9846 *J. Am. Chem. Soc.* **1992**, *114*, 9846-9851

Delocalization in Bimetallic Triple-Decker Complexes: Electrochemistry, ESR Spectroscopy, and Spectroelectrochemistry of (p-MeC$_6$H$_4$CHMe$_2$)$_2$Ru$_2$(Et$_2$C$_2$B$_3$H$_3$) and CpCo(Et$_2$C$_2$B$_3$H$_3$)Ru(p-MeC$_6$H$_4$CHMe$_2$) and Derived Ions

Jon W. Merkert,[†] James H. Davis, Jr.,[‡,§] William E. Geiger,[*,†] and Russell N. Grimes[*,‡]

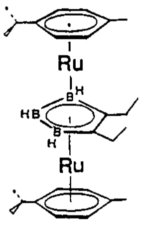
Contribution from the Departments of Chemistry, University of Vermont, Burlington, Vermont 05405, and University of Virginia, Charlottesville, Virginia 22901.

Received June 29, 1992

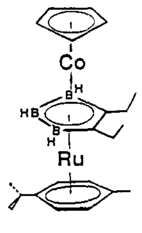
Abstract: The redox properties of the 30-e$^-$ triple-decker complexes (p-MeC$_6$H$_4$CHMe$_2$)$_2$Ru$_2$(Et$_2$C$_2$B$_3$H$_3$) (RuRu) and CpCo(Et$_2$C$_2$B$_3$H$_3$)Ru(p-MeC$_6$H$_4$CHMe$_2$) (CoRu) have been investigated by voltammetry, coulometry, optical spectroelectrochemistry, and electron spin resonance spectroscopy. The electron-transfer series RuRu^{2+} $\rightleftharpoons$ RuRu$^+$ $\rightleftharpoons$ RuRu $\rightleftharpoons$ RuRu$^-$ and CoRu$^+$ $\rightleftharpoons$ CoRu $\rightleftharpoons$ CoRu$^-$ $\rightleftharpoons$ CoRu^{2-} were detected. Electronic spectra over the range 300–2000 nm were obtained for the 29-e$^-$ mixed-valent ions RuRu$^+$ and CoRu$^+$ with the aid of an optically transparent thin-layer electrolysis cell. Analysis of the bandwidths of the near-IR absorptions of the cations, as well as the lack of dependence of the absorption energy on solvent dielectric, allows assignment of the ions as class III (totally delocalized) mixed-valent species. ESR studies of the 29-e$^-$ cations are consistent with a SOMO derived from a degenerate e$_2''$ orbital composed of a d$_{xy}$, d$_{x^2-y^2}$ pair. This orbital has greater Ru character than Co character in CoRu$^+$. The SOMO of the 31-e$^-$ anion CoRu$^-$ derives from a degenerate e$_2''$ orbital composed of a d$_{xz}$, d$_{yz}$ pair with significantly greater Co character than Ru character.

Introduction

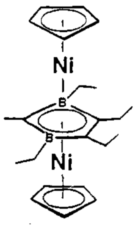
One rationale for the research interest surrounding carborane- and organoborane-bridged polydecker sandwich compounds[1,2] is that they are likely to possess delocalized electronic structures. This property is of potential utility in the design of molecules and devices which rely on facile electron transfer over long distances.[3] Electron-transfer series of triple- or tetra-decker complexes generally encompass several redox processes with fast electron-transfer reactions having well-separated formal potentials.[4-9] This observation implies, but does not prove, strong electronic communication between metal centers. There has, in fact, been little reported concerning the extent of metal–metal interactions in polydeckers. Perhaps the strongest evidence to date of electronic delocalization in a triple-decker complex comes from the NMR study by Zwecker et al.[6] on **3**, a 33-e$^-$ (formally mixed-valent) species in which the two metals are found to be equivalent on the experimental time scale.



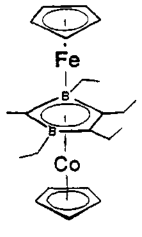
1



2



3



4

The situation with heterodinuclear complexes is even less well understood. Mossbauer spectra of 29-e$^-$ **4**$^+$ are "ferrocenium-like" in character even though INDO calculations on **4** and **4**$^+$ do not indicate a high-lying filled orbital with significant atomic density on Fe to account for such an observation.[5]

Given the need for studies in this area and the recent availability of homo- and heterobimetallic triple-decker complexes of Co and Ru,[10] we were interested in probing the delocalization in mixed-valent complexes derived from **1** and **2**. The monooxidized form of **1** contains formal Ru(II) and Ru(III) metals and is therefore an organometallic analogue of the Creutz–Taube ion.[11] This suggested the use of electronic spectroscopy to study its mixed-valent properties. We interpret the results of optical, electrochemical, and ESR spectroscopic investigations on 29-e$^-$ **1**$^+$ and isoelectronic **2**$^+$ [in which CpCo has replaced (arene)Ru] as strong evidence that the metals in these organometallic stacks are in intimate communication.[12]

The formal d-orbital configurations are d^6 [Ru(II) and/or Co(III)] for both metals in (p-MeC$_6$H$_4$CHMe$_2$)$_2$Ru$_2$(Et$_2$C$_2$B$_3$H$_3$), RuRu (**1**), and CpCo(Et$_2$C$_2$B$_3$H$_3$)Ru(p-MeC$_6$H$_4$CHMe$_2$), CoRu (**2**), where p-MeC$_6$H$_4$CHMe$_2$ = 4-methylisopropylbenzene (cymene).

Experimental Section

Chemicals. Complexes **1** and **2** were prepared as described previously,[10] as was [Cp$_2$Fe][PF$_6$].[13] Cp*$_2$Fe (Cp* = η^5-C$_5$Me$_5$) was purchased from Strem Chemicals. Solvents were purified by vacuum distillation from drying agents.[14] Manipulations were performed under dinitrogen, using either a Vacuum Atmospheres Corp. drybox or Schlenk procedures.

[†] University of Vermont.

[‡] University of Virginia.

[§] Present address: Brandeis University, Waltham, MA 02254.

(1) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251.

(2) (a) Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 943. (b) Siebert, W. *Pure Appl. Chem.* **1987**, *59*, 947.

(3) (a) Burdett, J. K.; Canadell, E. *Organometallics* **1985**, *4*, 805. (b) Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 857.

(4) Brennan, D. E.; Geiger, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 3399.

