

Dynamic NMR Studies of the Restricted Rotation of Thiophenes (Th) and Selenophenes (Seln) in the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ Complexes

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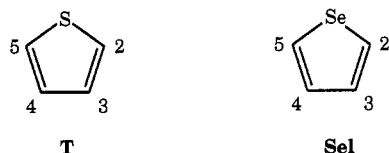
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The reaction of $\text{Cr}(\text{CO})_6$ with thiophenes (Th) and selenophenes (Seln) produced $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ (Th = T, 2-MeT, 2-EtT, 3-MeT, 2,5-Me₂T, and Me₄T) and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ (Seln = Sel, 2-MeSel, and 2,5-Me₂Sel). Variable-temperature ¹³C NMR spectra of these complexes in dimethyl ether indicated that there is restricted rotation about the Cr-Th and -Seln bonds. Band shape analyses of the ¹³C NMR spectra using DNMR5 gave activation parameters for ring rotation. Activation enthalpies (ΔH^\ddagger , kcal/mol) for these complexes increase in the following order: T (6.2), 3-MeT (6.5), 2-EtT (6.9), 2-MeT (7.1), Me₄T (7.4), 2,5-Me₂T (7.7), Sel (7.8), 2-MeSel (8.4), and 2,5-Me₂Sel (9.0). In general, alkyl substitution increases ΔH^\ddagger and α -substitution leads to a larger ΔH^\ddagger than β -substitution. Substitution of the S heteroatom by Se also increases ΔH^\ddagger . These results are discussed in terms of the relative electron densities on the heteroatom and the diene fragment, which were estimated using extended Hückel molecular orbital (EHMO) calculations. The structure of $\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{T})$ was established by a single crystal X-ray diffraction study. The rotational barriers for these complexes are larger than those of $\text{Cr}(\text{CO})_3(\eta^6\text{-arene})$ complexes presumably due to the strong interaction between the chromium and the heteroatom.

Introduction

Heterogeneous catalytic hydrodesulfurization (HDS) of petroleum-based feedstocks is crucial for both environmental and industrial reasons.² Of the organosulfur compounds present in petroleum, thiophene (T) and its



alkyl-substituted derivatives (Th) are among the most difficult to desulfurize, presumably due to their aromaticity.³ For that reason, thiophene compounds and their organometallic transition metal complexes have been the focus of many HDS studies.⁴ Use of selenophene (Sel) as

a model for HDS reactions is rather recent⁵ and is based primarily on the similarity of the chemistry of thiophenes (Th) and selenophenes (Seln).^{5,6} Selenophene compounds have the added benefit of an NMR active heteroatom (⁷⁷Se is a spin 1/2 nucleus that is 7.6% abundant)⁷ that could be useful in the elucidation of selenophene binding modes in transition metal complexes and on heterogeneous catalyst surfaces.⁵

Although it is widely accepted that T and Sel possess some degree of aromaticity, attempts to quantify the relative aromaticities of this family of five-membered heterocycles with respect to each other and benzene have yielded conflicting results.^{4b,6a,8} In general, however, studies indicate a decrease in aromaticity in the sequence benzene > T > Sel. Although this ordering indicates that T and Sel are less aromatic than benzene, it should be noted that the properties and reactivities of Th and Seln compounds are dominated by their aromaticity.^{6,9}

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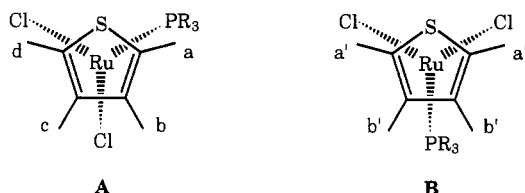
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Without exception, transition metal complexes of thiophenes with the stoichiometry $ML_3(\eta^5\text{-Th})$ have pseudooctahedral structures in which the L ligands are approximately *trans* to the sulfur or a double bond of the Th ligand.^{4b,10} This orientation of the Th rings can be interpreted as indicating localized metal–thiophene bonding through the two double bonds and sulfur; however, it is possible that the metal–thiophene bonding is better described in terms of a delocalized electron system of roughly cylindrical symmetry. The former case implies a significant energy barrier to thiophene ring rotation; the latter would presumably allow relatively free rotation of the thiophene ring.

