$Na(NaX)_n^+$ species, the nature of the products of reactions 3-6 will depend upon the breakdown curves for the given species.

In the CID spectra of the $[M+Na(NaX)_n]^+$ and $[M+xNa-(x-1)H]^+$ species for β-cyclodextrin (see Table III), fragment ions similar to those reported in Table I are observed; however, many more ionic product ions are observed in the CID spectra. The fact that numerous fragment ions are observed in the CID spectra is not surprising; i.e., the ions undergoing fragmentation in the CID experiment correspond to ions with a broad range of internal energies.[31] This contrasts with ions formed by low translational energy ion-molecule reactions (chemical ionization) where only specific product ions are observed. This interpretation is in qualitative agreement with studies reported by Allison.[40] For example, Allison observed specific, low-energy fragment ions when $K^+$ was allowed to react with a variety of organic molecules.

The general trend in the FTMS data can be explained quite readily by the mechanism given above for formation of the organoalkali metal ion clusters. For example, as the ion beam fluence is increased the "selvedge region"[39] density increases favoring formation of organoalkali metal ion species. Increases in the density of the "selvedge region" corresponds to increases in the thermal energy of the plasma, e.g., the internal energy of the alkali metal clusters. Reaction of the higher internal energy clusters with the organic sample produces a complex with sufficient internal energy to undergo fragmentation. The fact that the ionization of the organic molecule proceeds through an ion-molecule collision complex, i.e., ionization via a chemical ionization process, suggests that the fragment ions formed may differ from the fragment ions formed by gas-phase dissociation of $[M+H]^+$ and/or $[M+Na]^+$.

## Conclusions

The work reported here clearly illustrates the influence of the primary beam density on the DI mass spectrum. The results of these studies have important implications for DI-FTMS studies of large molecules. For example, at low primary beam densities the DI mass spectrum of β-cyclodextrin is dominated by the $[M+H]^+$ ion. At higher beam densities ions of the types $[M+Na]^+$ and $[M+xNa-(x-1)H]^+$ and fragment ions of the sodiated species dominate the high mass region of the spectrum. We interpret these results as evidence that DI with high beam densities occurs by a gas-phase (selvedge region) reaction between the neutral organic molecule and alkali metal halide ion clusters. Since the cluster emission ionization mechanism corresponds to a chemical reaction, it is feasible that fragmentation of $[M+Na]^+$ species may differ significantly from $[M+H]^+$ species. It may be feasible to utilize different DI conditions to obtain additional structural information on large molecules. That is, the fragmentation reactions of the organoalkali metal ions species may differ from the fragmentation reactions of the $[M+H]^+$ ion.[41] Based on the currently available data it is difficult to predict the fragmentation reactions for these species. Additional studies to establish the fragmentation reaction of the organoalkali metal ion species are underway.

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(41) A specific example of these differences is the CID spectrum of the $[M+H]^+$ and $[M+Na]^+$ ions formed by FAB ionization of hippuryl-histidyleucine. Of particular interest is the fact that the CID spectrum of the $[M+Na]^+$ ion contains more structurally significant fragment ions than the CID spectrum of the $[M+H]^+$ ion: Mallis, L. M.; Russell, D. H. *Anal. Chem.*, submitted for publication.

# Electrochemically Induced Changes in Hapticity in Mixed-Sandwich Compounds of Iridium and Rhodium†

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*Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05405.* *Received March 8, 1985*

**Abstract**: The electrochemical reductions of two sandwich complexes, $[(\eta^5\text{-}C_5Me_5)M(\eta^6\text{-}C_6Me_6)]^{2+}$ (M = Rh, Ir), are reported. The reduction of the rhodium complex occurs by two reversible one-electron transfers having $E°$ values separated by several hundred millivolts. The iridium complex reduces in a single two-electron step with cyclic voltammetric peak separations very dependent on electrode material. The neutral species of both metals have been isolated and the $^1H$ NMR spectra indicate the structure $[(\eta^5\text{-}C_5Me_5)M(\eta^4\text{-}C_6Me_6)]$. Thus these complexes undergo reversible $\eta^6 \rightleftharpoons \eta^4$ isomerization of the arene coordination with the transfer of two electrons. The relationship between the $E°$ values and the structure change is discussed, and a model is favored in which the slippage from $\eta^6$- to $\eta^4$-arene coordination occurs during the second electron transfer.

The structure and reactivity of $[\eta^6\text{-}C_6(CH_3)_6][\eta^4\text{-}C_6(CH_3)_6]Ru$ ($\mathbf{1}^0$) have been the subject of considerable interest. $\mathbf{1}^0$ was first prepared in 1970 by reduction of the 18-electron dicationic precursor $\mathbf{1}^{2+}$ with sodium in liquid ammonia.[1] X-ray crystallography confirmed[2] the remarkable fact, first suggested by NMR results,[1] that one of the arene rings in $\mathbf{1}^0$ is bent and donates only two pairs of electrons to the Ru, thereby retaining the formal 18-electron configuration of the metal. Whereas this was not the first $\eta^4$-

† Structural Consequences of Electron-Transfer Reactions. 11. Part 10: Geiger, W. E.; Rieger, P. H.; Tulyathan, B.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 7000.

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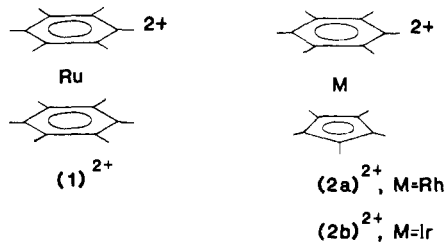


arene–metal complex prepared,[3,4] it did represent the first known system in which the arene could be either $\eta^4$ or $\eta^6$, depending on the oxidation state of the metal in the complex. This ability of the arene ring to change its coordination mode takes on special significance in light of proposals that $\eta^6 \rightarrow \eta^4$ bonding changes may be a key step in the catalytic hydrogenation of arenes.[5-7] Since addition of two electrons to a species like $\mathbf{1}^{2+}$ mimics the addition of dihydrogen, the factors controlling the redox-induced $\eta^6 \rightleftharpoons \eta^4$ isomerization may be of both fundamental and practical interest.

