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Redox-Induced Hapticity Changes: Effect of Substituents on Arene Bending in a Series of Rhodium Complexes[†]

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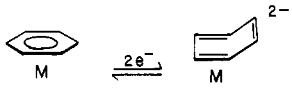
Electrochemical measurements have been performed on a series of rhodium arene complexes of the formula [(Me$_n$C$_6$H$_{6-n}$)RhCp*]$^{2+}$ (n = 0–6; Cp* = η^5-C$_5$Me$_5$). In general, two reduction waves are observed, corresponding to the Rh(III)/Rh(II) and Rh(II)/Rh(I) oxidation state changes. The Rh(I) complexes have been proposed to have a η^4-bonded arene, and this has been confirmed by X-ray crystallographic measurements on the hexamethylbenzene complex **6**. (η^4-C$_6$Me$_6$)RhCp* crystallizes in the space group *Pnma* with a = 16.724 (4) Å, b = 15.149 (4) Å, c = 7.963 (2) Å, V = 2017.5 (9) Å^{-3}, and Z = 4. The arene hinge angle is 41.8°. For nine of the complexes studied, both the Rh(II) monocation and the neutral Rh(I) complex have been detected. In all cases, the lifetimes of the Rh(II) complexes were less than the corresponding Rh(III) or Rh(I) complexes. Half-lives of the Rh(II) monocations steadily increased as the number of methyl groups on the arene increased, from about 5 ms for [(C$_6$H$_6$)RhCp*]$^+$ to >1800 s for [(C$_6$Me$_6$)RhCp*]$^+$. The standard reduction potential for the Rh(III)/Rh(II) couple decreased by about 28 mV for each Me group on the arene ring, and an analysis of previous literature data shows that this is the expected substituent effect when substituting Me for H in an arene complex. $E°$ values for the Rh(II)/Rh(I) couples are, however, virtually independent of the degree of arene methylation. The implication of this observation is that the arene hapticity change is thermodynamically favored with an increasing degree of arene methylation. The "natural" lowering of the potential due to the inductive effects of added Me groups is thus counterbalanced by a raising of the potential due to increased stabilization of the η^4 structure. The amount of stabilization of the η^4 structure is about 33 mV/Me group or about 0.7 (kcal/mol)/Me. The favoring of the η^4 structure with a higher degree of arene substitution may be due to decreased loss of resonance energies in the bending of the more highly substituted arene complexes.

Introduction

Hapticity changes due to ring slippage are important in many reactions of cyclic polyolefin metal complexes. Ring-slippage effects of the cyclopentadienyl ligand have been widely documented and have been widely documented and have been the subject of recent reviews.[1-3] Several η^3-cyclopentadienyl[4,5] or -indenyl[6-10] complexes have now been structurally characterized. Metal arene complexes[11,12] display analogous behavior, in that there may be either η^6 [13] or η^4 [14-28] bonding of the six-membered ring to the metal. The η^4, or "bent", arene complexes for which X-ray structures are available[21-28] may all be rationalized on the basis that the partial decoordination of the arene allows the metal to attain the 18-electron configuration.

Analogous to observations of enhanced reactivity of Cp complexes brought about by the η^5- to η^3-ring slippage of the five-membered ring,[29] slippage or bending of the six-membered ring has been proposed to be an important step in the substitution chemistry of metal arene complexes. The η^6- to η^4-ring slippage is thought to allow formation of a relatively low-energy intermediate or transition state in arene-exchange reactions and in the hydrogenation of arenes using soluble metal catalysts.[12,30-37]

Little quantitative information exists on the degree to which the η^4-arene configuration may stabilize an otherwise hypervalent metal complex.[12,31] In part, this is due to a lack of systematic routes to stable η^4 complexes, which are usually prepared by the thermal reaction of metal complexes with acetylenes. A more promising synthetic approach might be the two-electron reduction of η^6 complexes to the corresponding η^4 complexes



[†] Part 18 of the series "Structural Consequences of Electron-Transfer Reactions". Part 17: Brammer, L.; Connelly, N. G.; Edwin, J.; Geiger, W. E.; Orpen, A. G.; Sheridan, J. B. *Organometallics* 1988, *7*, 1259.

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Table I. Formal Reduction Potentials of (Arene)rhodium Complexes in Acetone[a]

complex		$E°_1$ (V)	$E°_2$ (V)	$E°_2 - E°_1$ (mV)
$[(C_6H_6)RhCp^*][PF_6]_2$	$\mathbf{0}^{2+}$	−0.42		
$[(MeC_6H_5)RhCp^*][PF_6]_2$	$\mathbf{1}^{2+}$	−0.45		
$[(1,4\text{-}Me_2C_6H_4)RhCp^*][PF_6]_2$	$\mathbf{2}^{2+}$	−0.46	−0.79	330
$[(1,2,3\text{-}Me_3C_6H_3)RhCp^*][PF_6]_2$	$\mathbf{3a}^{2+}$	−0.48	−0.77	290
$[(1,3,5\text{-}Me_3C_6H_3)RhCp^*][PF_6]_2$	$\mathbf{3b}^{2+}$	−0.50	−0.79	290
$[(1,2,3,4\text{-}Me_4C_6H_2)RhCp^*][PF_6]_2$	$\mathbf{4a}^{2+}$	−0.53	−0.80	270
$[(1,2,4,5\text{-}Me_4C_6H_2)RhCp^*][PF_6]_2$	$\mathbf{4b}^{2+}$	−0.52	−0.78	260
$[(Me_5C_6H)RhCp^*][PF_6]_2$	$\mathbf{5}^{2+}$	−0.55	−0.78	230
$[(Me_6C_6)RhCp^*][PF_6]_2$	$\mathbf{6}^{2+}$	−0.57	−0.77	200
$[(Me_6C_6)RhCp][PF_6]_2$	$\mathbf{7}^{2+}$	−0.35[b]	−0.63[b]	280[b]
$[(2,4,6\text{-}Me_3Aniline)RhCp^*][PF_6]_2$	$\mathbf{8}^{2+}$	−0.70	−0.99	290

[a] Potentials reported vs SCE; T = 298 K unless otherwise noted; supporting electrolyte was 0.1 M $[Bu_4N][PF_6]$. [b] Solvent = acetonitrile; T = 261 K.

