Dynamics of Agostic Complexes of the Type $C_5R_5(C_2H_4)M(CH_2CH_2\text{-}\mu\text{-}H)^+$. Energy Differences between and Ancillary Ligand Control of Agostic and Terminal Hydride Structures

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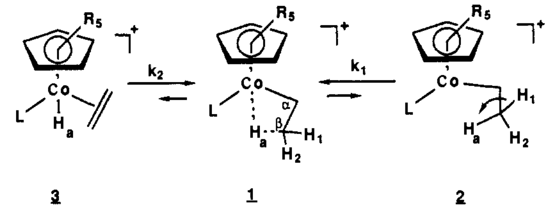
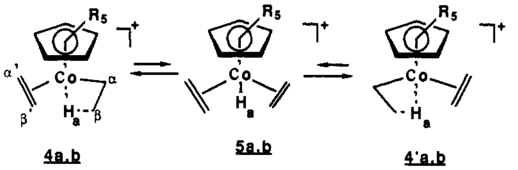
Abstract: The degenerate interconversions of the two enantiomeric forms of agostic $C_5R_5(C_2H_4)Co(CH_2CH_2\text{-}\mu\text{-}H)^+$ (**4a**, R = CH_3; **4b**, R = H) have been investigated by ^{13}C NMR spectroscopy at 100.6 MHz in the temperature range -80 to -100 °C. Very substantial line broadening of the olefinic carbon resonances is observed in this temperature range. By estimating ^{13}C chemical shifts for the static species and applying the fast-exchange equation, we determined free energies of activation for this process as ca. 5.3 kcal/mol for both **4a** and **4b**. Since the rearrangements must proceed via the symmetrical terminal hydrides $C_5R_5Co(C_2H_4)_2(H)^+$ (**5a,b**), 5.3 kcal/mol represents a maximum energy difference between the agostic and terminal hydride structures. The analogous rhodium complex has been shown to possess the agostic structure $C_5Me_5(C_2H_4)Rh(CH_2CH_2\text{-}\mu\text{-}H)^+$ (*6*), but the barrier for degenerate isomerization via the terminal hydride is <3.7 kcal/mol, indicating an even smaller difference between the terminal and agostic forms relative to the cobalt species. Since complexes of the type $C_5R_5(L)Rh(C_2H_4)H^+$ (L = PR_3, $P(OR)_3$) are terminal hydrides, these rhodium systems represent a unique case where agostic and terminal hydride structures are sufficiently close in energy that the stable form observed can be altered by small changes in the ancillary ligand.

Scheme I



L = PMe_3, $P(OMe)_3$, CH_2CH_2
R = H, CH_3

Scheme II



Intermediate or transition state

(a) R = CH_3
(b) R = H

Cobalt complexes of type **1** (see Scheme I) are among a growing class of transition-metal compounds that contain an agostic ethyl group involving a three-center, two-electron bond between the metal center and a β-CH bond.[1-14] These cobalt complexes[8-13] are of particular interest since they are homogeneous ethylene polymerization catalysts[9-11] whose mechanism of polymerization has been elucidated by ^1H and ^{13}C NMR spectroscopic studies.[10,11]

Dynamic NMR investigations of these complexes establish that H_a, H_1, and H_2 undergo site exchange with free energies of activation between 10.3 and 12.5 kcal/mol and that C_α exchanges with C_β with ΔG^* values between 12.2 and 15.6 kcal/mol.[1a,8-11,13] Exchange of H_a, H_1, and H_2 has been assumed to occur via the 16-electron species **2** (Scheme I). An "in-place" methyl rotation is also possible in which the C_β–Co bond distance remains essentially fixed during rotation.[13,15] The C_α,C_β averaging process must proceed via formation of a classical hydride **3**, followed by ethylene rotation and rebridging. Thus, as shown in Figure 1, the measured ΔG^* is the sum of ΔG_{eq}, the difference in free energies between the agostic and terminal hydride structures, and ΔG^*_{rot}, the free energy of activation for ethylene rotation.