Finke et al.[8,9] recently showed that $\mathbf{1}^{2+}$ could be reduced to $\mathbf{1}^0$ electrochemically. This suggested that electrochemical methods might be valuable in preparing new (metal reduced) $\eta^4$ complexes from their (metal oxidized) $\eta^6$ precursors in the generalized Scheme I. $\eta^4$-Arene complexes of Rh(I) have been reported in which the arene is highly substituted with an electron-withdrawing group, as in $CpRh[\eta^4\text{-}C_6(CF_3)_6]$[3,4,10] (Cp = $\eta^5\text{-}C_5H_5$), $(\eta^5\text{-}C_5Me_5)Rh[\eta^4\text{-}C_6(CO_2Me)_6]$,[11] and $CpRh[\eta^4\text{-}C_6Ph_3(CO_2Me)_3]$,[12] but no $\eta^6$ Rh(III) complexes of these complexes have been reported. On the other hand, Rh(III) complexes of $\eta^6$-arenes with electron-releasing groups have been reported, but no $\eta^4$ Rh(I) versions of this class are known. Thus the Rh (and Ir) isoelectronic analogues of $\mathbf{1}^{2+}$, namely $[(\eta^5\text{-}C_5Me_5)M(\eta^6\text{-}C_6Me_6)]^{2+}$ ($\mathbf{2}^{2+}$; M = Rh, Ir), appeared to be a likely system in which to further demonstrate that electrochemical methods are highly effective in promoting interconversion of $\eta^6$- and $\eta^4$-arene complexes. We report the successful preparation of the neutral $\eta^4$ complexes $\mathbf{2}^0$ by either stepwise (M = Rh) or concerted (M = Ir) two-electron reduction of their dicationic precursors.

## Experimental Section

Complexes $\mathbf{2}^{2+}$ were synthesized by literature methods,[13] reacting the $\{[\eta^5\text{-}C_5(CH_3)_5]MCl_2\}_2$ dimer with silver(I) in acetone in the presence of hexamethylbenzene.

Tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) was prepared by metathesis of $Bu_4NI$ and $NH_4PF_6$ in acetone/water, recrystallized three times from 95% ethanol, and dried under vacuum at 100 °C for 24 h.

*N,N*-Dimethylformamide (DMF), acetone, dimethyl sulfoxide ($Me_2SO$), and acetonitrile ($CH_3CN$) (Burdick and Jackson) were dried over type 4A molecular sieves. Tetrahydrofuran (THF) (Aldrich Gold Label) was distilled from Na/benzophenone, and methylene chloride (Burdick and Jackson) was distilled from $CaH_2$ immediately before use. *o*-Xylene-$d_{10}$ and benzene-$d_6$ (Aldrich) were stirred over a potassium mirror and distilled under vacuum immediately before use.

Voltammetry was performed under nitrogen. A three-electrode cell was used with the saturated calomel reference electrode (SCE) segregated from the test solution by a fine frit. The platinum bead electrode was pretreated by placing it in the vapor of refluxing nitric acid (5 min) followed by immersion in saturated aqueous ferrous ammonium sulfate and rinsing with distilled water. Triply distilled mercury from Bethlehem Apparatus Co. was used for the hanging mercury drop electrode (HMDE) and dropping mercury electrode (DME). Bulk electrolyses were performed in a nitrogen-filled Vacuum Atmospheres Co. drybox. Electrochemical instrumentation was PARC equipment and ancillary devices were described previously.[14,15] Decamethylcobaltocene was prepared by the literature method.[16]

**Chemical Reduction of $\mathbf{2a}^{2+}$.** $[\eta^5\text{-}C_5(CH_3)_5]_2Co(PF_6)$ (135 mg) was reduced to decamethylcobaltocene on a potassium mirror in THF for 20 min. The solution was filtered and the THF was removed under vacuum. The residue was then mixed with 100 mg of $\mathbf{2a}^{2+}\cdot(PF_6)_2$ dissolved in approximately 25 mL of $CH_2Cl_2$. After reaction for 5 min at 0 °C, the $CH_2Cl_2$ was removed under vacuum. The residue was extracted with hexane, the hexane solution was filtered, and the hexane was removed under vacuum, leaving orange $\mathbf{2a}^0$.

**Chemical Reduction of $\mathbf{2b}^{2+}$.** Because of the milder reduction potential of the iridium complex, cobaltocene was used as a reducing agent. The only other difference from preparation of the rhodium complex $\mathbf{2a}^0$ is that the final hexane solution was cooled on dry ice to precipitate $\mathbf{2b}^0$ as yellow crystals.

**Scheme I**

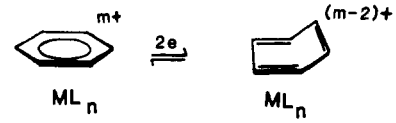


**Table I.** Dependence of $E°$ Potentials of $[C_5(CH_3)_5]Rh[\eta\text{-}C_6(CH_3)_6]^{2+/+/0}$ on Solvent[a]

| solvent | $-E_1°$, V | $-E_2°$, V | $E_2° - E_1°$ |
|---|---|---|---|
| dichloromethane | 0.50 | 0.87 | −0.37 |
| acetonitrile | 0.64 | 0.89 | −0.25 |
| acetone | 0.57 | 0.77 | −0.20 |
| *N,N*-dimethylformamide | 0.66 | 0.76 | −0.10 |
| dimethyl sulfoxide | 0.68 | 0.77 | −0.09 |

[a] Potentials given vs. SCE.

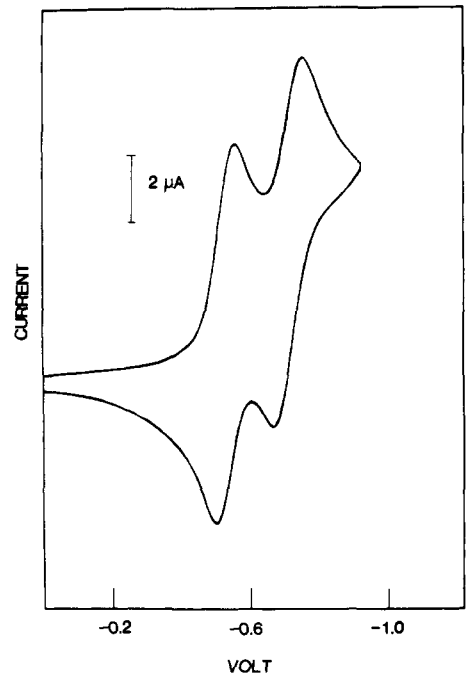


**Figure 1.** Cyclic voltammogram of $\{[\eta^5\text{-}C_5(CH_3)_5]Rh[\eta^6C_6(CH_3)_6]\}^{2+}$ ($\mathbf{2a}^{2+}$ 0.42 mM in acetone/0.1 M TBAHFP at a platinum bead electrode ($v$ = 0.1 V/s).