(5) Edwin, J.; Bochmann, M.; Boehm, M. C.; Brennan, D. E.; Geiger, W. E.; Kruger, C.; Pebler, J.; Pritzkow, H.; Siebert, W.; Swiridoff, W.; Wadepohl, H.; Weiss, J.; Zenneck, U. *J. Am. Chem. Soc.* **1983**, *105*, 2582.

(6) Zwecker, J.; Kuhlmann, T.; Pritzkow, H.; Siebert, W.; Zenneck, U. *Organometallics* **1988**, *7*, 2316.

(7) Fessenbecker, A.; Attwood, M. D.; Bryan, R. F.; Grimes, R. N.; Woode, M. K.; Stephan, M.; Zenneck, U.; Siebert, W. *Inorg. Chem.* **1990**, *29*, 5157.

(8) Fessenbecker, A.; Attwood, M. D.; Grimes, R. N.; Stephan, M.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Inorg. Chem.* **1990**, *29*, 5164.

(9) Michels, L.; Schmickler, W. *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *295*, 139.

(10) (a) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776. (b) *Ibid.* **1989**, *111*, 4784.

(11) (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988. (b) *Ibid.* **1973**, *95*, 1086.

(12) A preliminary account of this work was presented: Merkert, J.; Davis, J. H., Jr.; Grimes, R. N.; Geiger, W. E. *Abstracts of Papers*, 199th National Meeting of the American Chemical Society, Boston, MA, April 1990; American Chemical Society: Washington, DC, 1990; INOR-92.

(13) Quarmby, I. C.; Geiger, W. E. *Organometallics* **1992**, *11*, 436.

(14) Bowyer, W. J.; Merkert, J. W.; Geiger, W. E.; Rheingold, A. L. *Organometallics* **1989**, *8*, 191.

0002-7863/92/1514-9846$03.00/0 © 1992 American Chemical Society

Table I. Formal Potentials (V vs $Cp_2Fe^{0/+}$) of Triple-Decker Carboranes at Ambient Temperatures

complex	solvent	couple	potential
RuRu	CH_2Cl_2	0/1+	−0.34
RuRu	CH_2Cl_2	1+/2+	+0.61[a]
RuRu	CH_3NO_2	0/1+	−0.30
RuRu	THF	0/1−	−3.25
CoRu	CH_2Cl_2	0/1+	−0.16
CoRu	CH_2Cl_2	1+/?[b]	+0.86[c]
CoRu	CH_3NO_2	0/1+	−0.16
CoRu	THF	0/1+	−0.17
	THF	0/1−	−2.38
	THF	1−/2−	−3.12

[a] $T = 258$ K. [b] Multielectron irreversible process. [c] Peak potential. $v = 0.1$ V/s.

Electrochemistry. Electrochemical procedures were essentially the same as described earlier.[14] Potentials in this paper are referenced to the Cp_2Fe/Cp_2Fe^+ ($Fc^{0/+}$) couple. The laboratory reference electrode was either Ag/AgCl or the aqueous SCE, but the Fc potential was measured in an internal standard mode in each experiment. The supporting electrolyte was $[Bu_4N][PF_6]$, 0.1 M in voltammetry experiments and 0.2–0.5 M in spectroelectrochemical experiments. Voltammetry and coulometry experiments were conducted under an atmosphere of N_2 in a drybox at either Pt or Hg electrodes.

Standard criteria were employed for the diagnosis of mass transport control (measurement of the current function, $i_p/v^{1/2}$, as a function of scan rate v), chemical reversibility (i_{rev}/i_{fwd}), and electrochemical reversibility (ΔE_p compared to $Fc^{0/+}$). Details may be found elsewhere.[15]

Spectroelectrochemistry. The OTTLE (optically transparent thin-layer electrode) cell was of standard design[16] and was operated in the transmission mode with a 100 line/in. gold minigrid as the working electrode. Construction of the cell is described in ref 15. The optical path length was periodically calibrated with the ferrocene absorption at $\lambda_{max} = 436$ nm, using a molar absorptivity of 127 L mol^{-1} cm^{-1}. A typical path length was 0.04 cm. The electrochemical volume of the cell was calculated from coulometry on ferrocene as ca. 0.09 mL. Electrolysis to steady-state currents typically took ca. 200 s in this cell for 2–4 mM solutions. Cyclic voltammetry scans gave reasonably coherent responses with scan rates below ca. 20 mV/s and concentrations below 4 mM.

Spectroscopic Equipment. IR spectra were recorded on a Nicolet Model 6000 FT-IR spectrometer at 2-cm^{-1} resolution. Optical spectra were measured on either a Cary 14 or a Perkin-Elmer Lambda-6 spectrometer. A modified Varian E-4 spectrometer was utilized for ESR studies, and a Bruker instrument operating at 250 MHz for ^1H was employed for NMR work.

Chemical Oxidations and Reductions. A typical procedure was as follows. A 1.6-mg (2.8-μmol) sample of RuRu was dissolved in 7 mL of CH_2Cl_2, and 1.0 mg (3.0 μmol) of $[Cp_2Fe][PF_6]$ was added, whereupon the solution changed from red-orange to blue. A 2.4-mL portion (assumed to contain 0.96 μmol of $RuRu^+$) of this solution was placed in a 1-cm quartz cell in order to record the optical spectrum of $RuRu^+$. Back-reduction to RuRu was accomplished by addition of three successive 100-μL aliquots of a 4.1 mM solution of $Cp^*{}_2Fe$ (0.41 μmol in each aliquot). An optical spectrum was recorded after each addition. This process was repeated with CoRu in place of RuRu, but a complication in the back-reduction was spectral interference from the $Cp^*{}_2Fe^+$ absorption at $\lambda_{max} = 780$ nm.