The free energy difference between **1** and **3** is of importance with respect to developing a quantitative understanding of the energetics of agostic versus classical ethylene hydride structures. Analysis of various dynamic data[8,13] suggests ΔG_{eq} is probably less than ca. 7-10 kcal/mol. The most informative observations are those made by Brookhart, Green, and Pardy in connection with the rapid, degenerate equilibrium between **4a** and **4'a**

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Table I. ^{13}C Chemical Shifts and J Values for **4a**, **4b**, 6[a]

complex	C_β,C_β'	C_α,C_α'	C_5R_5	C_5R_5
4a	27.8 (151 Hz, $J_{C\text{-}H}$; 33 Hz, $J_{C\text{-}H_a}$)	52.5 (160 Hz, $J_{C\text{-}H}$)	100 (singlet)	9.0 (128 Hz, $J_{C\text{-}H}$)
4b	23.6 (154 Hz, $J_{C\text{-}H}$; 27 Hz, $J_{C\text{-}H_a}$)	48.2 (164 Hz, $J_{C\text{-}H}$)	89.2 (185 Hz, $J_{C\text{-}H}$)	
6	31 (153 Hz, $J_{C\text{-}H}$; 30 Hz, $J_{C\text{-}H_a}$; 5 Hz, $J_{Rh\text{-}C}$)	52 (160 Hz, $J_{C\text{-}H}$; 11 Hz, $J_{Rh\text{-}C}$)	103 (singlet)	9.0 (128 Hz, $J_{C\text{-}H}$)

[a] All spectra run at 100.586 MHz on a Varian XL-400 in CD_2Cl_2, −80 °C.

Table II. Line Widths of the C_β,C_β' and C_α,C_α' Resonances of **4a**, **4b**, and 6 as a Function of Temperature and Rate Constants and $\Delta G^\ddagger$ Values for Site Exchange

complex	T, °C	C_β,C_β' line width	k,[d] s^{-1}	$\Delta G^\ddagger$, kcal/mol	C_α,C_α' line width	k,[d] s^{-1}	$\Delta G^\ddagger$, kcal/mol
4a[a]	−99	104	8.5×10^5	5.3	21	2.9×10^6	4.9
	−89	69	1.5×10^6	5.4	16	4.3×10^6	5.1
	−79	35	4.8×10^6	5.3	11	8.5×10^6	5.1
4b[a]	−94	109	1.2×10^6	5.3	45	1.5×10^6	5.2
	−89	78	2.4×10^6	5.2	29	3.2×10^6	5.1
6[b]	−129	25[c]	$>8.6 \times 10^6$	<3.7	29[c]	$>4.2 \times 10^6$	<3.9

[a] CD_2Cl_2 used as the solvent. Spectra were acquired at 100.568 MHz. [b] A 50/50 CD_2Cl_2/Me_2O mixture was employed as a solvent. Spectra acquired at 100.568 MHz. [c] Within experimental error of the natural line width. [d] Calculated from the fast-exchange limit (eq 1); see text.

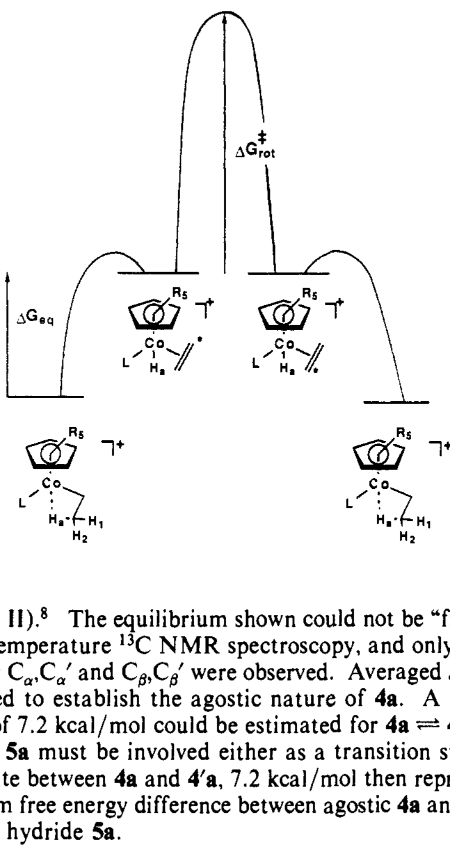


Figure 1.

(Scheme II).[8] The equilibrium shown could not be "frozen out" by low-temperature ^{13}C NMR spectroscopy, and only averaged shifts for C_α,C_α' and C_β,C_β' were observed. Averaged J_{CH} values were used to establish the agostic nature of **4a**. A maximum barrier of 7.2 kcal/mol could be estimated for **4a** $\rightleftharpoons$ **4'a**. Since classical **5a** must be involved either as a transition state or intermediate between **4a** and **4'a**, 7.2 kcal/mol then represents the maximum free energy difference between agostic **4a** and terminal ethylene hydride **5a**.