In the course of their investigations of the dimeric ruthenium–tetramethylthiophene (Me_4T) complex $[(\eta^5\text{-Me}_4\text{T})\text{RuCl}(\mu_2\text{-Cl})]_2$, Rauchfuss and co-workers^{10c} discovered striking differences in the ^1H NMR spectra of the $(\eta^5\text{-Me}_4\text{T})\text{RuCl}_2(\text{PR}_3)$ complexes for $\text{R} = \text{Me}$ or *n*-Bu versus $\text{R} = \text{Ph}$ or *p*-tolyl. The ^1H NMR spectra of the PMe_3 and $\text{P}(n\text{-Bu})_3$ complexes showed two very sharp resonances at 24 °C for the methyl peaks of Me_4T . The ^1H NMR of the PPh_3 and $\text{P}(p\text{-tolyl})_3$ complexes, however, showed two very broad resonances in the methyl region at room temperature. At –60 °C, these broad resonances decoalesced into four methyl peaks of equal intensity. This observation is consistent with slowed metal–ring rotation to give structure **A** in which the sulfur is *trans* to a Cl, rather than the other



rotamer **B** in which the PR_3 ligand is *trans* to the sulfur. It is not clear why **A** might be the most stable rotamer but the authors suggested that steric interactions between the Me_4T and PR_3 ligands are responsible for the relatively slow rate of rotation in the PPh_3 and $\text{P}(p\text{-tolyl})_3$ complexes.

Rotational barriers in $\text{Cr}(\text{CO})_3(\eta^6\text{-arene})$ complexes have been extensively studied and recently reviewed.¹¹ Generally, the barriers to arene rotation are low (less than 1 kcal/mol),¹² but in some cases the barrier can be substantially increased by steric¹³ or electronic¹⁴ modifications of the arene ligand. In particular, the chromium tricarbonyl complexes of aromatic rings that contain a distinct localization of the double bonds show relatively large rotational barriers of about 10 kcal/mol.^{14b,d} Given the fact that thiophene and selenophene are not as aromatic as benzene, it is not unreasonable to expect significant rotational barriers in the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes. The ^{13}C NMR signals for the carbonyl ligands in these complexes provide an opportunity to monitor the ring rotation. The three carbonyls are

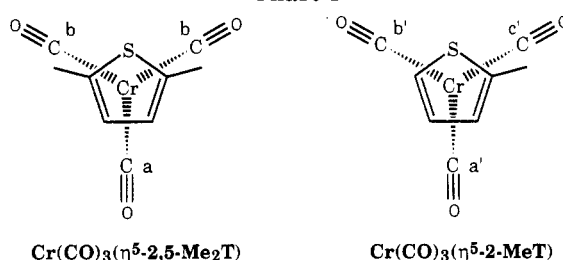
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Chart 1



equivalent when the ring rotates rapidly but become inequivalent when the rotation is slowed on the NMR time scale, as seen for the 2,5-dimethylthiophene (2,5- Me_2T) and 2-methylthiophene (2- MeT) chromium tricarbonyl complexes (Chart 1).

In this paper, we describe the synthesis and characterization of the series of $\eta^5\text{-Th}$ complexes $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$, where $\text{Th} = \text{T}$ (1), 2- MeT (2), 2-ethylthiophene (2- EtT) (3), 3-methylthiophene (3- MeT) (4), 2,5- Me_2T (5), and Me_4T (6), the $\eta^5\text{-Seln}$ complexes $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$, where $\text{Seln} = \text{Sel}$ (7), 2-methylselenophene (2- MeSel) (8), and 2,5-dimethylselenophene (2,5- Me_2Sel) (9), and the cationic, but isoelectronic, complex $[\text{Mn}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{-Sel})\text{OTf}](10, \text{OTf}^- = \text{CF}_3\text{SO}_3^-)$. The activation parameters (including ΔG_c^\ddagger , T_c , ΔH^\ddagger , and ΔS^\ddagger) for the restricted rotation of the thiophene and selenophene ligands in these complexes and the X-ray structure of $\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{T})$ are also reported.

