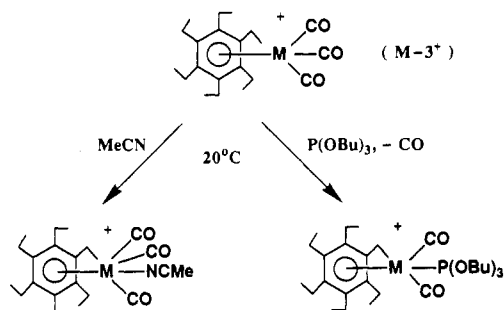
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Figure 2. Cyclic voltammograms of 1.0×10^{-3} M $(C_6Et_6)M(CO)_3$ in $CH_2Cl_2/0.10$ M Bu_4NPF_6 with (a) no added MeCN and (b) MeCN present at 0.040 M (Mo) and 0.10 M (W). The working electrode was a 1.6-mm-diameter platinum disk for Mo and a 100-μm-diameter platinum disk for W. The scan rate was 1.0 V/s (Mo) and 10 V/s (W). All potentials are relative to $E_{1/2}$(ferrocene) = 0.34 V.

Scheme I

1: Mo-3$^+$, $(5.0 \pm 1.5) \times 10^7$ M^{-1} s^{-1}; W-3$^+$, $(1.0 \pm 0.3) \times 10^7$ M^{-1} s^{-1}. Furthermore, the use of a 50-μm radius microelectrode at -75 °C and 100 V/s enabled the rate constant with W-3$^+$ to be determined as approximately 10^5 M^{-1} s^{-1} at this temperature, from which $\Delta H^{\ddagger}$ is calculated as ca. 20 kJ.

It was found that Cr-3$^+$ does not react with MeCN when this ligand is added to the original CH_2Cl_2 solution. However, Mo-3$^+$ and W-3$^+$ react cleanly to form the 19-electron *addition*

complex $(C_6Et_6)M(CO)_3(MeCN)^+$, which oxidizes spontaneously to the 18-electron dication. Thus, there is an overall 2-electron oxidation at higher MeCN concentrations. Figure 2 shows relevant CV's; note the increase in oxidation current when MeCN is present. The cathodic wave seen on the reverse scan is due to the 18-electron dication. A complete simulation and IR-spectroelectrochemical analysis, supported by steady-state voltammetry[9,12] with 2- and 5-μm microelectrodes, produced the rate constants summarized in Scheme I.

Ligand addition reactions to yield Mo(II) and W(II) complexes are well-known,[13] and it seems that Mo-3$^+$ and W-3$^+$ prefer this route (followed by oxidation to M(II)) rather than ligand substitution, unless the former pathway is excluded for steric reasons. The reactions reported here allow, for the first time, a direct comparison of the rate of ligand substitution of 17-electron complexes for a complete triad: Mo > W $\gg$ Cr (5×10^5:10^5:1). While this order does have a "steric" component, we believe that the same order will always obtain since the less congested complexes **1$^+$** and **2$^+$** have[3] W $\gg$ Cr by ca. 10^4:1. In dissociative reactions of 18-electron chromium triad complexes, the "normal" reactivity order is Mo > Cr > W. Steric effects only serve to increase the rate for Cr compared to W.[14] The much greater rate of W compared to Cr for associative reactions of 17-electron centers is likely due to the greater size of W (and Mo). It is apparent that the reactivity of 17-electron complexes can be *very* dependent on the metal within a triad. Information of this sort should be relevant to the study of stoichiometric and catalytic processes that may have organometallic radicals as intermediates. It is also useful to note that the present study illustrates how electroactivation can be used to synthesize complexes that are difficult to obtain via thermal or photochemical routes (e.g., (arene)W(CO)$_2$PR$_3$).[15]

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