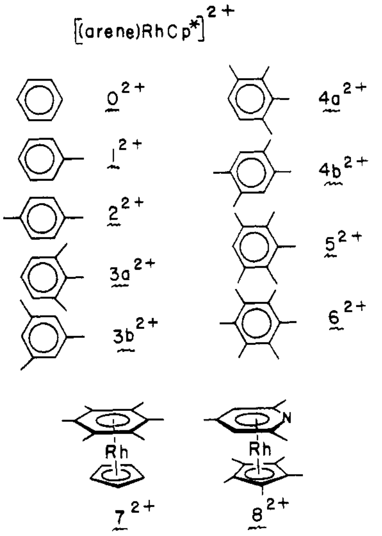
Table II. Half-Lives at 298 K of 19-Electron Rhodium(II) Monocations in Acetone/0.1 M $[Bu_4N][PF_6]$

complex		$t_{1/2}$ (s)
$[(C_6H_6)RhCp^*]^+$	$\mathbf{0}^+$	0.005[a]
$[(MeC_6H_5)RhCp^*]^+$	$\mathbf{1}^+$	0.01[a]
$[(1,4\text{-}Me_2C_6H_4)RhCp^*]^+$	$\mathbf{2}^+$	0.05[a]
$[(1,2,3\text{-}Me_3C_6H_3)RhCp^*]^+$	$\mathbf{3a}^+$	0.46[a]
$[(1,3,5\text{-}Me_3C_6H_3)RhCp^*]^+$	$\mathbf{3b}^+$	1.0[a]
$[(1,2,3,4\text{-}Me_4C_6H_2)RhCp^*]^+$	$\mathbf{4a}^+$	1.3[a]
$[(1,2,4,5\text{-}Me_4C_6H_2)RhCp^*]^+$	$\mathbf{4b}^+$	10[a]
$[(Me_5C_6H)RhCp^*]^+$	$\mathbf{5}^+$	$100 < t_{1/2} < 1000$[b]
$[(Me_6C_6)RhCp^*]^+$	$\mathbf{6}^+$	>1800[b]

[a] Measured by cyclic voltammetry using the method of Nicholson (*Anal. Chem.* **1965**, *37*, 1351) assuming a first-order decomposition reaction. [b] Semiquanitative values based on observations after bulk coulometric generation of the monocations from the corresponding Rh(III) dications.

since systematic preparations of the former are often available. This approach was first used to prepare $[(\eta^4\text{-arene})Ru(\eta^6\text{-arene})]$ from $[(\eta^6\text{-arene})Ru(\eta^6\text{-arene})]^{2+}$.[15,38,39] Similar strategy applied to $[(\eta^6\text{-}C_6Me_6)MCp^*]^{2+}$ (M = Co[40] or Rh[41]) showed that the Co and Rh compounds are reduced in two separate one-electron steps to the monocationic and neutral complexes but that only the rhodium species has a bent arene in the fully reduced complex.[41]

Since a series of complexes, $[(\eta^6\text{-arene})RhCp^*]^{2+}$, with different arenes, can be easily prepared,[42] we thought it would be useful to investigate the reduction of a series of such compounds. We sought to determine the effect of arene methyl substitution on the thermodynamic and kinetic stabilities of the 19-electron cations $[(\eta^6\text{-arene})RhCp^*]^+$ and the η^4 neutral complexes $(\eta^4\text{-arene})RhCp^*$. This paper reports electrochemical measurements on a series of nine (arene)rhodium complexes which differ in the number and/or position of methyl groups on the arene. They are labeled in the text according to the number of arene Me substituents and the charge on the complex. For example, $\mathbf{5}^{2+}$ represents $[(Me_5C_6H)RhCp^*]^{2+}$. Two related complexes, $\mathbf{7}^{2+}$ and $\mathbf{8}^{2+}$, are also included.



Arene methylation is shown to result in a thermodynamic destabilization but kinetic stabilization of the 19-electron Rh(II) monocation, which presumably retains the planar arene (vide infra). Of perhaps greater significance is that both the thermodynamic *and* kinetic stabilities of the η^4 neutral complexes increase with increasing arene methylation. The degree of thermodynamic stabilization is consistent with lower resonance energies for more highly methylated arene rings.

Experimental Section

All operations were conducted under a nitrogen atmosphere by using standard Schlenk or drybox techniques. The Rh(III) dications may be handled in the air. Samples that had been stored in the air were recrystallized and vacuum-dried before electrochemical experiments in order to minimize contamination of the solutions with moisture.

Chemicals. All of the Cp* dicationic complexes (Cp* = $\eta^5\text{-}C_5Me_5$) were prepared by the method of White et al.,[42] which involves the reaction of $[Cp^*RhCl_2]_2$ with $AgPF_6$ in acetone in the presence of the desired arene. They were recrystallized

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Table III. Crystal Data for (η^4-C_6Me_6)RhCp* (6)

formula	$C_{22}H_{33}Rh$
MW	400.41
cryst system	orthorhombic
space group	*Pnma*
Z	4
a, Å	16.724 (4)
b, Å	15.149 (4)
c, Å	7.963 (2)
V, Å^{-3}	2017.5 (9)
cryst dimens, mm	0.12 × 0.26 × 0.36
color	brown-red
T, K	296
D(calcd), g cm^{-3}	1.32
μ (cm^{-1})	8.16
λ (Å)	0.710 73 Mo Kα
scan type	θ–2θ
scan limit	4–50°
octants collected	h, 0–19; k, 0–18; l, 0–9
reflctns collected	1960
independent reflns	1861
obsd, $F_o \geq 5\sigma(F_o)$	1499
least-squares parameters	177
$R(F)$	0.0341
$R(\mathrm{w}F)$	0.0365
GOF	1.046
g^a	0.001
Δ/σ	0.004
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å^{-3})	0.488/−0.529

[a] $w^{-1} = \sigma^2(F_o) + gF_o^2$.

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	U^a
Rh	6126.2 (2)	2500	3864.7 (5)	33.8 (1)
C(1)	6074 (2)	2033 (3)	6331 (4)	45 (1)
C(2)	6764 (3)	1647 (3)	5544 (5)	50 (1)
C(3)	7553 (2)	2065 (3)	5921 (5)	57 (1)
C(4)	5388 (2)	1507 (4)	7072 (7)	80 (2)
C(5)	6758 (3)	662 (3)	5224 (5)	82 (2)
C(6)	8253 (2)	1493 (4)	6405 (4)	106 (3)
C(7)	5012 (3)	2500	2174 (7)	54 (2)
C(8)	5487 (3)	3245 (3)	1861 (5)	52 (1)
C(9)	6248 (2)	2966 (3)	1237 (5)	52 (1)
C(10)	4169 (4)	2500	2842 (9)	92 (3)
C(11)	5210 (5)	4188 (4)	1952 (9)	93 (3)
C(12)	6906 (5)	3548 (6)	583 (9)	94 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Selected Bond Distances and Angles for 6

(a) Bond Distances (Å)			
Rh–C(1)	2.089 (4)	C(2)–C(3)	1.494 (6)
Rh–C(2)	2.144 (4)	C(1)–C(1a)	1.416 (9)
Rh–C(7)	2.298 (6)	C(3)–C(3a)	1.316 (10)
Rh–C(8)	2.228 (4)	C(7)–C(8)	1.402 (5)
Rh–C(9)	2.217 (4)	C(8)–C(9)	1.430 (6)
C(1)–C(2)	1.437 (6)	C(9)–C(9a)	1.411 (10)

(b) Bond Angles (deg)			
C(1a)–C(1)–C(2)	114.0 (2)	C(7)–C(8)–C(9)	109.1 (4)
C(1)–C(2)–C(3)	116.7 (3)	C(8)–C(9)–C(9a)	107.2 (2)
C(2)–C(3)–C(3a)	115.1 (2)	C(8)–C(7)–C(8a)	107.3 (5)