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(15) $v$ = scan rate (cyclic voltammetry), $i_p$ = peak current (cyclic voltammetry), $E$ = potential, $E_p$ = peak potential (cyclic voltammetry), $\Delta E_p$ = potential separation between anodic and cathodic peaks, $I$ = diffusion current constant ($\mu A\ s^{1/2}\ mg^{-2/3}\ mM^{-1}$), $i_a/i_c$ = ratio of peak anodic and cathodic currents (cyclic voltammetry), and $i_p/v^{1/2}$ = current function of cyclic voltammetry.
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**Table II.** Electron-Transfer Rates of $[C_5(CH_3)_5]Rh(\eta\text{-}C_6(CH_3)_6]^{2+/+/0}$ ($k_s$, cm·s$^{-1}$) at Three Electrodes in Aceonitrile

| electrode | $k_{s1}$, cm·s$^{-1}$ | $k_{s2}$, cm·s$^{-1}$ |
|---|---|---|
| platinum | 0.16 | 0.011 |
| mercury | 0.24 | 0.14 |
| gold | 0.11 | 0.032 |

**$^1$H Nuclear Magnetic Resonance.** NMR spectra were recorded on a Bruker WM-250 NMR spectrometer. Variable-temperature spectra of **2b**$^0$ were recorded in *o*-xylene-$d_{10}$ in a sealed NMR tube under vacuum. The NMR sample of **2a**$^0$ was prepared in a nitrogen-filled drybox in benzene-$d_6$.

## Results

**Rhodium Complex 2a$^{2+}$.** $[(C_5Me_5)Rh(C_6Me_6)]^{2+}$ is well-behaved at electrode surfaces. It gave electrochemistry that was independent of electrode material (Hg or Pt) and virtually independent of solvent (dichloromethane, acetone, acetonitrile, dimethylformamide, and dimethyl sulfoxide). Small effects of solvent on $E°$ values (Table I) and on reactivity will be commented on where appropriate.

The Rh(III) dication **2a**$^{2+}$ undergoes two chemically reversible reductions at mild potentials, $E_1° = -0.57$ V and $E_2° = -0.77$ V. These data and much of that subsequently discussed refer to acetone solutions, which are reasonably conductive (minimizing errors due to ohmic effects) and do not react rapidly with either the Rh(II) or Rh(I) reduction products. Cyclic voltammetry measurements (Figure 1) over a range of scan rates from 20 to 500 mV/s showed a constant value of $i_p/v^{1/2}$ for both waves, demonstrating them to be diffusion controlled. A peak separation ($\Delta E_p$) of 60 mV was measured for the first wave and 90–100 mV for the second wave at a scan rate of $v = 100$ mV/s. These data were obtained at a Pt bead electrode but the results on a hanging mercury drop electrode (HMDE) were similar. Over the indicated range of scan rates, the first cathodic wave showed no change in peak potential and the second wave shifted very little (ca. 15 mV more negative). For both waves the anodic-to-cathodic current ratios were unity. These data indicate that each reduction results in a product stable on the CV time scale (ca. 20 s in the slowest scans) and that reactions 1 and 2 govern the reductive behavior of the Rh(III) dication:

$$(C_5Me_5)Rh(C_6Me_6)^{2+} + e^- \rightleftharpoons (C_5Me_5)Rh(C_6Me_6)^+ \qquad E_1° = -0.57 \text{ V} \quad (1)$$

$$(C_5Me_5)Rh(C_6Me_6)^+ + e^- \rightleftharpoons (C_5Me_5)Rh(C_6Me_6)^0 \qquad E_2° = -0.77 \text{ V} \quad (2)$$

The data also indicate that the first electron transfer (reaction 1) is rapid (reversible) and that the second (reaction 2) is slower (quasi-reversible). We attach no structural significance to this difference in charge-transfer rates, a point to which we will come back in our Discussion. Electron-transfer rates ($k_s$) for **2a**$^{2+/+/0}$ are recorded in Table II.

These electrode reactions were also investigated by double-potential-step chronoamperometry, pulse polarography, and differential pulse polarography. In each case, the diagnostic criteria for diffusion-controlled one-electron reversible processes were obeyed. For example, chronoamperometry experiments in which the potential was stepped from −0.3 to −1.0 V (beyond the second wave) gave a constant (±3%) value of $it^{1/2}$ and reversing the pulse gave $i_{rev}/i_{for}$ values that were the same as for a reversible standard, ferrocene. The $it^{1/2}$ value for the forward wave was twice that of a one-electron standard, the cobaltocenium ion. Taken together, these measurements confirm that the two reductions are diffusion-controlled, chemically reversible, one-electron processes. The voltammetric conclusions appear to be on firm grounds.

A polarographic diffusion current constant of $I = 2.58$ μA mM$^{-1}$ mg$^{-2/3}$ s$^{1/2}$ was measured on the plateau of the first wave (4.86 μA mM$^{-1}$ mg$^{-2/3}$ s$^{1/2}$ for the plateau of the second wave). The diffusion coefficient of the Rh(III) dication was calculated from this value and the Ilkovic equation to be $1.33 \times 10^{-5}$ cm/s.

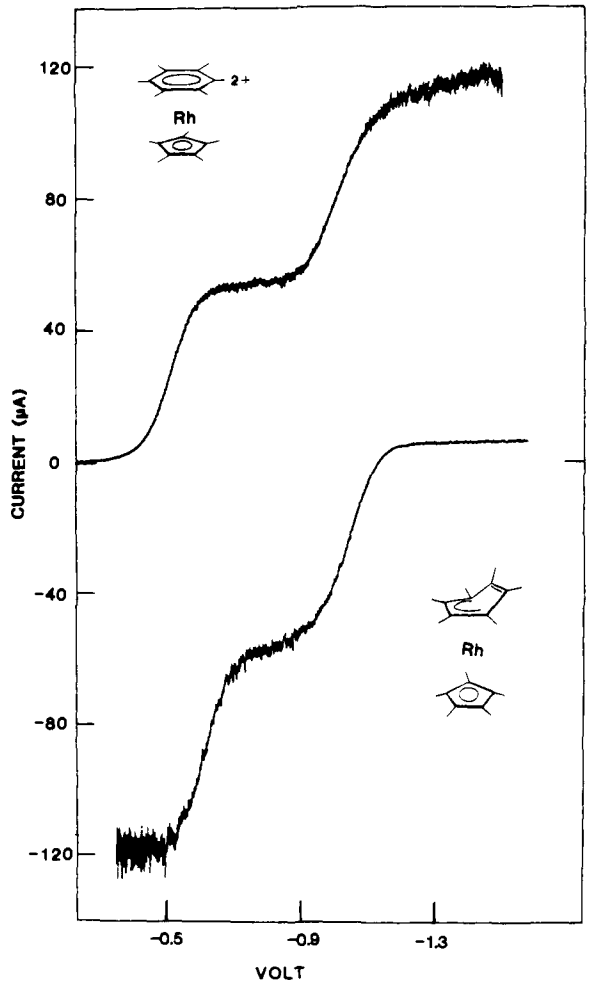



**Figure 2.** Voltammograms at a rotating platinum electrode in $CH_2Cl_2$/0.1 M TBAHFP: (top) initial, 1.5 mM **2a**$^{2+}$; (bottom) after electrolysis at −1.3 V to 95% depletion of electrolysis current at a platinum basket electrode to pass 1.93 *F*.