We report here very low temperature ^{13}C NMR studies of **4a** and its C_5H_5 analogue **4b** at high fields that allow the barriers of interconversion of the agostic species to be determined. In addition the structure and dynamics of the analogous agostic rhodium complex $Cp^*(C_2H_4)Rh(CH_2CH_2\text{-}\mu\text{-}H)^+$ (**6**) are described and compared with those of the cobalt systems. These results provide a quantitative assessment of the energy difference between agostic and terminal hydride structures and, in the case of the rhodium systems, show that small changes in the ancillary ligand can induce a change in the stable form of the hydride from agostic to terminal.

Results

A. Variable-Temperature Spectra of 4a,b. The complexes **4a** and **4b** were generated by protonation of the bis(ethylene) complexes $C_5Me_5Co(C_2H_4)_2$ and $C_5H_5Co(C_2H_4)_2$ with $HBF_4{\cdot}Me_2O$. ^{13}C spectra at 100.568 MHz were recorded between −50 and −109 °C. At −80 °C the equilibrium shown in Scheme II is rapid on an NMR time scale, and average resonances are observed for C_α,C_α' and C_β,C_β'. Complete ^{13}C data are summarized in Table I. Data for **4a** match those previously reported.[8] The shifts and J_{CH} values for C_α,C_α' and C_β,C_β' in **4b** are similar to those in **4a**. The averaged ^{13}C–H coupling between $^{13}C_\beta,C_\beta'$ and H_a of 27 Hz establishes the agostic structure for **4b**.

As the temperature is decreased, the sharp lines at 28 (**4a**) and 24 ppm (**4b**) of the C_β,C_β' averaged bands begin to broaden severely. The C_α,C_α' bands broaden, but to a lesser extent than the C_β,C_β' bands. The remaining lines in the spectrum (CH_3, C_{ring} for **4a**; C_{ring} for **4b**) remain sharp at all temperatures, indicating little viscosity broadening of the signals. The line-broadening process is completely reversible. Static spectra with separate signals for C_β,C_β' and C_α,C_α' could not be recorded because the salts precipitated and the solvent froze below −109 °C.

A summary of the C_β,C_β' and C_α,C_α' line widths at half-height for **4a** and **4b** as a function of temperature is given in Table II. Using these linewidths, one can apply the equation for two-site exchange in the fast-exchange region (eq 1) to determine the rate

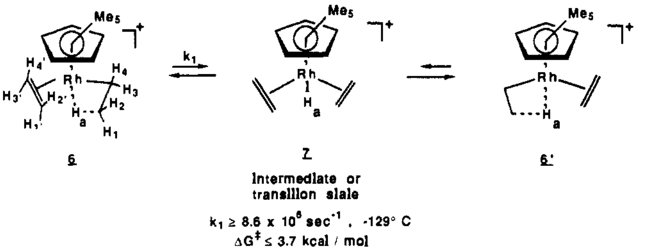
$$k = \frac{\pi(\nu_A - \nu_X)^2}{2(W - W_f)} \qquad (1)$$

of site exchange of C_β with C_β' and C_α with C_α'. In addition to the line widths, the resonance frequencies of C_β, C_β', C_α, and C_α' must be known in the static system to determine $\nu_A - \nu_X$. Although these cannot be measured due to temperature limitations, they can be accurately estimated. Complexes of type **1** (R = H, CH_3, L = PR_3, $P(OR)_3$) provide excellent models for the expected shifts of C_α and C_β. All C_β values fall in the range δ −4.7 to −9.6 while all C_α values fall in the range δ 20.4–26.5.[8-13] Using predicted values of δ −5.8 and 26.5 for C_β and C_α, respectively, of **4a** and the averaged C_β,C_β' and C_α,C_α' values (see Table I), one can estimate the shifts of C_β' and C_α' as δ 61.4 and 78.5. Thus $\nu_{C_\beta} - \nu_{C_\beta'} = 6758$ Hz and $\nu_{C_\alpha} - \nu_{C_\alpha'} = 5229$ Hz at 100.568 MHz. Similarly, for **4b** estimated values are C_α (δ 21.7), C_α' (δ 74.7), C_β (δ −9.2), C_β' (δ 56.4), $\nu_{C_\beta} - \nu_{C_\beta'} = 6597$ Hz, and $\nu_{C_\alpha} - \nu_{C_\alpha'} = 5330$ Hz.