Results and Discussion

Electrochemistry of Triple Deckers. The 30-e^- complexes RuRu (**1**) and CoRu (**2**) undergo reversible electron-transfer reactions involving at least four detected members of the electron-transfer series. The electrochemically-observed species are those with charges of 2+ through 1− for RuRu and 1+ through 2− for CoRu (eqs 1 and 2). Both complexes have an additional irreversible

$$[\text{irrev oxdn}] \leftarrow RuRu^{2+} \rightleftharpoons RuRu^+ \rightleftharpoons RuRu \rightleftharpoons RuRu^- \quad (1)$$

$$[\text{irrev oxdn}] \leftarrow CoRu^+ \rightleftharpoons CoRu \rightleftharpoons CoRu^- \rightleftharpoons CoRu^{2-} \quad (2)$$

oxidation. The formal potentials of the couples and approximate half-lives of the ions of the series are collected in Tables I and II, respectively. Without exception, these couples displayed near-Nernstian behavior, as diagnosed by cyclic voltammetry (CV) peak separations compared to those of reversible standards such as ferrocene(0/+) or cobaltocene(+/0), and their electrode characteristics were essentially independent of the working electrode composition. Except where noted, diffusional mass transport was observed over the CV time scale. Details are available.[15]

Table II. Estimated Half-Lives of Ions Derived from the 30-e^- Complexes RuRu and CoRu (T = Ambient) Based on Voltammetric Data

ion	solvent	$t_{1/2}$ (s)[a]	valence (e^-)
$CoRu^{2-}$	THF	0.6	32
$CoRu^-$	THF	persistent	31
$RuRu^-$	THF	0.4	31
$CoRu^+$	CH_2Cl_2	persistent	29
$RuRu^+$	CH_2Cl_2	persistent	29
$CoRu^{2+}$	CH_2Cl_2	<0.01	28
$RuRu^{2+}$	CH_2Cl_2	0.1 (T = 255 K)	28

[a] Half-lives were calculated from decomposition rate constants, assuming first-order kinetics, based on the values of i_{rev}/i_{fwd} measured by the semiempirical method of Nicholson: Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351, Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

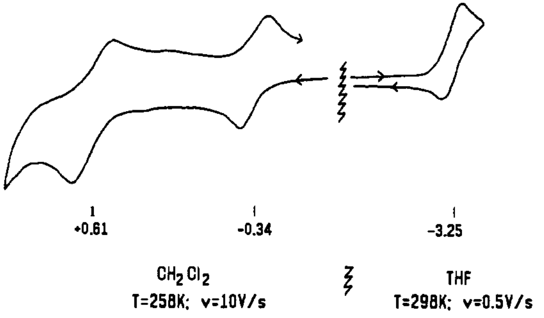


Figure 1. Cyclic voltammograms of ca. 0.5 mM RuRu at a Pt electrode: (left) in CH_2Cl_2, T = 258 K, v = 10 V/s; (right) in THF, T = 298 K, v = 0.5 V/s. Potentials are vs Fc.

The one-electron oxidation of RuRu in CH_2Cl_2 was facile ($E° = -0.34$ V vs Fc) and resulted in a stable monocation. Bulk electrolysis at 277 K ($E_{appl} = -0.1$ V) released 0.96 faraday/equiv and resulted in a blue solution characteristic of $RuRu^+$. The yield was apparently quantitative, judging from rotating Pt electrode (RPE) voltammograms prior to and after electrolysis. Reduction of the monocation ($E_{appl} = -0.5$ V) afforded the yellow-orange neutral complex with high efficiency. Similar results were obtained with CH_3NO_2 or THF (CV only) as solvents.

The second oxidation of RuRu was a chemically irreversible process at ambient temperatures. Voltammetry at 255 K showed that the current function ($i_p/Cv^{1/2}$) of the second wave decreased from that of a 2-e^- to that of a 1-e^- process as v, the scan rate, was increased.[17] Above about v = 20 V/s, the second oxidation was reversible (Figure 1), and a half-life of about 0.1 s was calculated for $RuRu^{2+}$ at 255 K (eq 3).

$$RuRu^{2+}\ (t_{1/2} = 0.1\text{ s}) \rightleftharpoons RuRu^+ \rightleftharpoons RuRu \rightleftharpoons RuRu^-\ (t_{1/2} = 0.4\text{ s}) \quad (3)$$

The cathodic process associated with this complex was only observed in THF owing to its quite negative potential ($E° = -3.25$ V). The 1-e^- nature of the reduction was established by comparison of its current function with that of $RuRu^{0/+}$. CV studies established a half-life of 0.4 s for $RuRu^-$ at 298 K, assuming a first-order decomposition rate.[18]

CoRu (**2**) also gave a completely reversible 1-e^- oxidation in CH_2Cl_2 ($E° = -0.04$ V), THF, or CH_3NO_2. Coulometric oxidation at 243 K in CH_2Cl_2 ($E_{appl} = 0.16$ V) resulted in a color

---

(15) Merkert, J. W. Ph.D. Dissertation, University of Vermont, 1992.

(16) Murray, R. W.; Heineman, W. R.; O'Dom, G. W. *Anal. Chem.* **1967**, *39*, 1666.

(17) The first wave characterized as $RuRu/RuRu^+$ served as a convenient 1-e^- standard.

(18) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

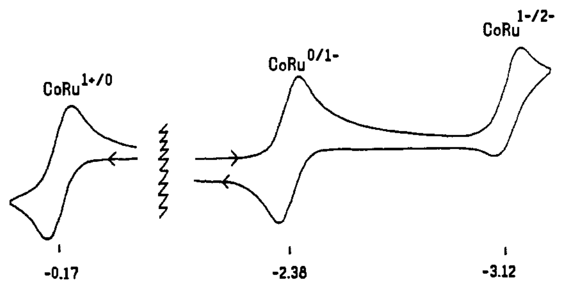


Figure 2. Cyclic voltammograms of ca. 0.5 mM CoRu in THF at ambient temperature (v = 0.2 V/s, Pt working electrode, potentials vs Fc).

Table III. Pertinent Electronic Spectral Data for RuRu and $RuRu^+$

complex	matrix	λ_{max} (nm)	$\bar{\nu}_{max}$ (10^3 cm^{-1})	a_M (10^3 cm^{-1} M^{-1})
RuRu	CH_2Cl_2	452	22.1	1.6
		362	27.6	5.6
RuRu	acetone	456	21.9	2.2
		367	27.2	8.4
$RuRu^+$	CH_2Cl_2/Bu_4NPF_6[a]	720	13.8	4.1
		560	17.9	1.6
		369	27.1	5.9
$RuRu^+$	CH_2Cl_2[b]	719	13.9	3.7
		562	17.8	1.4
$RuRu^+$	CH_3NO_2/Bu_4NPF_6[a]	725	13.8	4.0
		560	17.9	1.5
$RuRu^+$	acetone/Bu_4NPF_6[a]	725	13.8	4.9
		561	17.8	1.9
		373	26.8	5.9

[a] Sample prepared by electrolytic oxidation of RuRu in solvent containing 0.1 M supporting electrolyte. [b] Sample prepared by oxidation with equimolar $[Cp_2Fe][PF_6]$.

change from deep green to yellow-green with release of 1.1 faraday/equiv. Rereduction at E_{appl} = −0.2 V regenerated the original complex without decomposition. Bulk electrolysis in nitromethane gave a similar result at ambient temperatures. The second oxidation of CoRu was irreversible in CH_2Cl_2 (E_p = +0.9 V) with a multielectron peak height at scan rates up to 50 V/s.