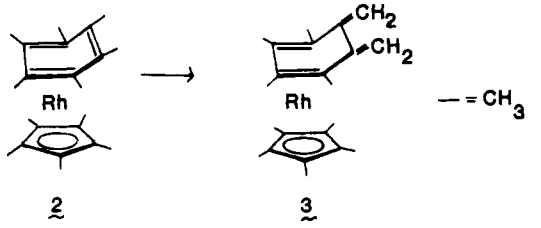
Bulk coulometry at a platinum basket electrode was performed in acetone with an applied potential of either −0.63 V (between the two $E°$ potentials) or −1.0 V (negative of the second $E°$). At 295 K, electrolysis at the first wave gave $n_{app} = 0.95$ e (two determinations) but indicated that the Rh(II) product was slightly unstable. At 273 K the Rh(II) monocation had a half-life of over 30 min. Electrolysis negative of the second wave at 235 K resulted in passivation of the platinum electrode before the Coulombic equivalent of one electron was passed. This electrode filming apparently arose from poor solubility of the Rh(I) neutral complex in acetone, leading us to do further experiments in dichloromethane.

**2a**$^{2+}$ exhibits no major changes in voltammetry between $CH_2Cl_2$ and acetone. The $E°$ potentials differ by an increased amount ($E_1° = 0.50$ V, $E_2° = -0.87$ V) and the second wave again exhibits a slightly larger $\Delta E_p$ than the first (65 mv for first wave and 105 mV for second when $v = 30$ mV/s. The half-life of the deep blue Rh(II) monocation produced coulometrically at −0.65 V was 13 min at 295 K, but the orange neutral Rh(I) complex [$\eta_{app} = 1.93$ e from electrolysis of **2a**$^{2+}$ at −1.3 V] was even longer lived ($t_{1/2} > 2$ h). The voltammetry of neutral $(C_5Me_5)Rh(C_6Me_6)$ was the complement of that of the beginning dication. That is, two oxidation waves were observed in place of the two reduction waves of **2a**$^{2+}$. Consistent with the observed quasi-reversibility of the second reduction wave of **2a**$^{2+}$ at platinum, the $E_{1/2}$ potential of the Rh(II)/Rh(I) wave (the first oxidation wave of the neutral complex) was shifted slightly positive of the same couple before coulometric reduction (Figure 2). CV scans showed a similar trend, with the peak positions of the Rh(III)/Rh(II) and Rh(II)/Rh(I) couples being close to the values before electrolysis.

The bulk electrolysis data are consistent with quantitative conversion of the Rh(III) dication to the corresponding Rh(I) complex in a chemically reversible process.

The neutral complex $(C_5Me_5)Rh(C_6Me_6)$ was isolated by evaporation of dichloromethane from the coulometrically reduced solution, extraction of the residue with hexane, filtration, and evaporation. The remaining orange solid gave an NMR spectrum in $C_6D_6$ with singlets at $\delta$ 1.64 (15 H, cyclopentadienyl methyl), 2.05 (6 H), 1.41 (6 H), and 1.27 (6 H). The last three resonances are typical of those observed for $\eta^4$-arene methyl groups.[1,17] Hence the twice-reduced neutral complex is assigned the $\eta^4$ structure $\mathbf{2a}^0$ (M = Rh). As a final check on the integrity of the isolation procedure, we observed that the electrochemical behavior of the orange solid used for the NMR experiment was identical with that of the reduced electrolysis solution prior to evaporation of the solvent.

The neutral Rh(I) complex was also prepared through reduction of $\mathbf{2a}^{2+}$ by 2 equiv of $(\eta^5\text{-}C_5Me_5)_2Co$ in $CH_2Cl_2$, going through a similar procedure of extraction with hexane and evaporation of the hexane to yield orange $\mathbf{2a}^0$, which gave the identical NMR spectrum. Over the course of several days in a capped but not sealed NMR tube in $C_6D_6$, the $^1H$ spectrum of $\mathbf{2a}^0$ was replaced by one in which there are two resonances in the methylene region [$\delta$ 5.15 (s, 2 H), 4.61, (s, 2 H)] and two in the methyl region [$\delta$ 1.66 (s, 6 H), 1.44 (s, 6 H)] in addition to the cyclopentadienyl methyl resonance at $\delta$ 1.64 (s, 15 H). This provides strong evidence that $\mathbf{2a}^0$ has converted to the *o*-xylylene complex **3** upon standing.[18] The most likely reason for formation of **3** is from




2 3

reaction of $\mathbf{2a}^0$ with oxygen that leaked into the NMR tube, since it has been shown that the closely related molecule bis(hexamethylbenzene)iron reacts with $O_2$ via H-atom abstraction to form the corresponding $(\eta^6\text{-arene})Fe[\eta^4\text{-}C_6Me_4(CH_2)_2]$ complex.[19] In tentative support of this hypothesis, introduction of $O_2$ into an electrochemical cell containing $\mathbf{2a}^0$ and **3** results in the disappearance of the CV waves of $\mathbf{2a}^0$ and an increase of the oxidation wave assigned to **3** (at ca. 0 V). Oxygen appears to react even more rapidly with the Rh(II) monocation generated in the first reduction of $\mathbf{2a}^{2+}$, since CV scans of $\mathbf{2a}^{2+}$ showed a single chemically irreversible reduction in the presence of deliberately admitted air, even at 220 K.