The rate constants for exchange calculated with eq 1 are listed in Table II for various temperatures.[16] $\Delta G^\ddagger$ values corresponding to these rate constants are also given. Several points should be noted about these calculations. First, since there is a much greater frequency difference between C_β and C_β' than between C_α and C_α', the C_β,C_β' line broadens much faster than the C_α,C_α' line. Thus rates calculated from the C_β,C_β' line widths are probably somewhat more accurate than those based on C_α,C_α'. In addition, since the shift difference between C_β and C_β' is so enormous, a moderate error in estimating shifts in the static spectrum will result in little change in the calculated rate. Similarly, line broadening is sufficiently large, especially for the C_β,C_β' line, that small errors in estimating W_f, the natural line width, will not result in significant errors in k.[17]

B. Variable-Temperature NMR Spectra of $C_5Me_5Rh(C_2H_4)_2H^+$ (6). Complex **6** was generated by protonation of $(C_5Me_5)Rh(C_2H_4)_2$ with $HBF_4{\cdot}Me_2O$ in CD_2Cl_2. To record spectra below −109 °C, solutions were diluted with ca. 50% Me_2O. Spectra

Scheme III



6

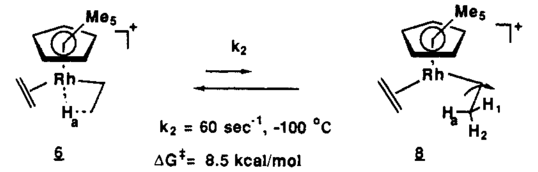
7

Intermediate or transition state

6'

$k_1 \geq 8.6 \times 10^6$ sec^{-1}, -129° C
$\Delta G^{\ddagger} \leq 3.7$ kcal / mol

Scheme IV



6

8

$k_2 = 60$ sec^{-1}, -100 °C
$\Delta G^{\ddagger} = 8.5$ kcal/mol

recorded in the temperature range of ca. -80 °C are quite similar to those of the cobalt complex **4** and are consistent with an agostic structure exhibiting very rapid interchange between **6** and **6'** (Scheme III). ^{13}C data for rapidly equilibrating **6** ⇌ **6'** are summarized in Table I. The observation of a 30-Hz coupling between H_a and C_β,C_β' clearly indicates an agostic structure with $J_{CH}(av) - [60 \text{ Hz } (J_{C_\beta H_a}) + 0 \text{ Hz } (J_{C_\beta H_a})]/2 = 30$ Hz. The ^1H NMR spectrum is consistent with **6** ⇌ **6'** and exhibits a high-field band for H_a at -8.6 ppm, four two-proton multiplets (2.73 (H_3,H_3' or H_4,H_4'), 2.56 (H_4,H_4' or H_3,H_3'), 1.85 (H_1,H_1' or H_2,H_2'), 1.38 (H_2,H_2' or H_1,H_1')), and a 15H methyl singlet at 1.75 ppm.

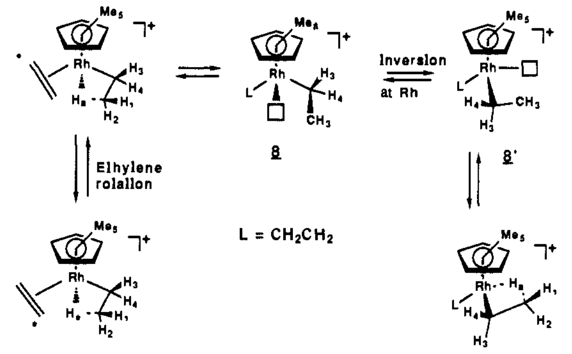
An attempt was made to assess the rate of interconversion of **6** with **6'** using the same ^{13}C NMR technique as was used for **4**. Very low temperature ^{13}C NMR spectra were recorded in an effort to detect line broadening of the C_β,C_β' and C_α,C_α' lines. However, even at temperatures as low as -129 °C these lines do not broaden noticeably relative to the CH_3 and C_{ring} lines. Line broadening of 10 Hz would have readily been detected. Assuming a broadening of <10 Hz, a minimum rate of interconversion of **6** ⇌ **6'** can be calculated by using the fast-exchange equation (eq 1) and making a similar estimation of $\nu_{C_\beta} - \nu_{C_\beta'}$ as with **4** ⇌ **4'**:

$$k_{min} = \frac{\pi(7380)^2}{2(10 \text{ s}^{-1})} = 8.6 \times 10^6 \text{ s}^{-1} \text{ at } -129 \text{ °C}$$