Reduction of CoRu was best studied using THF, in which two 1-e$^-$ waves were observed (Figure 2). Their one-electron nature was established through comparison of the voltammetric current functions of the cathodic peaks referenced to that of the anodic wave for the coulometrically characterized CoRu/$CoRu^+$ couple. The monoanion $CoRu^-$ was stable on the CV time scale, but decomposition of the dianion $CoRu^{2-}$ was apparent over the same time frame based on the diminished return wave of the $CoRu^-/CoRu^{2-}$ couple. Equation 4 describes the electron-transfer series involving persistent forms of the cobalt–ruthenium complex.

$$CoRu^+ \rightleftharpoons CoRu \rightleftharpoons CoRu^- \rightleftharpoons CoRu^{2-} \ (t_{1/2} = 0.6 \text{ s}) \quad (4)$$

Table IV. Pertinent Electronic Spectral Data for CoRu and $CoRu^+$

complex	matrix	λ_{max} (nm)	$\bar{\nu}_{max}$ (10^3 cm^{-1})	a_M (10^3 cm^{-1} M^{-1})
CoRu	CH_2Cl_2	604	16.6	0.6
		439 (sh)	22.8	0.9
CoRu	acetone	619	16.2	0.9
		441 (sh)	22.7	1.6
CoRu	CH_3NO_2	618	16.2	0.7
		444 (sh)	22.5	1.2
$CoRu^+$	CH_2Cl_2/Bu_4NPF_6[a]	846	11.8	0.4
		~665[b]	15.0	0.7
		452	22.1	0.9
$CoRu^+$	CH_2Cl_2[c]	847	11.8	0.7
		~710[b]	14.1	0.9
		460	21.7	1.8
$CoRu^+$	CH_3NO_2/Bu_4NPF_6	862	11.6	0.9
		700	14.3	1.1
		462	21.6	2.0
$CoRu^+$	acetone/Bu_4NPF_6	854	11.7	0.9
		~672[b]	14.9	1.2
		449	22.3	2.1

[a] Matrices listing Bu_4NPF_6 were electrolysis solutions. [b] Two overlapping bands make this value hard to specify. [c] $CoRu^+$ generated by oxidation with equimolar $[Cp_2Fe][PF_6]$.

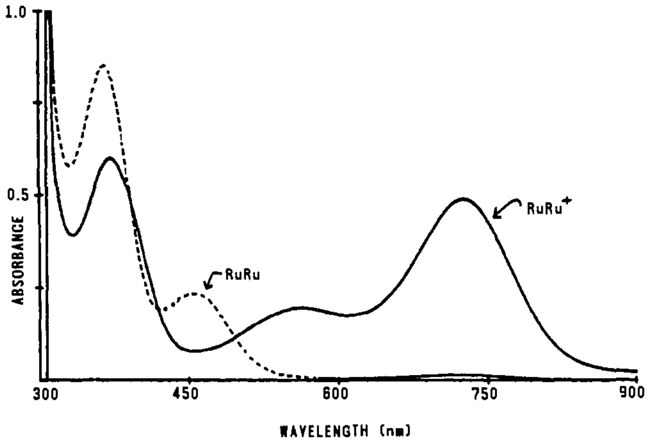


Figure 3. Optical spectra of RuRu and $RuRu^+$ obtained with the OTTLE cell in acetone/0.2 M Bu_4NPF_6, conc = 0.25 mM.

Electronic Spectra of Triple Deckers and Their Monocations. The optical spectra of RuRu, $RuRu^+$, CoRu, and $CoRu^+$ were recorded as a probe of mixed-valency type for the 29-e$^-$ monocations. Owing to the fact that the $E°$ of ferrocene is positive of that of either RuRu or CoRu, reaction of the neutral complexes with equimolar ferrocenium ion produced the desired monocations (eq 5). The triple-decker cations could be reduced back to the

$$M\text{-}M + Cp_2Fe^+ \rightarrow M\text{-}M^+ + Cp_2Fe \quad (5)$$

$$M\text{-}M^+ + Cp^*{}_2Fe \rightarrow M\text{-}M + Cp^*{}_2Fe^+ \quad (6)$$

neutral complexes by decamethylferrocene, which acts as a reducing agent owing to its $E°$ (ca. −0.57 V vs Fc) being negative of those of the triple deckers (eq 6). Quantitative conversions were obtained in all cases,[19] enabling studies of reasonably concentrated solutions (ca. 10 mM) at wavelengths down to 2000 nm with our Cary 14 spectrometer (details elsewhere[15]). Since the *lowest energy* band detected (λ_{max} = 862 nm, $\bar{\nu}$ = 11.8 × 10^3 cm^{-1}) was within the range of our more rapid scanning and more sensitive Perkin-Elmer spectrometer, a complete set of quantitative experiments was performed using the latter instrument, for which a transmission spectroelectrochemical cell (OTTLE) was fitted. The spectroelectrochemical experiments avoided the spectral interferences inherent to use of chemical oxidants and reductants. However, all spectral results are in agreement and internally consistent (Table III and IV).

Typical OTTLE spectra for RuRu and its oxidation products are shown in Figure 3. In the 1-e$^-$ oxidation, the visible bands of the neutral complex disappear (Figure 3, top) and two new bands appear in the (25–11) × 10^3 cm^{-1} range. The lowest energy band for $RuRu^+$ is an intense transition at $\bar{\nu}$ = 13.8 × 10^3 cm^{-1}, λ_{max} = 720 nm. This absorption was studied for possible assignment as an intervalence transition (IT) band.

Spectra of $RuRu^+$ generated in three different solvents (CH_2Cl_2, CH_3NO_2, acetone) showed no appreciable shift in the energy or shape of the long-wavelength band (Table III). Especially pertinent is the CH_2Cl_2 result, since its optical dielectric constant is appreciably different from that of either of the other two solvents. The solvent independence of this absorption argues against its being assigned as an IT band.[20]

---

[19] An exception involves $RuRu^+$ in acetone, which was shown by spectroelectrochemistry to result in significant amounts of a side product with $\bar{\nu}$ = 15.1 and 18.9 × 10^3 cm^{-1}, the half-life of $RuRu^+$ being 5–10 min in this solvent.

[20] Creutz, C. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley and Sons: New York, 1983; Vol. 30, p 1.