Experimental Section

General Procedures. All reactions were performed under a nitrogen atmosphere in purified solvents of reagent grade using standard Schlenk techniques¹⁵ unless otherwise stated. Hexanes, methylene chloride (CH_2Cl_2), chloroform (CHCl_3), and *n*-butyl ether (*n*- Bu_2O) were distilled from CaH_2 , and THF was distilled under nitrogen from Na/benzophenone. The solvents were stored over 4-Å molecular sieves under nitrogen. The neutral alumina (Brockman, Activity I, 150 mesh) used for chromatography was deoxygenated at room temperature in high vacuum for 16 h and then deactivated with 5 wt % nitrogen-saturated water, shaken, and stored under nitrogen.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Nicolet NT-300 and a Varian VXR-300 spectrometer, respectively, using CDCl_3 (unless otherwise stated) as the solvent and internal lock. The ^1H NMR spectra (Table 1) were referenced to internal SiMe_4

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Table 1. ^1H NMR Chemical Shifts (δ) and Coupling Constants (Hz) for the Complexes in CDCl_3

complex	H2	H3	H4	H5	Me	CH_2	$J_{2,5}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	J_{Et}
$\text{Cr}(\text{CO})_3(\eta^5\text{-T})$	5.37 (m)	5.59 (m)	5.59 (m)	5.37 (m)							
$\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeT})$		5.33 (d)	5.52 (dd)	5.21 (d)	2.28			2.7		3.3	
$\text{Cr}(\text{CO})_3(\eta^5\text{-2-EtT})$		5.35 (d)	5.53 (dd)	5.24 (d)	1.24 (t)	2.58 (q)		2.9		3.4	7.4
$\text{Cr}(\text{CO})_3(\eta^5\text{-3-MeT})$	5.13 (d)		5.49 (d)	5.37 (dd)	2.28		1.6			3.3	
$\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{T})$		5.27	5.27		2.22						
$\text{Cr}(\text{CO})_3(\eta^5\text{-Me}_4\text{T})$					2.16 ^{a,b}						
$\text{Cr}(\text{CO})_3(\eta^5\text{-Sel})$	5.95 (m)	5.79 (m)	5.79 (m)	5.95 (m)							
$\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeSel})$		5.47 (d)	5.74 (dd)	5.80 (d)	2.36			3.1		3.7	
$\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})$		5.43	5.43		2.31						
$[\text{Mn}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})]\text{OTf}^c$		6.60	6.60		2.57						
T	7.31 (m)	7.10 (m)	7.10 (m)	7.31 (m)							
2-MeT		6.74 (dd)	6.87 (dd)	7.05 (dd)	2.48			3.4	1.3	5.1	
2-EtT		6.79 (dd)	6.91 (dd)	7.10 (dd)	1.31 (t)	2.86 (q)		3.4	0.8	5.0	7.5
3-MeT	6.87 (d)		6.88 (d)	7.18 (dd)	2.26		3.0			4.8	
2,5-Me ₂ T		6.51	6.51		2.40						
Me ₄ T					2.00 ^a						
					2.30 ^b						
Sel	8.01 (m)	7.34 (m)	7.34 (m)	8.01 (m)							
2-MeSel		6.91 (d)	7.09 (dd)	7.74 (d)	2.58			3.7		5.4	
2,5-Me ₂ Sel		6.65	6.65		2.50						