This minimum rate corresponds to a maximum free energy difference between agostic hydride **6** and terminal hydride **7** of 3.7 kcal/mol.[16]

As the temperature is raised, two other dynamic processes can be detected by ^1H and ^{13}C NMR spectroscopy. These processes have close analogy in the cobalt system **4a**. The first involves averaging of H_a with H_1,H_1',H_2,H_2'. The rate of this process can be measured by applying the slow-exchange equation to the broadening of H_a in the temperature range -90 to -100 °C. Values of the line width at half-height (corrected for the natural line width) are 19 (-100 °C) and 175 Hz (-90 °C), which correspond to rate constants k_2 of 60 (-100 °C) and 550 s^{-1} (-90 °C) and $\Delta G^{\ddagger}$'s of 8.5 and 8.3 kcal/mol, respectively. The simplest mechanism that explains this averaging process is migration of H_a to C_β to form the 16-electron complex **8** (Scheme IV). This migration coupled with the rapid **6** ⇌ **6'** process results in scrambling of the five hydrogen atoms H_a, H_1, H_2, H_1', and H_2'.

Scheme V



8

8'

L = CH_2CH_2

An alternate mechanism involves "in-place" rotation[13,15] of the agostic methyl group in **6** coupled with rapid **6** ⇌ **6'**.

The last dynamic process results in averaging of all ten hydrogens and the four carbons C_α, C_α', C_β, and C_β'. Complex **6** is substantially more thermally stable than **4**, and higher temperature spectra can be recorded. Thus at -20 °C a broad 9H signal is observed at 1.05 ppm, which corresponds to the average of H_1, H_1', H_2, H_2', H_3, H_3', H_4, H_4', and H_a. The signal sharpens as the sample is warmed. The activation barrier for the 9H exchange process is determined by low-temperature ^1H NMR. At -90 °C the two ^1H NMR signals for H_3,H_3', and H_4,H_4' are sharp, while those of H_1,H_1', H_2,H_2', and H_a are severely broadened due to the rapid 5H exchange process. As the temperature is increased from -90 to -70 °C, the α-hydrogen signals broaden as the rate of the 9H scrambling process increases. This rate can be measured by applying the slow-exchange equation to the line broadening of H_3,H_3' and H_4,H_4' resonances. Rate constants k_3 of 198 (-70 °C) and 60 s^{-1} (-80 °C) were determined, which correspond to a $\Delta G^{\ddagger}$ of 9.6 kcal/mol.

The mechanism of the 9H exchange process involves the coupling of the lower energy 5H exchange process with either an ethylene rotational process or an inversion of the Rh center in the 16-electron intermediate **8** (Scheme V).

Discussion

The results presented here support the following observations with respect to fundamental aspects of the structure and dynamics of the agostic cobalt and rhodium ethyl complexes.

(1) For the first-row cobalt systems **4a** and **4b**, there is at most a ca. 5.3 kcal/mol free energy difference between the symmetrical terminal hydride structure and the more stable agostic isomer. If the terminal hydride is an *intermediate* between **4a,b** and **4'a,b**, then the difference between the terminal and agostic hydride structures is even smaller. Substitution of ethylene by PR_3 or $P(OR)_3$ in the cobalt systems[10-13] does *not* result in a change in the stable form from the bridged to terminal structure, in contrast with the behavior of the rhodium system (see below).