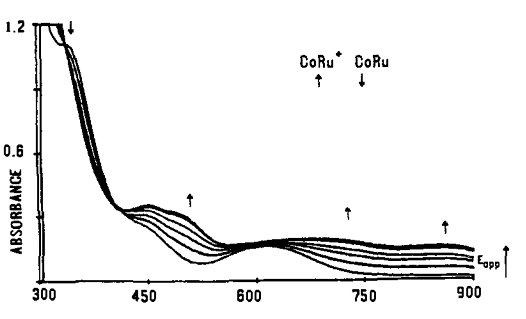


Figure 4. Optical spectra of CoRu and CoRu$^+$ obtained with the OTTLE cell poised at increasingly positive values of E_{appl}. From botton to top. E_{app} (V vs Ag/AgCl) = +0.20. +0.24. +0.26. +0.28, +0.30, +0.34; electrolyte = acetone/0.2 M Bu_4NPF_6.

Another key diagnostic is the bandwidth of the absorption, which should follow eq 7 for an IT band[21] (where $\Delta\nu_{1/2}$ is the width at half-height.

$$\Delta\nu_{1/2} = (2310\bar{\nu})^{1/2} \qquad (7)$$

The measured bandwidth of ca. 2.4 × 10^3 cm^{-1} is less than half that required for an IT band of this energy (5.6 × 10^3 cm^{-1}) for a class II[21] mixed-valent complex.

The optical spectra of RuRu$^+$ are therefore *inconsistent* with a trapped-valent class I or class II[22] characterization of this ion. We conclude that RuRu$^+$ must be classified as a class III (totally delocalized) mixed-valent complex with two formally Ru(II^1/$_2$)-valent metals.

Clean OTTLE spectra of CoRu$^+$ were also generated. Figure 4 gives typical spectra at various applied potentials. A Nernst plot[23] of the absorbance at 11.8 × 10^3 cm^{-1} as a function of E_{appl} gave the expected 1-e$^-$ slope. These spectra contain at least five bands in the vis–near-IR region. In considering whether they are indicative of trapped valence, the absorbances at energies below 16 × 10^3 cm^{-1} are crucial. Invoking trapped valence (class I or class II behavior) would require assignment of these bands either as (a) IT processes or (b) transitions localized on the oxidized redox site of one metal center, either a CpCo^{IV} or (arene)Ru^{III} site. A direct test of (b) was not possible because mononuclear analogues in these oxidation states (e.g., CpCo^{IV}(carboranyl) or (arene)Ru^{III} (carboranyl)) have lifetimes insufficient for facile spectral characterization.[23,24] However, other experiments and arguments strongly favor a class III mixed-valent description.

The lowest energy band again shows neither solvent dependence of its position (Table IV) nor the breadth expected for an IT band.[26] Furthermore, it is not expected that a Co(IV) or Ru(III) trapped valence site would give rise to such low-energy absorption bands. These points argue forcibly for a class III (delocalized) behavior in CoRu$^+$.

Electron Spin Resonance Spectra of RuRu$^+$, CoRu$^+$, and CoRu$^-$. ESR spectra of the 29-e$^-$ monocations were obtained at 77 K on frozen-solution samples prepared by oxidation of the 30-e$^-$ complexes with either [Cp_2Fe][PF_6] or anodic electrolysis, with identical results. Superior spectra of CoRu$^+$ were obtained when the solvent was a 1:1 mixture of CH_2Cl_2 and $C_2H_4Cl_2$ rather than CH_2Cl_2. Neither cation gave detectable fluid solution ESR spectra, but each was NMR active.[27] The 31-e$^-$ complex CoRu$^-$ was very air-sensitive and was prepared under vacuum by alkali metal reduction.

Table V. ESR Data on Frozen Solutions (T = 77 K) of Triple-Decker Ions from This work

ion	no. of valence e^{-1}	g values	A(Co) (10^{-4} cm^{-1})
RuRu$^+$	29	$g_\parallel = 2.293$	
		$g_\perp = 2.053$	
CoRu$^+$	29	$g_1 = 2.287$	44
		$g_2 = 2.067$	~0
		$g_3 = 2.020$	16
CoRu$^-$	31	$g_1 = 2.151$	121
		g_2. A_2 unresolved	
		$g_3 = 1.863$	65

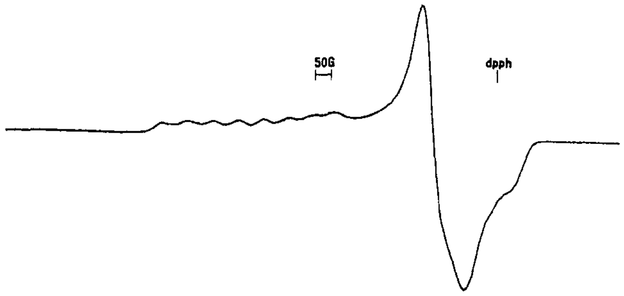


Figure 5. ESR spectrum of ca. 1 mM CoRu$^+$ in a 1:1 CH_2Cl_2:$C_2H_4Cl_2$ mixture at 77 K, prepared by oxidation of CoRu with equimolar [Cp_2Fe][PF_6].

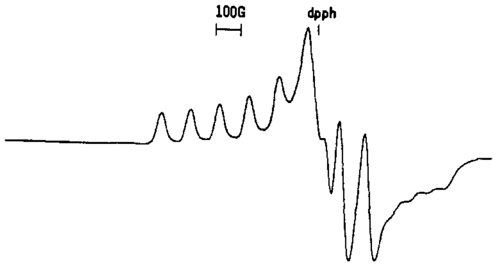


Figure 6. ESR spectrum of ca. 2 mM CoRu$^-$ in 2-MeTHF at 77 K, prepared by reduction of CoRu over a Na mirror at 200 K.

The **g** tensor of RuRu$^+$ was strictly axial: $g_\parallel$ = 2.293 and $g_\perp$ = 2.053, confirmed by simulations (Table V). The spectrum of CoRu$^+$, on the other hand, displays a rhombic **g** tensor (Figure 5). Simulations gave g_1 = 2.287, $g_2 \approx$ 2.067, and g_3 = 2.020. The cobalt hyperfine splitting ($I = {}^7/_2$, 100%) was 44 × 10^{-4} cm^{-1} for the low-field component A_1(Co); an estimate of 16 × 10^{-4} cm^{-1} was obtained from simulations for the high-field splitting, A_3(Co). These observations are consistent with a singly-occupied orbital (SOMO) in the monocations which is derived from a nearly degenerate pair of d_{xy}, $d_{x^2-y^2}$ orbitals (of e_2'' origin) which are delocalized over both metals (vide infra).