**Iridium Complex.** $[(C_5Me_5)Ir(C_6Me_6)]^{2+}$ ($\mathbf{2b}^{2+}$), in contrast to its rhodium congener, exhibits complex electrode behavior. Large variations in CV shapes and $\Delta E_p$ values are found at different electrodes in different solvents. We have obtained an array of data which will be the subject of a separate paper, but for present purposes we note that although large variations in heterogeneous charge-transfer rates were observed, the reduction of $\mathbf{2b}^{2+}$ is a *chemically reversible* overall *two-electron* process in all solvents and at all electrodes studied. Reaction 3 therefore

$$(C_5Me_5)Ir(C_6Me_6)^{2+} + 2e^- \rightleftharpoons (C_5Me_5)Ir(C_6Me_6)^0 \quad (3)$$

describes the overall electrode process, which is undoubtedly composed of two one-electron transfers in which $E_2°$ (for the Ir(II)/Ir(I) couple) is positive of $E_1°$. Some data from CV experiments are offered in support of this statement.

The charge transfer is very rapid on a mercury electrode. In $CH_2Cl_2$ a peak separation of 33 mV is observed at a HMDE ($E°$ = −0.60 V, $v$ = 0.050 V/s). The electrode process is diffusion

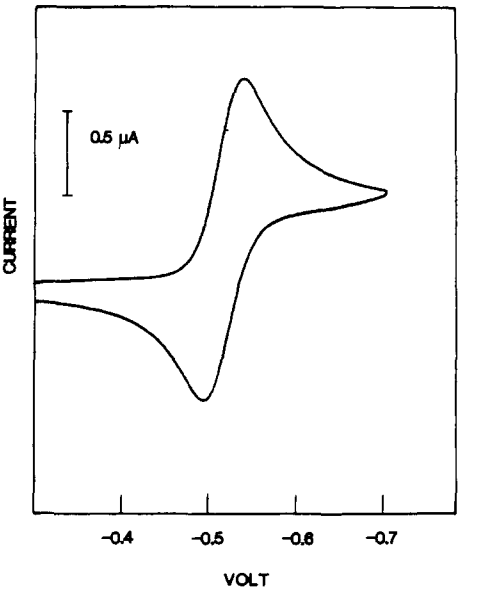



**Figure 3.** Cyclic voltammogram of $\{[\eta^5\text{-}C_5(CH_3)_5]Ir[\eta^6\text{-}C_6(CH_3)_6]\}^{2+}$ ($\mathbf{2b}^{2+}$) 0.10 mM in $CH_2Cl_2$/0.1 M TBAHFP at a hanging mercury drop electrode ($v$ = 0.1 V/s).

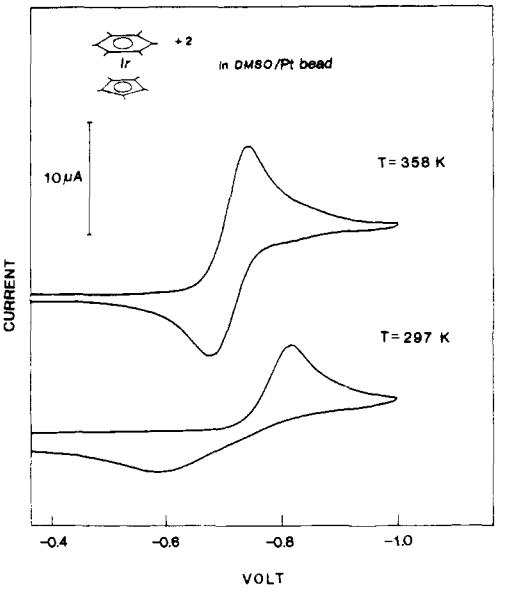



**Figure 4.** Cyclic voltammogram of $\{[\eta^5\text{-}C_5(CH_3)_5]Ir[\eta^6\text{-}C_6(CH_3)_6]\}^{2+}$ ($\mathbf{2b}^{2+}$) 0.38 mM in $Me_2SO$/0.1 M TBAHFP at a platinum bead electrode ($v$ = 0.13 V/s, temperature 358 (top) and 297 K (bottom)).

controlled (constant value of $i_p/v^{1/2}$) and chemically reversible ($i_a/i_c$ = 1.0). At $v$ = 20 mV/s in $CH_3CN$, the peak separation was 30 mV (Figure 3). These data are consistent with a process in which two electrons are transferred in sequence (an EE mechanism), with the second $E°$ being positive of the first, so that the Ir(II) monocation $[(C_5Me_5)Ir(C_6Me_6)]^+$ is only a thermodynamically unstable intermediate between the Ir(III) and Ir(I) complexes. If $E_2°$ were equal to or negative of $E_1°$, a minimum peak separation of 42 mV would have been observed.[20] In this light, it was important to establish that adsorption of the electrode product or reactant is not responsible for narrowing the peak separation. This was ensured through double-potential-step chronocoulometry, which showed with certainty that no specific adsorption of either the Ir(III) dication or the neutral Ir(I) complex was present on the mercury electrode. Direct-current polarography in acetonitrile gave a diffusion-controlled wave of two-electron height ($I$ = 5.54 μA $mM^{-1}$ $mg^{-2/3}$ $s^{1/2}$) with a slope of 30 mV in

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the plot of $-E$ vs. log $[i/(i_d - i)]$. On mercury electrodes, the reduction is reversible in both the chemical and electrochemical sense. The chemical reversibility of the Ir(III)/Ir(I) couple was confirmed by double-potential-step chronoamperometry at a HMDE and at a platinum disk electrode.

Cyclic voltammetry of $\mathbf{2b}^{2+}$ at solid electrodes gave decidedly non-Nernstian behavior. Typical are the scans shown in Figure 4, bottom, taken in dimethyl sulfoxide ($Me_2SO$) at a platinum electrode. $\Delta E_p$ values of several hundred millivolts are found, increasing with increasing scan rate, and a very broad anodic return wave is observed. Again, reverse pulse chronoamperometry shows that this electrode process is simply the chemically reversible couple of reaction 3, now exhibiting slow charge-transfer kinetics. As a test of this hypothesis, the $\Delta E_p$ was measured *above* ambient temperatures. Our reasoning was that if the electrode process involves slow charge transfer between stable Ir(III) and Ir(I) electrode reactant and product, respectively, then higher temperatures would increase the charge-transfer rate and decrease the $\Delta E_p$ value. Consistent with this, the couple became increasingly electrochemically reversible at higher temperatures (Figure 4, top), the $\Delta E_p$ value falling to 56 mV at 388 K, $v$ = 130 mV/s. The value of $RT/F$ at this temperature predicts a $\Delta E_p$ of 37 mV for a Nernstian two-electron process. The symmetric shape of the voltammogram also argues for a reversible electrode process, again demonstrating that reaction 3 describes the electrode behavior of the Ir(III) dication at different electrode surfaces and solvents.