(2) The analogous second-row rhodium system $C_5Me_5Rh(CH_2CH_2)(CH_2CH_2\text{-}\mu\text{-}H)^+$ is agostic but with an even lower free energy difference between agostic and terminal hydride forms (<3.7 kcal/mol). This is in line with the general expectation that second-row metal complexes will favor terminal hydride structures relative to their first-row analogues.[1]

(3) Rhodium systems of the general type $(C_5Me_5)(L)Rh(CH_2CH_2)(H)^+$ represent a unique case where the energy difference between the agostic and terminal hydride forms is so small that the precise structure that the complex adopts can be controlled by small variations in the ancillary ligand, L. While the complexes $C_5R_5(L)Rh(CH_2CH_2)H^+$ (C_5H_5, L = PMe_3;[18] C_5Me_5, L = PMe_3,[19] PPh_3,[19] $P(OMe)_2(Ph)$,[19] $P(OMe)_3$[20]) are all terminal hydrides, substitution of PR_3 by C_2H_4 results in the agostic structure, **6**, being the more stable isomer. This change is most simply explained by supposing that the increased π-acidic character

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[16] The rate constants calculated refer to the degenerate rates of interconversion of **4a,b** with **4'a,b**; i.e., *k* for **4a,b** ⇌ **4'a,b** (see Scheme II). If the diene hydride **5a,b** is a true *intermediate* in the interconversion of **4a,b** and **4'a,b**, then the rate of formation of **5a,b** from **4a,b** (or **4'a,b**) is twice the exchange rate since, once formed, **5a,b** has an equal probability of returning to **4a,b** or giving **4'a,b**. A similar analysis applies to the rhodium system shown in Scheme III.

[17] For example, when one calculates the rate constant *k* and $\Delta G^{\ddagger}$ for $C_5Me_5Co(CH_2CH_2)(CH_2CH_2\text{-}\mu\text{-}H)^+$ using broadening of C_α, a 25% error in the estimation of $\nu_A - \nu_X$ results in a ±0.15 kcal/mol change in $\Delta G^{\ddagger}$. A 25% error in the measurement of ΔW results in a ±0.20 kcal/mol change in $\Delta G^{\ddagger}$.

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[19] Lincoln, D. M.; Brookhart, M., unpublished results.

[20] Brookhart, M.; Lincoln, D. M. *J. Am. Chem. Soc.* **1988**, *110*, 8719.

of C_2H_4 renders the rhodium center more electrophilic, which favors a bridging M- - -H- - -C interaction.

Experimental Section

General Information. All complexes were manipulated under an atmosphere of dry, oxygen-free nitrogen within a Vacuum Atmospheres drybox or using standard Schlenk technique. Solvents were dried and degassed prior to use. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer. $C_5Me_5Co(CH_2CH_2)_2$, $C_5Me_5Rh(CH_2CH_2)_2$, and $C_5H_5Co(CH_2CH_2)_2$ were prepared by published procedures.[21-23]

Generation and NMR Characterization of Complexes 4a, 4b, and 6. $Co(C_5Me_5)(CH_2CH_2)(CH_2CH_2\text{-}\mu\text{-}H)^+BF_4^-$ (4a). $C_5Me_5Co(CH_2CH_2)_2$ (30 mg, 0.12 mmol) was dissolved in 5 mL of diethyl ether, and the solution was cooled to −30 °C. $HBF_4{\cdot}Me_2O$ (0.156 mmol) dissolved in 2.0 mL of ethyl ether was slowly syringed into the ether solution of the cobalt complex. $C_5Me_5Co(CH_2CH_2)(CH_2CH_2\text{-}\mu\text{-}H)^+BF_4^-$ began immediately to precipitate from solution. The solution was cooled to −78 °C and allowed to stand for 15 min to ensure complete precipitation. The ether was decanted from the precipitate, and the precipitate was washed with two 5-mL portions of cold ether. The precipitate was dried under vacuum at −30 °C, cooled to −78 °C, and dissolved in 0.8 mL of CD_2Cl_2. The solution was transferred by cannula to a precooled (−78 °C) 5-mm NMR tube equipped with a side arm and blanketed by nitrogen. The sample was sealed under vacuum at liquid nitrogen temperatures. The NMR tube was warmed to −78 °C prior to introduction into a precooled (−80 °C) NMR probe. ^{13}C NMR (−80 °C, CD_2Cl_2) δ 27.8 (td, J_{CH} = 151, 33 Hz, C_β,C_β'), 51.0 (t, J_{CH} = 150 Hz, C_α,C_α'), 100.0 (s, C_5Me$_5$), 9.0 (q, J_{CH} = 128 Hz, C$_5Me_5$). The ^1H NMR spectrum matches that previously reported.[8]

$Co(C_5H_5)(CH_2CH_2)(CH_2CH_2\text{-}\mu\text{-}H)^+BF_4^-$ (4b). NMR samples of **4b** were prepared as for **4a** using 30 mg (0.17 mmol) of $C_5H_5Co(CH_2CH_2)_2$ and 1.3 equiv (0.21 mmol) of $HBF_4{\cdot}Me_2O$. ^{13}C NMR (−90 °C, CD_2Cl_2) δ 23.6 (td, J_{CH} = 154 Hz, 27 Hz, C_β,C_β'), 48.2 (t, J_{CH} = 164 Hz, C_α,C_α'), 89.2 (d, J_{CH} = 185 Hz, C_5H_5).