In the absence of a full theoretical treatment for d^5 Co(IV) in a ligand field of approximate cylindrical symmetry, and given the ambiguity of the signs of the Co hfs (since fluid solutions were ESR-silent), we make no estimate of the spin density on each metal in CoRu$^+$. Qualitatively, the splittings are rather small and suggest less Co character in the SOMO of the 29-e$^-$ cation than is found (vide infra) in the SOMO of 31-e$^-$ CoRu$^-$.

---

[21] Hush. N. S. In *Progress in Inorganic Chemistry*; Cotton. F. A., Ed.; John Wiley and Sons: New York. 1967; Vol. 8. p 391.

[22] Robin. M. B.; Day. P. In *Advances in Inorganic Chemistry and Radiochemistry*; Emeleus. H. J., Sharpe. A. G., Eds.; Academic Press: New York. 1967; Vol. 10. p 247.

[23] (a) Heineman. W. R.; Norris. B. J.; Goelz. J. F. *Anal. Chem.* **1975**, *47*, 79. (b) DeAngelis. T. P.; Heineman. W. R. *J. Chem. Educ.* **1976**, *53*, 594.

[24] [CpCo^{IV}($C_2B_4H_6$)]$^+$ and analogues: Geiger. W. E.; Brennan. D. E. *Inorg. Chem.* **1982**, *21*, 1963.

[25] [(*p*-MeC$_6$H$_4$CHMe$_2$)Ru(Et$_2$C$_2$B$_4$H$_4$)]$^+$: Merkert. J. W.; Geiger. W. E.; Attwood. M. D.; Grimes. R. N. *Organometallics* **1991**, *10*, 3545.

[26] For a heterodinuclear IT band. the width is predicted to be: $\Delta\bar{\nu}_{1/2} = [2310(\bar{\nu} - \Delta E°)]^{1/2}$, where $E°$ is the separation of potentials (in cm^{-1}) for the formal couples in the charge-transfer transition (see ref 21 and: Dowling. N.; Henry. P. M.; Lewis. N. A.; Taube. H. *Inorg. Chem.* **1981**, *20*, 2345). Assuming that a class II IT transition for CoRu$^+$ would involve a Co(III)–Ru(III) to Co(IV)–Ru(II) transition. a value of $\Delta E°$ = 2400 cm^{-1} (0.3 eV) may be used in this equation, based on Ru(II)/Ru(III) and Co(III)/Co(IV) potentials of sandwich carboranes given in refs 24 and 25. The observed half-bandwidths of (2.4–2.5) × 10^3 cm^{-1} are still much smaller than that predicted (4.6 × 10^3 cm^{-1}) and are therefore incompatible with assignment of this band as an intervalence transition.

[27] In CD_2Cl_2 at ambient temperature. RuRu$^+$ and CoRu$^+$ showed several broad proton resonances in the range +40 to −20 ppm. This behavior is typical of paramagnetic triple-decker complexes and is likely due to a rapid electronic relaxation rate of the complex.

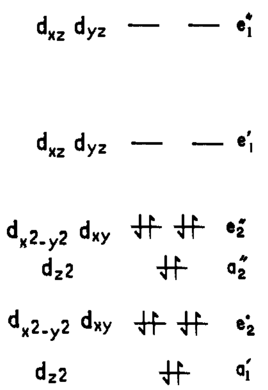


Figure 7. MO ordering proposed for RuRu and CoRu on the basis of the calculations of Lauher et al.[32] and modified to put e_2'' above a_2'', as required by ESR results on the 29-e^- complexes $RuRu^+$ and $CoRu^+$. Occupancy shown is for 30-e^- systems.

Spectra of $CoRu^-$ in frozen THF display two well-resolved components (Figure 6) with $g_1 = 2.151$, $A_1(Co) = 121 \times 10^{-4}$ cm^{-1}, and $g_3 = 1.863$, $A_3(Co) = 65 \times 10^{-4}$ cm^{-1}. Deviation from axial symmetry is apparent, but simulations of the g_2 component failed to yield values in which we had confidence. Fluid solutions in THF were ESR-silent. These spectral features are reminiscent of those observed for cobaltocene and its analogues.[28,29]

Cobaltocene has the same formal electronic configuration [d^7, Co(II)] as does $CoRu^-$ if we assign the SOMO in the latter to a predominantly Co orbital. A nearly-degenerate d_{xz}, d_{yz} pair is the likely candidate for the SOMO in both cases (vide infra). Ammeter has shown that interpretation of A and g values in terms of metal covalency factors is difficult for orbitally-degenerate or nearly-orbitally-degenerate radicals.[30] However, a number of such systems have been found to show a linear correlation between the values of Δg_z (= $g_e - g_z$) and A_z, assuming a constant metal covalency (orbital reduction) factor of 0.8.[31] Taking the g_z component from g_3[28], a value of $A_3(Co) = 76 \times 10^{-4}$ cm^{-1} is predicted for $CoRu^-$ from this relationship, close to the value of 65×10^{-4} cm^{-1} which is measured. We conclude that the SOMO of $CoRu^-$ is "cobaltocene-like" in character, with perhaps somewhat less electron density on Co than is found in Cp_2Co.

Electronic Structures and Ground States. Several theoretical treatments of the bonding in triple-decker complexes have appeared.[32-34] The original calculations by Lauher et al.[32] appear to be most relevant to the present situation, since they refer to complexes with a bridging ligand, $C_5H_5^-$, electronically similar to our $Et_2C_2B_3H_3^{4-}$[35] and predict the existence of complexes with >30 e^-.[36] The ESR results are nicely accommodated by this treatment.

A set of tightly packed d-orbitals, derived from the t_{2g} sets of the CpM fragments, is filled below the e_1' level in 30-e^- complexes (Figure 7). Occupancy of the weakly antibonding e_1' level allows complexes with up to 34-e^- counts. This level is expected to be destabilized somewhat in the carborane complexes. We show the e_2'' level as the HOMO in the 30-e^- complexes, whereas Lauher et al. computed this level to be slightly lower than the a_2''.[32] In all published treatments, these two levels are very close, and our ESR data on both 29-e^- systems is inconsistent with an a_2'' SOMO. Our data do not rule out an a_2'' HOMO in the *30*-e^- complexes, since orbital relaxation effects could invert the ordering of the two pertinent levels in the oxidized system.