(usually from acetone/dichloromethane) and checked for purity by NMR. The complex [(η^6-Me_6C_6)RhCp][PF_6]$_2$ is apparently a new compound and was prepared as follows. [(η^6-C_6H_6)RhCp][BF_4]$_2$[43] (0.10 g; Cp = η^5-C_5H_5) and 0.53 g of hexamethylbenzene were combined in 5 mL of trifluoroacetic acid and heated for 19 h at 338 K. The mixture was filtered after addition of ether, and the resulting solid was washed with cold acetone to give 0.04 g of white [(η^6-Me_6C_6)RhCp][BF_4]$_2$. This material was dissolved in acetone and treated with an acetone solution of [NH_4][PF_6] to yield the desired [7][PF_6]$_2$ (tan solid). Its identity was confirmed by ^{1}H NMR [(acetone-d_6) δ 6.89 (s, 5 H), 2.92 (s, 18 H)][44] and by elemental analysis [Calcd for $C_{17}H_{23}RhP_2F_{12}$: C, 32.9; H, 3.71. Found (Robertson Laboratories): C, 33.2; H, 3.98].

Neutral 6 was prepared through reduction of 6^{2+} by cobaltocene. Slightly less than 2 equiv of freshly sublimed Cp_2Co was added to a slurry of 6^{2+} in pentane. As the mixture was stirred, the color of the solution changed from purple (Cp_2Co) to red [(η^4-C_6Me_6)RhCp*] and Cp_2Co^+ precipitated. After 1 h the solution was filtered and evaporated, leaving an oily red solid which was pure by NMR spectroscopy and which was also used for crystal growth.

Electrochemistry. Electrochemical measurements were performed largely as previously described.[41] All experiments except those on complex 7^{2+} employed acetone/0.1 M [Bu_4N][PF_6] as the electrolyte medium. 7^{2+} was not very soluble in acetone, so CH_3CN was used in that case. Voltammetry was performed at platinum bead electrodes, except in a few cases, specifically mentioned in the text, in which a hanging mercury drop electrode was used. The working electrode for controlled-potential electrolyses was a Pt gauze cylinder. Coulometry experiments were taken to >98% completion to measure n values, and temperature control for those experiments employed a constant-temperature bath inside a Vacuum Atmospheres Drilab (1° temperature precision). Voltammetry scans at scan rates in excess of 0.5 V/s were recorded on a Hewlett-Packard digital recorder (HP 7090A).

The aqueous saturated calomel electrode was the operational reference electrode, and all potentials in this study are reported vs the SCE. The potential of the ferrocene/ferrocenium couple in acetone/0.1 M [Bu_4N][PF_6] was 0.48 V vs SCE. Therefore the potentials in Table I can be converted to the Cp_2Fe^+/Cp_2Fe reference by addition of *minus* 0.48 V.

X-ray Crystallography of (η^4-C_6Me_6)RhCp* (6). Table III contains the parameters for the structural determination of 6. A red-brown crystal grown by slow evaporation under N_2 of a *sec*-butyl alcohol solution of 6 was mounted on a glass fiber with epoxy. Exact cell parameters were determined through centering and least-squares refinement of 25 reflections ($20 \geq 2\theta \leq 25$). Data were collected on a Nicolet R3m/μ diffractometer with a graphite monochromator (Mo Kα, λ = 0.710 73 Å). Systematic absences in the diffraction data were consistent with either of the orthorhombic space groups, *Pnma* or *Pn*2_1*a*. The centrosymmetric alternative was suggested by the proposed structure which is found to possess a crystallographic mirror plane.

The structure was solved through a Patterson map which located the Rh atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses and least-squares refinements. No absorption correction was necessary (μ = 8.16 cm^{-1}). Hydrogen atoms were calculated and updated ($U = 1.2U$ of attached C atom, $d_{\mathrm{C-H}}$ = 0.96 Å). Non-hydrogen atoms were refined with anisotropic thermal parameters.

All of the programs which were used are contained in the SHELXTL (5.1) program libraries (G. Sheldrick, Nicolet XRD, Madison, WI). The molecular structure and numbering scheme of $C_{22}H_{33}Rh$ is shown in Figure 4. Table IV lists atomic coordinates and isotropic thermal parameters; bond lengths and angles are found in Table V.

Results

General Reduction Mechanism. This class of Rh(III) dications undergoes two sequential one-electron transfers to give successively, the Rh(II) monocation and the Rh(I) neutral complex. These reactions are represented by eq 1 and 2, respectively. The reduced forms of the complexes

$$[(\text{arene})\text{Rh}^{\text{III}}\text{Cp*}]^{2+} + e^- \rightleftharpoons [(\text{arene})\text{Rh}^{\text{II}}\text{Cp*}]^+ \quad (E°_1) \tag{1}$$

$$[(\text{arene})\text{Rh}^{\text{II}}\text{Cp*}]^+ + e^- \rightleftharpoons (\text{arene})\text{Rh}^{\text{I}}\text{Cp*} \quad (E°_2) \tag{2}$$

were more stable (in the kinetic sense) with increasing methyl substitution on the arene ring. In an earlier report[41] we presented NMR data indicating that the overall two-

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[43] Johnson, B. F. G.; Lewis, J.; Yarrow, D. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2084.

[44] Compare with reported NMR spectrum of the analogous Co complex: Fairhurst, G.; White, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1531.

electron reduction of the complex in which the arene was hexamethylbenzene resulted in η^4 coordination of the arene in the neutral Rh(I) complex. This conclusion is confirmed by the present crystallographic study. It is quite likely that the η^6 to η^4 rearrangement is general for this class of compounds, and our electrochemical data are interpreted under that assumption.

Relative Stabilities of Rh(II) and Rh(I) Species. With all of the complexes investigated in this study, it was observed that the neutral Rh(I) complexes were more stable (longer lived) than their monocationic Rh(II) relatives. This is understandable in light of the η^4-arene structure of the former, which allows the metal to regain the rare-gas configuration. The effect of the greater reactivity of the Rh(II) complexes on the CV curves is that the first reduction wave of the Rh(III) complex (eq 1) has lower chemical reversibility than does the second reduction wave (eq 2). Only complexes $\mathbf{5}^{2+}$ and $\mathbf{6}^{2+}$ failed to follow this trend; these two compounds are sufficiently stable in all three oxidation states that both waves are chemically reversible down to the lowest scan rates employed.

It is worth noting that even though the second reduction wave, due to the Rh(II)/Rh(I) couple, exhibits a high degree of *chemical* reversibility, it is less *electrochemically* reversible than the first [Rh(III)/Rh(II)] couple. This effect arises from slower heterogeneous electron transfer of the Rh(II)/Rh(I) couple and is manifested in larger peak separations for the more negative wave. This property was noted earlier[41] for the $\mathbf{6}^{2+}/\mathbf{6}^{+}/\mathbf{6}$ redox sequence and will be commented on in the Discussion.