$Rh(C_5Me_5)(CH_2CH_2)(CH_2CH_2\text{-}\mu\text{-}H)^+BF_4^-$ (6). The NMR sample was prepared as for **4a** using 30 mg (0.10 mmol) of $Rh(C_5Me_5)(CH_2CH_2)_2$ and 1.3 equiv (0.13 mmol) of $HBF_4{\cdot}Me_2O$. The following variations in sample preparation were used. The extraction of the salt with CD_2Cl_2 was performed with 0.4 mL of CD_2Cl_2 for the preparation of 6. Me_2O (0.4 mL) was condensed into the NMR tube (−78 °C) and mixed with 0.4 mL of the CD_2Cl_2 solution of the cationic rhodium complex prior to sealing the sample. The Me_2O lowered the solution freezing point to ca. −135 °C. ^1H NMR (−110 °C, CD_2Cl_2) δ −8.6 (br, s, H_a), 1.38 (m, H_1,H_1' or H_2,H_2'), 1.85 (m, H_2,H_2' or H_1,H_1'), 2.56 (m, H_3,H_3' or H_4,H_4'), 2.73 (m, H_4,H_4' or H_3,H_3'), 1.75 (s, C$_5Me_5$). ^{13}C NMR (−129 °C, CD_2Cl_2/Me_2O) δ 8.5 (q, J_{CH} = 128 Hz, C$_5Me_5$), 103.5 (s, C_5Me$_5$), 52.0 (dt, J_{CH} = 160 Hz, J_{RhC} = 11 Hz, C_α,C_α'), 31.0 (ddt, J_{CH} = 153, 30 Hz, J_{RhC} = 5 Hz, C_β,C_β').

Acknowledgment is made to the National Science Foundation (Grant CHE-8705534) and Johnson Matthey for the gift of $RhCl_3$.

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Photochemical Generation of Radical Cations from α-Terthienyl and Related Thiophenes: Kinetic Behavior and Magnetic Field Effects on Radical-Ion Pairs in Micellar Solution[1]

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Abstract: The photochemistry of α-terthienyl (αT) and related compounds has been examined in homogeneous solution and in anionic micelles in the presence of electron acceptors. The absorption spectra of the radical cations from four thiophenic substrates have been characterized; for example, those derived from α-bithienyl (αB) and αT show absorption maxima at 420 and 530 nm, respectively. Triplet quenching by acceptors such as methyl viologen (MV^{2+}) and tetracyanoethylene approaches diffusion control ($k > 5 \times 10^9\ M^{-1}\ s^{-1}$). Quenching by oxygen, which is known to be dominated by singlet oxygen sensitization, involves electron transfer only to a minor extent; the highest efficiency, for αB, was only 6%. In micellar systems the behavior of the radical-ion pairs produced via electron transfer involves the competition of geminate and exit processes which occurs in the 10^{-7}–10^{-6} s time domain. Both processes are slower in the larger micelles. Geminate processes are dramatically affected by magnetic fields. A model is proposed where the rate of geminate processes is suggested to depend upon the intramicellar reencounter frequency for the pair and the degree of singlet character in the triplet-derived radical-ion pair. The magnetic field effects observed are consistent with such a model.

α-Terthienyl (αT) and structurally related compounds are secondary plant metabolites[3] which are the subject of considerable interest because of their phototoxicity and possible insecticidal applications.[4-6] It is now well established that the lowest triplet states of αT and its analogues are excellent singlet oxygen sensitizers,[6,7] and their energy-transfer properties have been studied in considerable detail.[7e,f,8] It is now believed that the phototoxicity of αT in vivo is a direct result of αT's ability to generate singlet oxygen.[7f,9]

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(1) Issued as NRCC 30759.

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