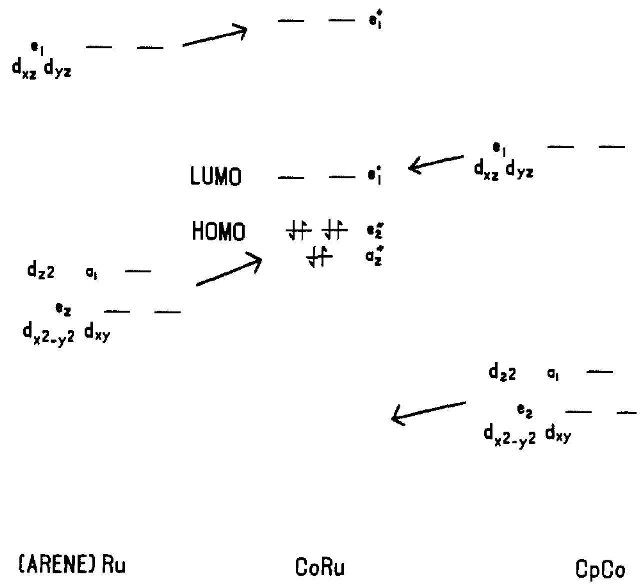


Figure 8. Qualitative MO interactions between the t_{2g} sets of (arene)Ru and (cyclopentadienyl)Co leading to the frontier orbitals shown for CoRu. Inclusion of the bridging carborane orbitals does not affect the order of the orbitals designated in this figure. The HOMO is predominantly Ru in character; the LUMO is predominantly Co.

The 29-e^- Cations $[(p\text{-}MeC_6H_4CHMe_2)_2Ru_2(Et_2C_2B_3H_3)]^+$ and $[CpCo(Et_2C_2B_3H_3)Ru(p\text{-}MeC_6H_4CHMe_2)]^+$. The two reasonable candidates for the SOMO in $RuRu^+$ and $CoRu^+$ are a_2'' (mostly d_{z^2}) and e_2'' (the $d_{x^2-y^2}$, d_{xy} pair). The former is characterized by (1) g values close to but below that of g_e, the free spin value, and (2) relatively sharp-line ESR spectra in fluid solutions arising from long electronic relaxation times. The latter have large g value anisotropies and rapid relaxation processes, making for very broad (and often undetectable) fluid solution spectra.[37] Clearly, $RuRu^+$ and $CoRu^+$ fit the expectations of radicals in the e_2'' ground state.[38]

The 31-e^- Anion $CpCo[Et_2C_2B_3H_3)Ru(p\text{-}MeC_6H_4CHMe_2)]^-$. When isolobal CpCo replaces (arene)Ru, the major changes in the MO scheme arise from differences in energy of the (π-ligand)M t_{2g} sets, rather than differences in metal–ligand covalency, since the pertinent orbitals have almost pure metal character. This simplifies our consideration of the qualitative MO scheme for $CpCo(Et_2C_2B_3H_3)Ru(p\text{-}MeC_6H_4CHMe_2)$.

Two factors indicate that the t_{2g} set for CpCo will be at lower energy than that of (arene)Ru: the first-row nature of the metal and the higher formal oxidation state. Mixing between the two t_{2g} sets is still symmetry allowed, but the bonding/antibonding pairs will retain more of the character (in orbital makeup and energies) of the sets from which they were derived. As shown in Figure 8, this means that the HOMO in 30-e^- CoRu will have more Ru character; the LUMO will have more Co character. Our ESR results are completely consistent with this description.

Concluding Remarks

Although a number of triple deckers with bridging hydrocarbons (Cp^- or arene) have been reported,[39] all reasonably stable odd-electron triple deckers contain group III or group V atoms in the

---

[28] Ammeter, J. H.; Swalen, J. D. *J. Chem. Phys.* **1972**, *57*, 678.

[29] (a) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882. (b) Castellani, M. P.; Geib, S. J.; Rheingold, A. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 1703.

[30] Ammeter, J. H. *J. Magn. Reson.* **1978**, *30*, 299.

[31] Ammeter, J. H.; Brom, J. M., Jr. *Chem. Phys. Lett.* **1974**, *27*, 380.

[32] Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

[33] Chesky, P. T.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 5186.

[34] (a) Tremel, W.; Hoffmann, R.; Kertesz, M. *J. Am. Chem. Soc.* **1989**, *111*, 2030. (b) Jemmis, E. D.; Reddy, A. C. *Organometallics* **1988**, *7*, 1561.

[35] Grimes, R. N. In *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH Publishers: New York, 1988; Chapter 11, pp 235–263 and references therein.

[36] The treatment of Tremel et al.,[34a] relating to triple deckers with a bridging P_5 central ring, resulted in a calculated inversion of the ordering of bonding a and e levels and favored lower stable electron counts: [$Cp^*Cr(\mu\text{-}P_5)Cp^*Cr$] and the corresponding cation have 28-e^- and 27-e^- counts, respectively.

[37] Warren, K. D. In *Structure and Bonding*; Dunitz, J. D., et al., Eds.; Springer-Verlag: Berlin, 1976; Vol. 27, p 45.

[38] Splitting of the e_2'' set into its two components is, of course, expected, with the separation of $d_{x^2-y^2}$ and d_{xy} being larger in the lower symmetry complex $CoRu^+$. We retain the e_2'' label in this treatment to follow the origin of this energy pair, consistent with common practice.

[39] Leading references to this family of compounds may be found in refs 33 and 34.

J. Am. Chem. Soc. **1992**, *114*, 9851–9858 9851

bridge.[1,40] The increased sturdiness of the heterocyclic-bridged polydeckers is central to their appeal as models for the study of delocalization in extended metal–π stacks.

The magnetic properties and ESR spectra of a number of odd-electron triple deckers with $C_3B_2R_5$ bridges were reported by Edwin and co-workers.[5] The 29-e⁻ complex $Cp_2FeCo(C_3B_2R_5)^+$ was shown to have a $^2E_{2g}$ ground state analogous to that of Cp_2Fe^+ (when proper allowance is made for reduction of symmetry upon substitution of $C_3B_2R_5^{3-}$ for $C_5H_5^-$).

Our 29-e⁻ systems $RuRu^+$ and $CuRu^+$ are isoelectronic with the above FeCo cation, and we draw a similar conclusion about the electronic ground state. [In fact, in these complexes, the e_2'' level is expected to split into a close-lying a′ ($d_{x^2-y^2}$) and a″ (d_{xy}) pair owing to the reduction of symmetry from D_{5d}. A single-crystal ESR study would be necessary to distinguish between the two possibilities.] Although the Mossbauer spectra of the FeCo cation suggested a large amount of Fe character in the SOMO, a Co hyperfine splitting in the low-field *g* component was observed (ca. 50×10^{-4} cm⁻¹). We find a similar feature in the ESR spectrum of $CoRu^+$. These observations suggest that, in 29-e⁻ triple deckers of Co and Fe (or Ru), the half-filled orbital is distributed over both metals, with the *dominant* contribution being from the iron-group metal.