For a given complex, both the individual E°_1 and E°_2 values, as well as the differences between the standard potentials, $E^\circ_1 - E^\circ_2$, vary with the solvent employed. Earlier work[41] on the hexamethylbenzene complex $\mathbf{6}^{2+}$ showed that differences of up to several hundred millivolts in $E^\circ_1 - E^\circ_2$ could arise from changing solvents. Since we wanted to eliminate the possibility of solvation changes affecting the various compounds in different ways, we sought a "universal" solvent for these measurements. Our choice was based on considerations of the solubility and stability of the three oxidation state complexes and electrochemical characteristics of the solvent. Although CH_2Cl_2 showed the least tendency to displace the arene from the complex, some of the dications did not dissolve in it. Therefore, acetone was employed for E° measurements since it provided good solubility and a reasonably inert medium. Dichloromethane was occasionally used for bulk coulometry.

Reduction of $[(Me_5C_6H)RhCp^*]^{2+}$ ($\mathbf{5}^{2+}$). This complex gave two diffusion-controlled reversible reductions, as shown by the usual criteria[45] from cyclic voltammetry, dc polarography, and double-potential-step chronoamperometry experiments. Reduction potentials for this and other complexes are in Table I. Details of the voltammetric measurements are available.[46] Bulk reduction of $\mathbf{5}^{2+}$ negative of the first wave gave a transient blue solution due to the presence of the Rh(II) cation $\mathbf{5}^{+}$, but the radical decomposed fairly rapidly. Reduction to the neutral complex was therefore accomplished by electrolysis of the dication at the second wave, a procedure which reduces the monocation by another electron as soon as it is formed in solution. At 295 K in CH_2Cl_2 this electrolysis consumed only 1.2 F, but 1.8 F was passed at 273 K. The difference between these coulometric values and the theoretical one (2.0 F) is due to the instability of the Rh(II) species. In the lower temperature experiment, conversion to the neutral complex was reasonably efficient, and an orange solution of **5** was produced that showed no decomposition over 40 min at 273 K. Ambient temperature electrolysis led to decomposition of the Rh(II) radical, and the resulting yellow solution had an unassigned reduction wave at −1.6 V (irreversible).

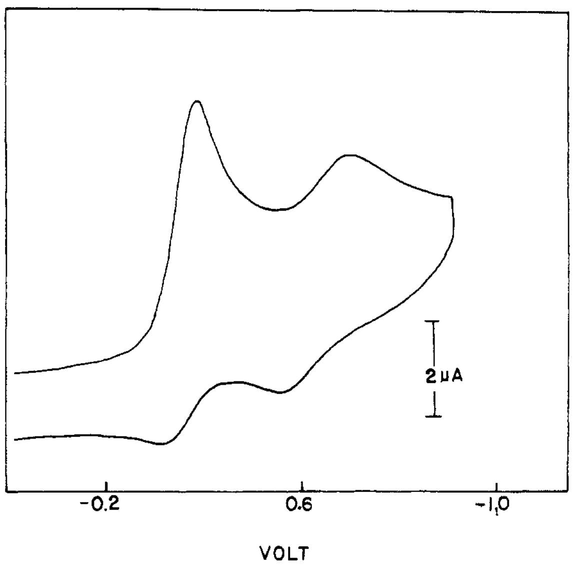

Figure 1. CV scan of 0.40 mM $[(1,2,3,4\text{-}Me_4C_6H_2)RhCp^*]^{2+}$ ($\mathbf{4a}^{2+}$) in acetone/0.1 M Bu_4NPF_6 at a Pt electrode with v = 0.1 V/s, at 298 K, showing the smaller Rh(II)/Rh(I) wave due to Rh(II) decomposition.

Reduction of the Tetramethylbenzene Complexes $\mathbf{4a}^{2+}$ and $\mathbf{4b}^{2+}$. For both of these complexes the Rh(II) intermediate displays limited stability on the time scale of slow-sweep cyclic voltammetry. Therefore the first Rh(III)/Rh(II) wave has only limited chemical reversibility, and the second Rh(II)/Rh(I) wave is smaller than the first, both effects arising from the partial decomposition of the Rh(II) species during the scan. Figure 1 is representative of this behavior. The Rh(II) intermediate is somewhat more stable for the 1,2,4,5 isomer than for the 1,2,3,4 isomer (see tabulated half-lives in Table II). Electrolysis at 243 K of the 1,2,4,5 isomer gave about a 75% in situ yield of the neutral complex **4b** as the solution changed from colorless to blue to orange with passage of 1.52 F. **4b** was stable at this temperature but decomposed within 10 min when the solution was warmed to 283 K. Decomposed solutions of these and the other arene complexes had unassigned cathodic waves at −1.4 and −1.6 V. Half-lives of the Rh(II) intermediates, calculated from CV data, were dramatically lower than those of the corresponding penta- or hexamethylarene derivatives (Table II).

Reduction of the Trimethylarene Complexes $\mathbf{3a}^{2+}$ and $\mathbf{3b}^{2+}$. The Rh(II) mesitylene complex had a half-life of about 0.5 s. Intermediates of this lifetime lend themselves to facile quantitative evaluation by a variety of voltammetric methods. $\mathbf{3b}^{2+}$ was therefore convenient to study in order to confirm the adequacy of the model we are using to interpret the redox behavior of these compounds, namely, an EE sequence (eq 1 and 2) in competition with an EC process involving irreversible decomposition of the first electrode product [the Rh(II) intermediate].

dc polarographic measurements were consistent with this mechanism. The first wave had a diffusion current constant of 2.95 uA mM^{-1} $mg^{-2/3}$ $s^{1/2}$, appropriate for a one-electron reactant with a diffusion coefficient of 1.75×10^{-5} cm/s.[47] The additional current for the second wave was

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[45] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

[46] Bowyer, W. J. Ph.D. Dissertation, University of Vermont, 1985.

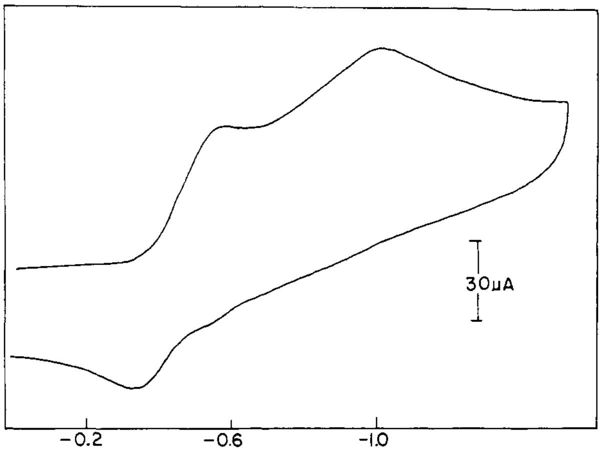

Figure 2. CV scan of 0.94 mM $[(MeC_6H_5)RhCp^*]^{2+}$ (1^{2+}) in acetone/0.1 M Bu_4NPF_6 at a Pt electrode with v = 100 V/s. At this relatively high scan rate the Rh(III)/Rh(II) couple is chemically reversible, but the Rh(II)/Rh(I) wave is spread out due to slow heterogeneous charge transfer.

smaller than the first, but it underwent a comparative increase at shorter mercury drop times (dt). The ratio of limiting plateau currents, i_{l2}/i_{l1}, was 0.29 with dt = 2 s and increased to 0.39 with dt = 0.5 s. The increased current at shorter drop times is due to the higher concentration of Rh(II) under conditions of shorter reaction (decomposition) times.