One remarkable observation coming out of the $Me_2SO$ experiments is that even at 388 K the ratio $i_a/i_c$ was unity, meaning that on the CV scale (ca. 10 s) the neutral Ir(I) complex did not exhibit any decomposition. Given the elevated temperatures and strong ligating solvent of the matrix, the neutral Ir(I) complex appeared to be a very stable species. Not surprisingly, therefore, it was easily isolated by chemical reduction of $\mathbf{2b}^{2+}$. Since the $E°$ of the Ir(III)/Ir(I) reduction is −0.60 V, cobaltocene ($Cp_2Co$) is a sufficiently strong reductant to reduce the Ir dication to the neutral complex. Reduction in $CH_2Cl_2$, using 2 mol of $Cp_2Co$ per mol of Ir(III) complex, followed by evaporation and extraction with hexane gave yellow $(C_5Me_5)Ir(\eta^4\text{-}C_6Me_6)$. The $\eta^4$-arene configuration is assigned on the basis of the NMR spectrum, which shows three types of methyl arene resonances, $\delta$ 2.19 (s, 6 H), 1.74 (s, 6 H), and 1.66 (s, 6 H), as well as the cyclopentadienyl methyl resonance at $\delta$ 1.91 (s, 15 H), closely analogous to the spectra of $(C_6Me_6)Ru(\eta^4\text{-}C_6Me_6)$[1] and $(C_5Me_5)Rh(\eta^4\text{-}C_6Me_6)$. The spectrum was unchanged at 390 K in *o*-xylene.

The electrochemical behavior of the isolated Ir(I) complex was identical with that of the Ir(I) complex produced by bulk coulometry. Reduction of 8 mg of $\mathbf{2b}^{2+}$ at a platinum electrode ($E_{app}$ = −1.0 V) was done in 10:1 $CH_2Cl_2/CH_3CN$ (the $CH_3CN$ was added to solubilize the reactant dication). A voltammogram at the rotating platinum electrode (RPE) before electrolysis gave $E_{1/2}$ = −0.65 V and a slope of $-E$ vs. log $[i/(i_d - i)]$ of 42 mV. After passage of 1.84 e per mol of Ir(III) dication, an anodic RPE wave with $E_{1/2}$ = −0.50 V and slope = 136 mV was observed, the shift in $E_{1/2}$ and slope being consistent with the quasi-reversible charge-transfer reaction and separation of $E°$'s. The half-life of the Ir(I) complex in the $CH_3CN/CH_2Cl_2$ mixture was 2.2 h. No decomposition of a chemically prepared sample of $\mathbf{2b}^0$ is noted after more than 1 h in pure $CH_2Cl_2$.

## Discussion

The $\eta^4$-coordination of arenes to transition metals results in an important class of complexes; $\eta^4$-arene intermediates have been proposed in arene exchange reactions,[21,24] ligand substitution,[25] catalytic cycles,[5-7,17,23,26] and isomerizations.[27] However, there are few characterized $\eta^4$-arene complexes relative to the number of proposed $\eta^4$-arene intermediates. $(C_5Me_5)M(\eta^4\text{-}C_6Me_6)$ (M = Rh, Ir) and their $\eta^6$-arene dicatonic precursors are only the second class of metal compounds in which an arene can be either $\eta^6$- or $\eta^4$-bonded, depending on the formal oxidation state of the metal. Taken together with the earlier work on bis(arene)ruthenium complexes,[1,8,9] these results indicate that redox chemistry may provide a systematic approach to investigate the tendency of metals to form $\eta^4$-arene complexes. While empirical observation of the varieties of $\eta^4$-arene complexes synthesized may suggest certain trends, the $E°$'s of reductions from $\eta^6$- to $\eta^4$-arene complexes are a systematic measure of thermodynamic stabilities (vide infra).

Since there are two electrons transferred in reactions 1 and 2 involving the conversion from a $d^6$ metal with an $\eta^6$-arene to a $d^8$ metal with an $\eta^4$-arene, the question arises as to whether the structural change occurs after the first electron transfer (i.e., in the $d^7$ intermediate) or after the second. Direct evidence on this question is lacking, since neither $[(C_5Me_5)M(\eta\text{-}C_6Me_6)]^+$ (M = Rh, Ir) nor $[(\eta^6\text{-}C_6Me_5)Ru(\eta\text{-}C_6Me_6)]^+$ has been isolated. The related $d^7$, 19e, system $(C_5Me_5)Fe(\eta^6\text{-}C_6Me_6)$ has been structurally characterized and shown to have a planar arene ring,[28,29] symmetrically bonded to the iron atom. On the other hand, ESR spectra of the recently studied isoelectronic system $[(\eta\text{-}C_6H_6)_2Cr]^-$ suggest a distortion of one arene based on the observation of three sets of proton hyperfine splittings for one ring[30] (although the nature of the arene distortion cannot be specified from the ESR data alone). However, neither the iron nor the chromium complex structures are directly pertinent to the structure of the $d^7$ Rh, Ir, or Ru complexes because the first-row transition metals do not show the tendency toward formation of $\eta^4$-arene complexes exhibited by second- and third-row metals (vide infra).

Although no direct structural evidence is available, the $E°$ values suggest that the structure change from $\eta^6$ to $\eta^4$ occurs with the second electron transfer. If one assumes that formation of the $\eta^4$-arene results in thermodynamic stabilization of the complex, a reduction will be facilitated by a concomitant structure change, and the $E°$ will shift positive. If the $\eta^4$ stabilization occurs in the first electron transfer ($d^6 \rightarrow d^7$), the $E_1°$ will be shifted positive and $E_1° - E_2°$[31] will be larger than it would be if no distortion occurs in any oxidation state. However, if the $\eta^4$ stabilization occurs in the second electron transfer, $E_2°$ will shift positive and $E_1° - E_2°$ will decrease.

The $E°$ values of $\mathbf{2}^{2+}$ may be compared with $E°$ values of two analogous systems in which no $\eta^4$ distortion takes place. One is $(C_5Me_5)Co(\eta\text{-}C_6Me_6)^{2+/+/0}$ (**4**), in which all three oxidation states apparently retain the $\eta^4$ planar arene.[32,33] The second is the metallocenes of the cobalt group, since these closely analogous compounds are believed to retain the symmetrical sandwich through the $d^6$, $d^7$, and $d^8$ electron configuration.[34]

The separation of $E°$ values is −1.0 V for the cobalt-mixed-sandwich complex **4**,[32] ca. −0.3 V for our Rh complex **2a**, and >0 V for the Ir complex **2b**. A similar positive shift of $E_2°$ relative to $E_1°$ is also observed for the Fe and Ru complexes $(\eta\text{-}C_6Me_6)_2M^{2+/+/0}$, in which $\Delta E°$ = −1.0 V for Fe and ca. −0.2 V for Ru.[8,35] However, this decrease of the $E°$ separation in going

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from first-row to second- and third-row complexes cannot be interpreted as being due simply to $\eta^4$ distortional stabilization of the $d^8$ complex, since that interpretation would ignore differences in metal ionization potentials.