The 31-e⁻ heterodinuclear complexes may also be compared: the present $CoRu^-$ with $Cp_2FeCo(C_3B_2R_5)^-$ and $Cp_2CoNi(C_3B_2R_5)^+$.[5] In all three cases, the observation of an ESR *g* component with a value of less than g_e eliminates a d_{z^2} SOMO[41] and argues strongly for d_{xz} or d_{yz}, descendant from the e_1' pair. However, the cobalt splittings vary greatly in this set of complexes. The iron-group complexes $CoRu^-$ and $Cp_2FeCo(C_3B_2R_5)^-$ have a large low-field splitting of ca. 120×10^{-4} cm⁻¹, whereas the same splitting in $Cp_2CoNi(C_3B_2R_5)^+$ is only 27×10^{-4} cm⁻¹. A tentative conclusion is that although these triple deckers show spin-delocalization when possessing odd-electron counts, the distribution of the unpaired electron is dependent on nuclear properties of the metals, and possibly on the properties of the bridging or capping ligands. Further investigation of these possibilities is warranted.

If these molecules are viewed as pentagonal bipyramidal clusters, our results also confirm two key predictions of Johnston and Mingos[42] for such systems, namely that (1) the HOMO/LUMO spacing of 30-e⁻ clusters is small, allowing electron counts in excess of 30, and (2) the LUMO of the 30-e⁻ system will always be doubly degenerate (or nearly so, depending on symmetry), whereas the HOMO may either be doubly degenerate (e-type) or singly degenerate (a-type).[42]

Finally, the observation of completely delocalized $RuRu^+$ and $CoRu^+$ cations is encouraging with respect to the construction of electroactive (and possibly magnetoactive) polymers incorporating carborane-bridged triple-decker or tetra-decker sandwich units.

Acknowledgment. We are grateful to the National Science Foundation for support of this research at both the University of Vermont (Grant CHE 86-03728 and 91-16332) and the University of Virginia (Grant CHE 90-22713).

---

(40) For stable 27-e⁻ complexes with bridging P_5 ligands, see: (a) Scherer, O. J.; Schwalb, J.; Wolmershaeuser, G.; Kaim, W.; Gross, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 363. (b) Scherer, O. J.; Schwalb, J.; Swarowsky, H.; Womershaeuser, G.; Kaim, W.; Gross, R. *Chem. Ber.* **1988**, *121*, 443.

(41) Reference 37, pp 110 ff.

(42) Johnston, R. L.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1987**, 647.

Mechanism of Formation of C–C Bonds in the Ring Opening and Coupling of Thiophene by $(C_5Me_5)Rh(C_2H_4)_2$

William D. Jones* and R. Martin Chin

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. *Received June 1, 1992*

Abstract: Thermolysis of $(C_5Me_5)Rh(C_2H_4)_2$ in the presence of thiophene leads to the formation of the new product. $[(C_5Me_5)Rh]_2[1,2,3,4\text{-}\eta^4\text{-}5,6,7,10\text{-}\eta^4\text{-}S(CH)_8S]$. The related reaction with dibenzothiophene leads first to the sulfur-bridged C–S-inserted cis dimer $[(C_5Me_5)Rh(\mu_2\text{-}\eta^2\text{-}SC_{12}H_8)]_2$ and then to the trans dimer of the same formula. These complexes have been structurally characterized, with the cis complex crystallizing in monoclinic space group $C2/c$ with $a = 16.323$ (6) Å, $b = 15.355$ (5) Å, $c = 14.646$ (5) Å, $\beta = 92.61$ (3)°, $Z = 4$, and $V = 3666.8$ (4.1) Å³. The trans isomer crystallizes in triclinic space group $P\bar{1}$, with $a = 9.995$ (3) Å, $b = 10.290$ (2) Å, $c = 11.230$ (2) Å, $\alpha = 112.02$ (1)°, $\beta = 97.99$ (2)°, $\gamma = 114.66$ (2)°, $Z = 1$, and $V = 911.2$ (1.1) Å³. The reaction of $(C_5Me_5)Rh(C_2H_4)_2$ with 2-methoxythiophene is found to lead to the monomer $(C_5Me_5)\overline{\mathrm{Rh}[\mathrm{C(OMe)}{=}\mathrm{CHCH}{=}\mathrm{CHS}}]$, which is in equilibrium with the corresponding cis and trans sulfur-bridged dimers. The rate of cleavage of the cis dimer to give the monomer at 22 °C is 3.12 (12) × 10^{-3} s⁻¹. The rate of cleavage of the trans dimer to give the monomer at 22 °C is 1.25 (4) × 10^{-5} s⁻¹. Equilibrium parameters for the cis ⇌ monomer equilibrium are $\Delta H° = 7.0$ (0.7) kcal/mol and $\Delta S° = 19$ (2) eu. Equilibrium parameters for the trans ⇌ monomer equilibrium are $\Delta H° = 10.4$ (0.7) kcal/mol and $\Delta S° = 28$ (2) eu. An X-ray structural determination of the cis dimer shows the complex to crystallize in triclinic space group $P\bar{1}$, with $a = 8.335$ (4) Å, $b = 10.096$ (3) Å, $c = 19.832$ (5) Å, $\alpha = 89.54$ (2)°, $\beta = 78.49$ (3)°, $\gamma = 67.97$ (3)°, $Z = 2$, and $V = 1511.9$ (2.1) Å³. The trans dimer crystallizes in triclinic space group $P\bar{1}$, with $a = 10.814$ (3) Å, $b = 10.816$ (5) Å, $c = 16.301$ (4) Å, $\alpha = 84.79$ (3)°, $\beta = 88.15$ (2)°, $\gamma = 68.79$ (3)°, $Z = 2$, and $V = 1770.1$ (2.2) Å³. These structures are discussed with regard to the mechanism of the C–C bond forming reaction.

Introduction

The reactions of thiophenes with transition metals as models for studying the hydrodesulfurization of petroleum have become of increased interest over the past few years.[1] A variety of coordination modes of thiophene have been exhibited and structurally characterized,[2] and reactions in which the ring has been cleaved by attack of external reagents have been reported.[3] More

---

(1) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387–394. Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394–400.

(2) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61–76. Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259–329.

0002-7863/92/1514-9851$03.00/0