Reduction of the Less Highly Methylated Complexes 2^{2+}, 1^{2+}, and 0^{2+}. For each of these complexes, the Rh(II) intermediate was quite short-lived and difficulties were encountered in detecting the subsequent reduction of Rh(II) to Rh(I). Fast CV scans outran the decomposition of the Rh(II) complex and allowed calculation of the half-lives of these three complexes in the intermediate oxidation state (Table II). Data on the benzene complex may be taken as typical. For the couple $0^{2+}/0^{+}$ at a scan rate of 50 V/s, the ratio i_a/i_c was 0.68, and the peak separation was 86 mV.[49] The high scan rates necessary to observe reversibility for the first wave unfortunately resulted in very drawn-out peaks for the second wave, which has a lower heterogeneous charge-transfer rate (see Figure 2). Because of this problem, we judged the measurement of the $E°$ potentials for the $1^{+}/1^{0}$ and $0^{+}/0^{0}$ couples to be too approximate to be included in our analysis, and hence these values are missing from Table II. Scans of the two waves for 1^{2+} and 0^{2+} at Hg electrodes gave sharper second peaks, but other voltammetric difficulties, possibly arising from electrode filming, were encountered, and attempts at measurement of the $E°_2$ values for the benzene and toluene complexes were abandoned.

Reduction of the Cyclopentadienyl Complex $[(Me_6C_6)RhCp]^{2+}$ (7^{2+}). This compound was investigated to observe the effect on the electrochemical behavior when it is the methylation of the 5-membered ring which is changed. This complex was not soluble in acetone, so its voltammetry was investigated in acetonitrile. It showed two waves shifted to more positive potentials than the Cp* analogues (Table I) but having similar overall characteristics. At slow scan rates the Rh(III)/Rh(II) reduction was irreversible at 295 K, but reversible at subambient temperatures (Figure 3). Quantitative comparison of $E°$ values and radical lifetimes to those of the Cp* complexes was not pursued because of the change in solvent, which adds a variable of unknown effect.

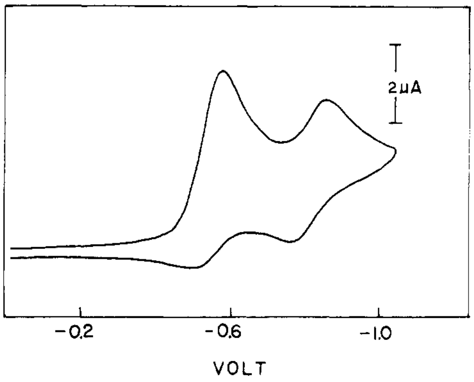

Figure 3. CV scan of ca. 0.3 mM $[(Me_6C_6)RhCp]^{2+}$ (7^{2+}) at a Pt electrode with v = 0.3 V/s at 261 K in CH_3CN/0.1 M Bu_4NPF_6.

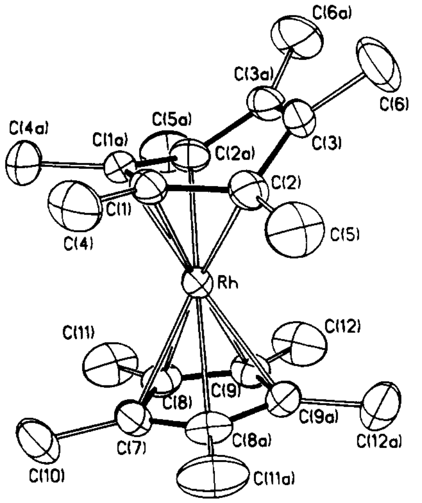

Figure 4. Molecular structure of (η^4-Me_6C_6)RhCp* (6).

Structure of the η^4 Complex (η^4-Me_6C_6)RhCp* (6). The structure of neutral 6 (Figure 4) consists of a Rh(I) metal atom π-bonded to an η^5-Cp ring and an η^4-hexamethylbenzene ring. The complex crystallizes as eight half-molecules per unit cell related by a crystallographic mirror plane. The distances from the metal to the centers of the π-bonded carbons is 1.722 Å for the arene and 1.886 Å for the C_5Me_5. The length of the uncoordinated arene C(3)–C(3a) bond is 1.316 (10) Å, as expected for a free carbon–carbon double bond. The Cp unit shows two long C–C bonds [1.430 (6) Å] and three short bonds [one pair of 1.402 (5) Å and one of 1.411 (10) Å]. The lack of uniform C–C distances in the Cp ring is reminiscent of that found in other Rh(I) or Co(I) cyclopentadienyl complexes.[50] The atoms on the hinge of the η^4-arene, C(2) and C(2a), are farther from the Rh atom [Rh–C(2) = 2.144 (4) Å] than are the other coordinated carbon atoms [Rh–C(1) = 2.089 (4) Å], whereas the Rh–C bonds to the C_5Me_5 ring are longer than both [2.217 (4), 2.228 (4), 2.298 (6) Å].

The dihedral angle of the arene "hinge" is 41.8°. This value is consistent with those found for other η^4-arenes. It is within 2° of the reported hinge angles for arenes

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(47) The diffusion coefficient was calculated from the diffusion constant. See ref 45, p 147, and ref 48.

(48) Heyrovsky, J.; Kuta, J. *Principles of Polarography*; Academic: New York, 1965; Chapter VI.

(49) A mercury electrode was used for these scans, since the electron-transfer rates of the complex were faster at a Hg surface than at Pt.

(50) (a) Dahl, L. F.; Wei, C. H. *Inorg. Chem.* **1963**, *2*, 713. (b) Bennett, M. J.; Churchill, M. R.; Gerloch, M.; Mason, R. *Nature (London)* **1964**, *201*, 1318. (c) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277. (d) Olson, W. L.; Nagaki, D. A.; Dahl, L. F. *Organometallics* **1986**, *5*, 630. (e) Lichtenberger, D. L.; Calabro, D. C.; Kellogg, G. E. *Organometallics*, **1984**, *3*, 1623.

η^4-bonded to Ta,[26] Fe,[24] and Ru.[21-27]

Discussion

Kinetic Stabilites of Rh(II) Monocations. We will first look at how the kinetic stabilities of the Rh(II) monocations and Rh(I) neutral complexes depend on the arene substituents, without explicitly considering the role of the hapticity change in the electron-transfer sequence. Then we will consider thermodynamic data which argue strongly that the arene slippage occurs in the Rh(II)/Rh(I) step.