Comparison of the redox potentials of our mixed-sandwich complexes with those of the metallocenes suggests that the decreasing $\Delta E°$ of $\mathbf{2}^{2+/+/0}$ on descending the table is not merely due to decreasing stability of the $d^7$ configuration. Both the $d^6 \rightarrow d^7$ and $d^7 \rightarrow d^8$ couples $Cp_2Rh^{+/0}$ and $Cp_2Rh^{0/-}$, respectively, are more negative than those of the Co congener, by ca. 0.5 and 0.25 V, respectively.[36,37] The $\Delta E°$ values are −1.0 V for Co and −0.75 V for Rh. This is in contrast to our mixed-sandwich compounds, in which the $d^6 \rightarrow d^7$ couple for Rh is *negative* of that of the Co congener, but the $d^7 \rightarrow d^8$ Rh wave is *positive* of the Co wave. Comparing mixed-sandwich $\Delta E°$ values (−1.0 V for Co and −0.3 V for Rh) with those of the metallocene analogues, we reason that the $\eta^4$ distortion of the arene stabilizes the $d^8$ complex by about 0.4 V, or about 9 kcal/mol.

This analysis should be viewed with caution, since it is based on a limited number of comparative potentials. Electrochemical data on $\pi$ complexes of Rh are rare and of Ir virtually nonexistent. For example, no redox potentials are known even for $Cp_2Ir^+$.[38] We encourage efforts to study the redox properties of other heavy-metal polyolefin complexes.

The above thermodynamic analysis assumes that the kinetics of the arene distortion are fast compared to the time scale of the voltammetry experiments.[39] If the arene distortion occurs concomitant with the electron transfer, it would be expected that the activation barrier to electron transfer would include an inner-sphere reorganizational energy that would slow down the electron-transfer process and lead to a lower $k_s$ value.[20] These Marcus-like arguments have been traditionally used to rationalize slow electrode kinetics. The larger CV peak separation in $CH_2Cl_2$ of the $[(\eta\text{-}C_6Me_6)_2Ru]^{+/0}$ couple than that of $[(\eta\text{-}C_6Me_6)_2Ru]^{2+/+}$ was suggested to originate from a $\eta^4$ distortion in the $d^7 \rightarrow d^8$ process.[8] Even though we also observe larger peak separations for the second reduction wave of $[(C_5Me_5)Rh(C_6Me_6)]^{2+}$ on a Pt electrode, we caution against interpreting this as evidence for distortional retardation of the charge-transfer reaction. There is increasing realization that heterogeneous charge-transfer kinetics seldom give unambiguous information about inner-sphere contributions to the electron-transfer energy barrier.[40] Even processes once considered to be paradigmatic of the relationship between slow charge-transfer kinetics and redox-initiated structural changes, such as the reduction of the tub-shaped cyclooctatetraene to its planar anion radical, are now known to be complicated by double-layer effects and the type of electrode used.[41,42] Indeed, the second reduction of $\mathbf{2a}^{2+}$ is faster at mercury than at platinum. Some results of the $k_s$ values calculated for the Rh complex from CV data on Pt, Hg, and Au are given in Table II.

Variations in electron-transfer rates from one metal to another are to be expected and probably reflect differences in the surface condition of the metals.[42] It remains, however, that the second electron transfer is slower than the first on all three metals, and it cannot be ruled out that the arene distortion is playing a role in the slowing down of the second electron transfer. A study of the electron-transfer kinetics of a series of Rh, Ir, and Ru complexes is planned to test the generality of this observation.

It is relevant to discuss these redox processes in the language previously used to describe isomerizations occurring during multi-electron-transfer reactions. Reductions of bianthrone and lucigenin occur in two-electron processes in which significant folding of the two coupled ring systems is involved.[43,44] Reduction of the binuclear complex $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ involves a two-electron wave and a change from a structure having one tetrahedral and one square-planar Rh atom (neutral complex) to one having two tetrahedral Rh atoms (dianionic complex). In each of these cases the isomerization in one oxidation state was slow enough to allow direct voltammetric monitoring of both isomers. In the first two cases,[43,44] an EEC mechanism was assigned, in which the isomerization occurs after the second electron transfer

$$A + e^- \rightleftharpoons A^- \quad E$$

$$A^- + e^- \rightleftharpoons A^{2-} \quad E$$

$$A^{2-} \rightarrow B^{2-} \quad C$$

In the last case, the isomerization follows the first electron transfer, in an ECE process

$$A + e^- \rightleftharpoons A^- \quad E$$

$$A^- \rightarrow B^- \quad C$$

$$B^- + e^- \rightleftharpoons B^{2-} \quad E$$

The present metal–arene system differs from these previously studied systems in that it appears to be adequately treated as an EE process. Strictly speaking, this assumes that the $\eta^6 \rightarrow \eta^4$ slippage occurs concomitant with one of the electron-transfer reactions (most likely the second, as discussed above). If the arene slippage is to be viewed as separate from the second electron transfer (an EEC process), it must be still very rapid and reversible, probably having forward and backward rate constants in excess of $10^3$ $s^{-1}$. A lower value would be inconsistent with the observation of a nearly Nernstian second wave, unless the $\eta^6$- and $\eta^4$-neutral isomeric complexes had identical $E°$ values, and this is viewed as highly unlikely.

The kinetic stabilities of the three oxidation states of the Rh complex are interesting by comparison, in that reduction of the stable dicationic $d^6$ complex by one electron yields a monocation which is less stable ($t_{1/2}$ in $CH_2Cl_2$ of 13 min) than the twice-reduced, neutral complex ($t_{1/2} > 120$ min). Apparently, the $d^7$ monocation is subject to radical reactions and its reaction pathways are being investigated. The isoelectronic 19e iron complex $CpFe(\eta^6\text{-}C_6Me_6)$ undergoes hydrogen-atom abstraction from a methyl group to give the reactive exo-methylene complex **5**.[28,29,46] As noted above, the neutral complex $(C_5Me_5)Rh(\eta^4\text{-}C_6Me_6)$ slowly converted to the bis(exo-methylene) complex $(C_5Me_5)Rh[\eta^4\text{-}C_6Me_4(CH_2)_2]$ (**3**).