Table II lists the half-lives of the Rh(II) radical intermediates $[(\text{arene})\text{RhCp}^*]^+$, insofar as they could be determined by either cyclic voltammetry or controlled-potential coulometry experiments. Immediately obvious is that complexes with more Me groups on the arenes are longer lived. This is not unexpected, for metal–arene complexes are well-known to display increased stability with greater numbers of electron-pushing groups on the arene.[31,40,42,51] This observation has been made previously in both synthetic[40,42,51,52] and thermodynamic contexts.[30,31,53]

What is remarkable about the data in Table II is the range of lifetimes for the Rh(II) complexes, which extends from 5 ms for arene = benzene to over 1800 s for arene = hexamethylbenzene, an increase of about a millionfold. This appears to be the first systematic data showing how arene methylation affects the kinetic stabilities of metal–arene odd-electron complexes.

Thermodynamic Effects: Dependence of $E°$ on Arene Substituents. The methyl substituent effect on the formal reduction potential of the first wave [representing the Rh(III)/Rh(II) couple] is considered in Figure 5. The linear negative shift of $E°_1$ with an increased number of Me groups is unremarkable and is significant for that reason, especially in light of the different behavior found for the second wave (vide infra). Our discussion will center on the observation that the methyl substituent shift on the Rh(III)/Rh(II) couple is as expected for a simple inductive effect but that explanation of the substituent effect on the Rh(II)/Rh(I) couple must also invoke a stabilization of the η^4-arene structure with increasing numbers of Me groups on the arene.

Although the present study appears to be the most comprehensive to date on the effect of alkyl substitution on metal–arene reduction potentials and the first to include arenes having one through six methyl groups, a number of other investigators have addressed this question. The largest data sets are those on $[(\text{arene})_2\text{Cr}]^{+/0}$,[54] $[(\text{arene})\text{CoCp}]^{2+/+/0}$,[40] $[(\text{arene})\text{CoCp}^*]^{2+/+/0}$,[40] $[(\text{arene})\text{FeCp}]^{+/0}$,[55] and $[(\text{arene})\text{Cr(CO)}_3]^{+/0}$.[56] The last study shows trends that are virtually identical with the others, but the results are not included in our graphical analysis because the reported potentials are $E_{1/2}$ values, rather than $E°$ values, and could introduce a factor of uncertainty since the $[(\text{arene})\text{Cr(CO)}_3]^{+/0}$ couple is now known to have limited reversibility.[57]

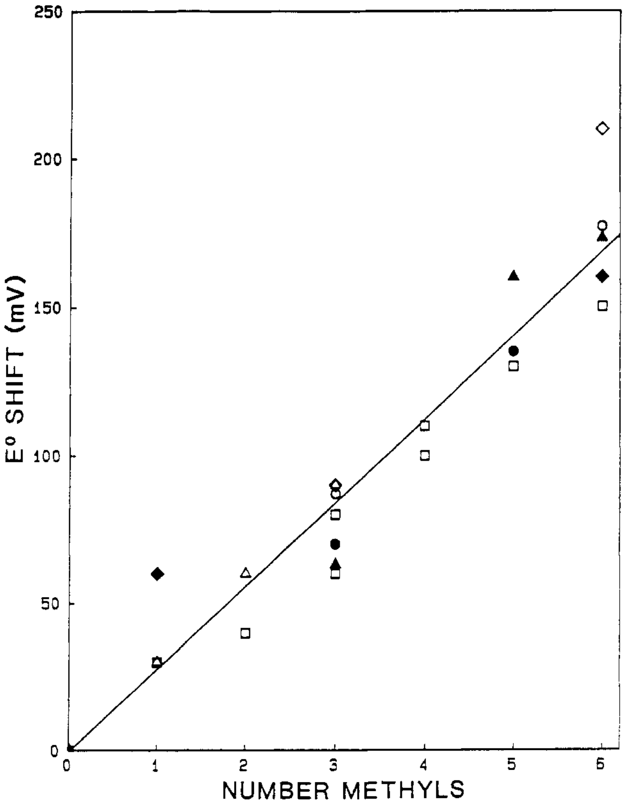

Figure 5. Shift of the formal reduction potential for a methyl-substituted arene complex from the potential of the C_6H_6 complex, plotted as a function of the number of methyl groups on the arene. Legend: ◆, $[(\text{arene})\text{FeCp}]^{+/0}$ (ref 55); △, $[(\text{arene})_2\text{Cr}]^{+/0}$ (ref 54); ●, $[(\text{arene})\text{CoCp}]^{2+/+}$ (ref 40); ▲, $[(\text{arene})\text{CoCp}]^{+/0}$ (ref 40); ○ $[(\text{arene})\text{CoCp}^*]^{2+/+}$ (ref 40); ◇, $[(\text{arene})\text{CoCp}^*]^{+/0}$ (ref 40); □, $[(\text{arene})\text{RhCp}^*]^{2+/+}$ (present data). The straight line is a least-squares line with slope = −28.2 mV/Me group (correlation coefficient 0.975).

Data on seven different redox couples, including our Rh(III)/Rh(II), $[(\text{arene})\text{RhCp}^*]^{2+/+}$, are plotted in Figure 5. The ordinate is defined as the shift in $E°$ from the value for the C_6H_6 complex. A linear correlation is found with a slope of −28 mV per added Me group. Therefore, the Rh(III)/Rh(II) couple behaves like other systems in which the inductive (or hyperconjugative) effect of the methyl group has been viewed as responsible for the negative $E°$ shifts for more highly substituted arene rings.[58]

We do not find a similar trend for $E°_2$ vs. the number of Me groups. Instead, the Rh(II)/Rh(I) potential is virtually *independent* of the degree of arene methylation (Table I). This behavior stands in sharp contrast to the linear substituent dependence revealed for the other redox couples in Figure 5 and is apparently unique among all metal arene redox couples studied to this point. Further analysis allows us to attribute this effect to preferential stabilization of the η^4-arene structure by more highly methylated arenes. Consider the following.

It can be assumed that in the absence of any unusual structural changes, the Rh(II)/Rh(I) wave would shift negative by 25–30 mV per added Me group. The generality of this electronic shift is suggested by the 22 data points in Figure 5, which encompass three different metals, three different oxidation states, and three different absolute molecular charges. The difference between the assumed inductive shift and the measured $E°$ shift gives the stabilization of the Rh(II)/Rh(I) couple due to the arene hapticity change. For the system under study, the per-

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(53) Skinner, H. A.; Connor, J. A. *Pure Appl. Chem.* **1985**, *57*, 79.

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(55) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758.

(56) Lloyd, M. K.; McCleverty, J. A.; Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1768.

(57) (a) Rieke, R. D.; Tucker, I.; Milligan, S. N.; Wright, D. R.; Willeford, B. R.; Radonovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 938. (b) Stone, N. J.; Sweigart, D. A.; Bond, A. M. *Organometallics* **1986**, *5*, 2553 provide leading references.

(58) Leading references may be found in ref 40.

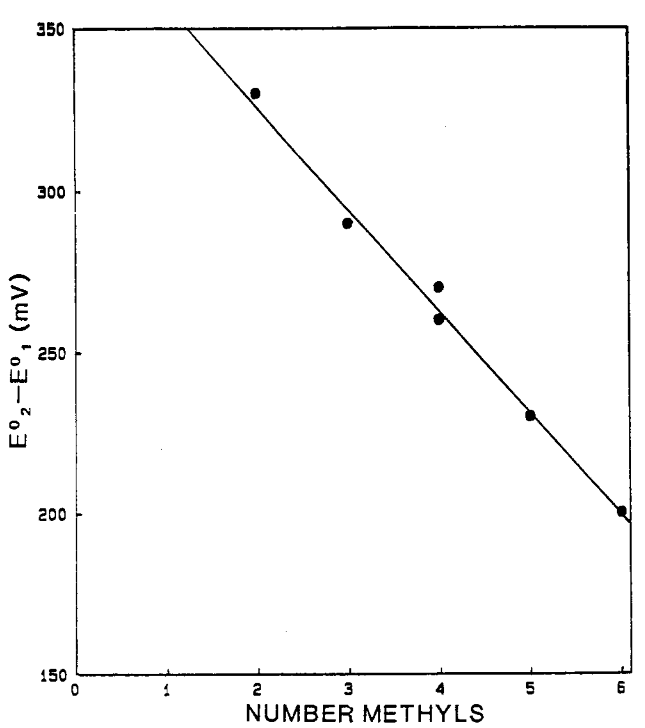

Figure 6. Separation of the formal potentials for the Rh(III)/Rh(II) and Rh(II)/Rh(I) couples ($E^\circ_1 - E^\circ_2$) as a function of the number of methyl groups on the arene of $[(\text{arene})\text{RhCp*}]^{2+/+/0}$.

tinent variable is $E^\circ_2 - E^\circ_1$, the difference between the first and second reduction potentials of the $[(\text{arene})\text{RhCp*}]^{2+/+/0}$ series. This quantity (Table I) when plotted against the degree of arene methylation (Figure 6) gives a straight line of slope +33 mV/Me group. That is, each additional methyl group stabilizes the η^4 Rh(I) complex by an additional 33 mV. When translated into thermochemical language, addition of each CH_3 group stabilizes the bent arene form by about 0.7 kcal/mol.

We offer the following hypothesis accounting for the stabilization of the bent (or slipped) arene form by increased methylation of the ring. Alkyl-substituted free arenes are thought to possess less aromatic resonance energy with an increased degree of substitution,[59] perhaps due to distortions of arene planarity.[60] If this effect were operative in the complexes under study, it would decrease the additional (negative potential) energy needed to reduce the Rh(II) planar arene complex to the Rh(I) bent arene complex as more Me groups were added to the arene, thereby decreasing the separation of the two waves, as is observed. Two different methods of calculating arene resonance energies[59] give an order of magnitude of 0.5–1.5 kcal/mol per Me group for this effect, in the proper range to account for our measured η^4-stabilization energy of 0.7 kcal/mol per Me. Quantitative correlations are excluded by the uncertainties in calculated resonance energies for the arenes and by the relatively small changes in energy for which we are trying to account. Still, this model should be testable with arenes having greater differences in resonance energies. If found to be correct, it might allow estimations of arene resonance energies from metal complex E° potentials.

It may be of interest to note that the $E^\circ_2 - E^\circ_1$ values of isomeric complexes were found to be very similar. Two such comparisons were made by using the 1,2,3- and 1,3,5-Me_3 complexes $\mathbf{3a}^{2+}$ and $\mathbf{3b}^{2+}$, respectively, and the 1,2,3,4- and 1,2,4,5-Me_4 complexes $\mathbf{4a}^{2+}$ and $\mathbf{4b}^{2+}$. Earlier qualitative arguments by Muetterties, Bleeke, and Sievert[31] suggested that the stereochemistry of alkyl substituents would more likely affect the stability of a η^4 rather than η^6 complex. Within the precision of our analysis, we cannot confirm this, since the two pairs of isomers mentioned have E° separations within experimental error (±10 mV or ±0.2 kcal/mol).

Finally, we wish to comment on the slower heterogeneous charge-transfer rates seen for the Rh(II)/Rh(I) couple as compared to the Rh(III)/Rh(II) couple. This is of special interest in light of the fact that the energy barrier for reorganization of the arene from planar to bent is expected to contribute to the increased activation energy for the Rh(II)/Rh(I) couple. The Rh(II)/Rh(I) couple shows electrode kinetics that are particularly prone to variations at different electrode surfaces. Therefore, electrode kinetics at solid electrode surfaces such as Pt or Au apparently reflect interfacial as well as geometric factors.[41,61]

Conclusions

A number of conclusions can be made concerning the kinetic and thermodynamic stabilities of these rhodium arene complexes.

1. In the overall two-electron reduction of Rh(III) to Rh(I) in the complexes $[(Me_nC_6H_{6-n})\text{RhCp*}]^{2+/+/0}$, the intermediate Rh(II) species is directly observable by electrochemical methods for $n = 0$ through $n = 6$. The kinetic stability of the Rh(II) complex decreases from $n = 6$ to $n = 0$, with the hexamethylbenzene complex being over 10^5-fold longer lived than the benzene complex.

2. The twice-reduced Rh(I) complex is in each case longer lived than the corresponding Rh(II) complex, apparently due to the hapticity change of the arene in the second reduction process which produces an 18-electron Rh(I) η^4 complex.

3. The Rh(III)/Rh(II) wave follows the expected negative shift of E° with added Me groups, consistent with previous studies of other arene metal complexes. A 22-point analysis of the present and literature data shows that the average shift is −28 mV in E° per added Me group.

4. The E° of the Rh(II)/Rh(I) process is virtually independent of the number of alkyl substituents. This can be traced to the fact that additional Me groups result in greater thermodynamic stabilization of the η^4 arene structure, roughly balancing the methyl inductive effect. This appears to be the first thermodynamic confirmation of the idea that η^4 structures are favored for arenes having increased ring substitution. The amount of stabilization of the η^4 structure imparted by a methyl group is the same order of magnitude as differences in resonance energies of the free arenes.

Acknowledgment. We are grateful to the National Science Foundation for generous support of this work (NSF CHE-86 03728) and for providing funds to the University of Delaware for purchase of its diffractometer. We also thank the Johnson/Matthey Corp. for a loan of rhodium trichloride.