**Comparison with Other $\eta^4$-Arenes.** In spite of the analogy of $\mathbf{2}^0$ with $\mathbf{1}^0$, the new complexes represent a rather rare example of a $\eta^4$-arene with electron-pushing substituents on the arene. The great majority of isolated $\eta^4$-arene complexes contain strongly electron-withdrawing groups on the arene[3,4,10-12] (especially $CF_3$ or $CO_2Me$). Whether there is an electronic preference for $\eta^4$-coordination due to an electron-withdrawing effect or if this situation has arisen from the synthetic routes available to their preparation is a matter to be clarified. Along these lines, however, it can be noted that the arene ring is $\eta^4$ in $CpCo[C_6(CF_3)_6]$[10] but $\eta^6$ in $(C_5Me_5)Co(C_6Me_6)$.[33] The former is one of the few examples of $\eta^4$-arene coordination to a first-row transition metal.[3,4,10-12,23,33,48]

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If the $\eta^4$-arene represents a much lower energy, as suggested by $E°$ data, for $\mathbf{1}^0$ and $\mathbf{2}^0$, then it is interesting that $[C_6(CH_3)_6]_2Fe$,[35,48] $[C_5(CH_3)_5]Co[C_6(CH_3)_6]$,[32,33] and $[C_6(CH_3)_6]_2Co$[49] all retain the $\eta^6$-coordination of the arene and are 20e complexes. Apparently, the stabilization energy gained by Jahn–Teller distortion to the 18e $\eta^4$-arene complexes[47] is less than the destabilization resulting from loss of arene aromaticity in these cases. The $E°$ data, as well as the structurally characterized 20e $\eta^6$-arene complexes, suggest that in many cases $\eta^4$-arene complexes are not sufficiently likely as intermediates to warrant their being so frequently proposed, especially for first-row metal complexes lacking strongly electron-withdrawing groups.

## Conclusions

(1) The mixed-sandwich rhodium and iridium complexes **2a** and **2b** represent only the second class of complexes that undergo $\eta^6 \rightleftharpoons \eta^4$ change in arene coordination on change of the oxidation state of the metal.

(2) Electrochemical investigations of the electron-transfer reactions and the concomitant structural changes provide a good method for a systematic probe of the redox reaction.

(3) The separation of the $E°$ values of the reductions decreases and the tendency toward formation of $\eta^4$-arene complexes increases for $(C_5Me_5)M(C_6Me_6)^{2+}$ complexes on descending the periodic table.

(4) The electron-transfer kinetics of the complexes do not suggest in which step the structure change occurs, but the $E°$ data indicate that the structure change occurs predominantly between the cationic metal $d^7$ and neutral metal $d^8$ species. This is consistent with the earlier suggestion[8] that $[(C_6Me_6)_2Ru]^{n+}$ undergoes its $\eta^6$-arene $\rightarrow$ $\eta^4$-arene change when the complex is reduced from $n = 1$ to $n = 0$.

Investigation of a variety of $(Cp)M(arene)^{2+}$ is being pursued to study the effect of the arene substituents on the structure change.

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**Registry No.** $\mathbf{2a}^{2+}\cdot(PF_6)_2$, 12715-84-3; $\mathbf{2a}^{2+}$, 51539-75-4; $\mathbf{2a}^{+}$, 97732-09-7; $\mathbf{2a}^{0}$, 97732-08-6; $\mathbf{2b}^{2+}$, 51539-74-3; $\mathbf{2b}^{+}$, 97732-11-1; $\mathbf{2b}^{0}$, 97749-34-3; **3**, 97732-10-0; $[\eta^5\text{-}C_5(CH_3)_5]_2Co(PF_6)$, 79973-42-5; $[\eta^5\text{-}C_5(CH_3)_5]_2Co$, 74507-62-3; $(\eta^5\text{-}C_5H_5)_2Co$, 1277-43-6; Pt, 7440-06-4; Hg, 7439-97-6; Au, 7440-57-5; dichloromethane, 75-09-2; acetonitrile, 75-05-8; acetone, 67-64-1; *N*,*N*-dimethylformamide, 68-12-2; dimethyl sulfoxide, 67-68-5.

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# Reactions of Organic Halides with ($\pi$-Allyl)nickel Halide Complexes: A Mechanistic Study

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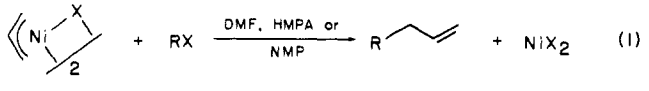
**Abstract:** The mechanism of allyl transfer reactions between ($\pi$-allyl)nickel halides and organic halides was studied. Extensive redistribution of ($\pi$-2-methallyl)nickel bromide (**1**) occurs in dimethylformamide (DMF), producing an equilibrium which involves nickel(II) bromide, bis($\pi$-methallyl)nickel, and a symmetrical ($\pi$-methallyl)nickel bromide species. The degree of allyl redistribution is a function of temperature and total nickel concentration—decreasing the temperature or addition of nickel(II) bromide to the solution suppressed the formation of bis($\pi$-methallyl)nickel. The position of this equilibrium affects the rate of cross-coupling reactions between **1** and organic halides since the rate of product formation increases when nickel(II) bromide is dissolved in the reaction mixture. Initiation of cross-coupling results when catalytic amounts of reducing agent are added to the reaction mixture or when it is exposed to a source of light. The presence of less than 1 mol % of *m*-dinitrobenzene inhibits the formation of cross-coupled material regardless of the type of organic halide used. The evidence indicates that the cross-coupling reaction proceeds by an electron transfer catalyzed mechanism. A mechanism utilizing common nickel(1+) intermediates in the reactions of alkyl, aryl, and vinyl halides and not involving free carbon-centered radicals has been proposed.

($\pi$-Allyl)nickel halide complexes[1] (**1**) undergo facile reaction with organic halides to substitute the allyl group for the halogen (eq 1).[2] This process has an unusual order of reactivity, with aryl and vinyl halides being substantially more reactive than alkyl halides, and with a substrate halide reactivity order of I > Br ≫ Cl, OTs. This coupling reaction requires the use of a polar,



(1)

coordinating solvent such as dimethylformamide (DMF), hexamethylphosphoramide (HMPA, $(Me_2N)_3PO$), or *N*-methylpyrrolidone (NMP). Since a wide variety of ($\pi$-allyl)nickel halide complexes can be readily prepared and since a wide range of organic halides are suitable substrates, this process has been used extensively in organic synthesis.[3] Recent examples include the synthesis of perillenal from furanyl halides,[4] myrcene, tagetol, and

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