Registry No. $\mathbf{0}^+$, 117340-47-3; $\mathbf{0}^{2+}$, 65074-04-6; $\mathbf{1}^+$, 117340-48-4; $\mathbf{1}^{2+}$, 65074-06-8; **2**, 117340-58-6; $\mathbf{2}^+$, 51151-27-0; $\mathbf{2}^{2+}$, 117340-34-8; **3a**, 117340-59-7; $\mathbf{3a}^+$, 117340-49-5; $\mathbf{3a}^{2+}$, 117340-36-0; **3b**, 117340-56-4; $\mathbf{3b}^+$, 117340-50-8; $\mathbf{3b}^{2+}$, 59714-86-2; **4a**, 117340-60-0;

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(60) (a) Vorozhtsov, N. N., Jr. *Isomerization of Organic Compounds*: Daniel Davey and Co.: New York, 1965; pp 101–103. (b) Badger, G. M. *Aromatic Character and Aromaticity*; Cambridge University: Cambridge, 1969; p 51 ff.

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4a$^+$, 117340-51-9; **4a**$^{2+}$, 117340-38-2; **4b**, 117340-61-1; **4b**$^+$, 117340-52-0; **4b**$^{2+}$, 117340-40-6; **5**, 117340-62-2; **5**$^+$, 117340-53-1; **5**$^{2+}$, 117340-42-8; **6**, 97732-08-6; **6**$^+$, 97732-09-7; **6**$^{2+}$, 12715-84-3; **7**, 117340-57-5; **7**$^+$, 117340-54-2; **7**$^{2+}$, 117340-44-0; **8**, 117340-63-3; **8**$^+$, 117340-55-3; **8**$^{2+}$, 117340-46-2.

Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters for **6** (4 pages); a listing of structure factors (11 pages). Ordering information is given on a current masthead.

Rhenium Carbonyl Phosphine Dinitrogen Complexes $(\eta^5\text{-}C_5Me_5)Re(CO)(PR_3)(N_2)$

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The new rhenium dinitrogen complexes $(\eta^5\text{-}C_5Me_5)Re(CO)(PR_3)(N_2)$ (**3a–f**) have been synthesized for PR_3 = (**a**) PMe_3, (**b**) $P(n\text{-}Bu)_3$, (**c**) PCy_3 (Cy = cyclohexyl), (**d**) PPh_3, (**e**) $P(OMe)_3$, and (**f**) $P(OCH_2)_3CMe$ by treatment of the corresponding *p*-methoxyphenyldiazenido complexes $[(\eta^5\text{-}C_5Me_5)Re(CO)(PR_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**2a–f**) with *t*-BuLi. These cationic phosphine complexes **2a–f** were synthesized from the cationic acetonitrile complex $[(\eta^5\text{-}C_5Me_5)Re(CO)(NCMe)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**1a**) and the appropriate phosphine. The compounds have been characterized spectroscopically, including unambiguous ^{15}N and ^{14}N NMR assignments of the N_α and N_β resonances of the aryldiazenide and dinitrogen ligands. Comparisons are made with the properties of the related known dicarbonyl compounds $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ and $(\eta^5\text{-}C_5Me_5)Re(CO)_2(N_2)$. It is shown that the ^{15}N label in $^{15}N_\alpha$-labeled **2a** and **2e** is retained exclusively at the N_α position in the dinitrogen complexes **3a** and **3e**; however, an equimolar mixture of $^{15}N_\alpha$- and $^{15}N_\beta$-labeled $(\eta^5\text{-}C_5Me_5)Re(CO)_2(^{15}N^{14}N)$ results when this dinitrogen complex is synthesized from exclusively $^{15}N_\alpha$-labeled $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(p\text{-}^{15}N^{14}NC_6H_4OMe)][BF_4]$. Hexane or cyclohexane solution IR spectra of **3d** (PR_3 = PPh_3) and **3e** (PR_3 = $P(OMe)_3$), but not of the remainder, show two ν(NN) absorption bands. This is attributed to the existence of more than one possible conformation of the PR_3 ligand in these complexes. The N_2 ligand in **3a** (PR_3 = PMe_3) is remarkably inert, as it is not displaced by PPh_3 at room temperature in diethyl ether solution and shows no exchange with nitrogen gas when pressurized.

Introduction

Previous publications from this laboratory have described the syntheses of the dinitrogen compounds $CpRe(CO)_2(N_2)$[1] and $Cp^*Re(CO)_2(N_2)$[2] (Cp = $\eta^5\text{-}C_5H_5$, Cp* = $\eta^5\text{-}C_5Me_5$) by the treatment of the corresponding cationic aryldiazenido (N_2Ar) complexes $[CpRe(CO)_2(N_2Ar)]^+$ or $[Cp^*Re(CO)_2(N_2Ar)]^+$ with a variety of reagents including I^-, BH_4^-, MeLi, and *t*-BuLi. Elsewhere,[3] we have described the synthesis of the cationic acetonitrile-substituted aryldiazenido complexes $[Cp'Re(CO)(NCMe)(N_2Ar)]^+$ (where Cp′ = Cp or Cp*) by means of eq 1.

$$[Cp'Re(CO)_2(N_2Ar)]^+ \xrightarrow[\text{MeCN}]{\text{PhIO}} [Cp'Re(CO)(NCMe)(N_2Ar)]^+ \quad (1)$$

These acetonitrile complexes readily undergo substitution of the acetonitrile by a variety of ligands. In this paper we describe a series of phosphine complexes of the type $[Cp^*Re(CO)(PR_3)(N_2Ar)]^+$ synthesized in this way. We have found that these carbonyl phosphine complexes, just like the dicarbonyls mentioned above, also undergo the transformation of the N_2Ar ligand into N_2 when treated with *t*-BuLi. This has allowed us to synthesize the series of carbonyl phosphine dinitrogen complexes $Cp^*Re(CO)(PR_3)(N_2)$ that is unobtainable from $Cp^*Re(CO)_2(N_2)$ and PR_3 because of preferential substitution of N_2 by PR_3. Some properties of the PMe_3 complex $Cp^*Re(CO)(PMe_3)(N_2)$, particularly the photodissociation of N_2 and subsequent C–H activation chemistry of the intermediate, have been communicated already.[4] Here, we provide details of the characterization of these complexes and make some comparisons with the dicarbonyl compound $Cp^*Re(CO)_2(N_2)$.

Experimental Section

All reactions were carried out under dry N_2 in Schlenk apparatus connected to a double manifold providing low vacuum or nitrogen. Solvents were purified and dried by conventional methods, distilled under nitrogen, and used immediately. Infrared spectra were measured by using a Perkin-Elmer Model 983-G instrument, usually as solutions in CaF_2 cells. Variable-temperature IR spectra were run on a Bruker IFS-85 FT-IR instrument by using a Specac variable-temperature IR cell. ^1H, ^{13}C, ^{31}P (referenced to external 85% H_3PO_4), ^{15}N, and ^{14}N (referenced to external $MeNO_2$) NMR spectra were measured by using a Bruker WM-400 instrument. The ^{15}N NMR spectra were obtained for 96% ^{15}N isotopically enriched samples. Mass spectra were obtained with a Hewlett-Packard Model 5985 mass spectrometer with electron-impact (EI) or fast atom bombardment (FAB; Phrasor Scientific Inc. accessory) sources. Masses are quoted for the ^{187}Re isotope. Microanalyses were performed by the Simon Fraser University Microanalytical Laboratory.

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