^a Me(3,4). ^b Me(2,5). ^c In CD_3NO_2 .Table 2. $^{13}\text{C}\{^1\text{H}\}$ NMR Chemical Shifts (δ) for the Complexes in CDCl_3

complex	C2	C3	C4	C5	Me	CH_2	CO
$\text{Cr}(\text{CO})_3(\eta^5\text{-T})$	85.87	91.24	91.24	85.87			232.79
$\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeT})$	106.58	91.58	92.19	84.79	15.54		233.26
$\text{Cr}(\text{CO})_3(\eta^5\text{-2-EtT})$	114.69	89.89	92.24	84.68	15.30	23.30	233.32
$\text{Cr}(\text{CO})_3(\eta^5\text{-3-MeT})$	84.15	109.34	93.93	86.60	15.23		233.41
$\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{T})$	105.44	92.16	92.16	105.44	15.80		233.68
$\text{Cr}(\text{CO})_3(\eta^5\text{-Me}_4\text{T})$	100.32	108.69	108.69	100.32	13.24, ^a 14.23 ^b		234.74
$\text{Cr}(\text{CO})_3(\eta^5\text{-Sel})$	91.63	91.91	91.91	91.63			233.04
$\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeSel})$	113.82	92.64	92.68	91.01	18.08		233.44
$\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})$	113.27	93.11	93.11	113.27	18.40		233.86
$[\text{Mn}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})]\text{OTf}^c$	128.92	100.10	100.10	128.92	18.07		218.37
T	125.13	126.87	126.87	125.13			
2-MeT	139.60	125.13	126.89	123.05	15.05		
2-EtT	147.44	123.27	126.69	122.67	16.09	23.29	
3-MeT	120.48	137.55	129.23	125.16	15.45		
2,5-Me ₂ T	137.38	124.77	124.77	137.38	15.22		
Me ₄ T	127.80	133.04	133.04	127.80	12.74 ^a		
					13.05 ^b		
Sel	129.41	130.37	130.37	129.41			
2-MeSel	146.48	127.64	129.34	128.42	17.89		
2,5-Me ₂ Sel	144.33	127.12	127.12	144.33	18.14		

^a Me(3,4). ^b Me(2,5). ^c In CD_3NO_2 .Table 3. Infrared Absorptions (cm^{-1}) for the Complexes in CH_2Cl_2

complex	$\nu(\text{CO})^a$
$\text{Cr}(\text{CO})_3(\eta^5\text{-T})$	1968, 1886, 1870
$\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeT})$	1963, 1880, 1870
$\text{Cr}(\text{CO})_3(\eta^5\text{-2-EtT})$	1962, 1878, 1865
$\text{Cr}(\text{CO})_3(\eta^5\text{-3-MeT})$	1964, 1883, 1868
$\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{T})$	1958, 1870, 1862
$\text{Cr}(\text{CO})_3(\eta^5\text{-Me}_4\text{T})$	1951, 1868, 1849
$\text{Cr}(\text{CO})_3(\eta^5\text{-Sel})$	1967, 1890, 1869
$\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeSel})$	1963, 1884, 1863
$\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})$	1958, 1878, 1859
$[\text{Mn}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})]\text{OTf}$	2069, 2011, 2000

^a Relative intensities are vs, s (br), and s (br).

and the ^{13}C NMR spectra (Table 2) were referenced to CDCl_3 (δ 77.0 ppm). The infrared spectra of the complexes (Table 3) were measured in CH_2Cl_2 using a Nicolet 710 FT-IR spectrometer. Electron impact mass spectra (EIMS) were performed on a Finnigan 4000 or a Kratos MS-50 mass spectrometer. The photochemical reactions were performed under nitrogen in a quartz tube equipped with a nitrogen bubbler using a 450 W mercury UV lamp. The temperature of the photochemical reactions was maintained at -16°C by a Lauda RK 20 constant-temperature circulator.

The low-temperature ^{13}C NMR studies were performed on ^{13}C -enriched samples (without spinning) using a Bruker WM-

200 spectrometer. Temperatures were measured using a copper-constantan thermocouple, which was calibrated to within 1 K. The temperature-dependent ^{13}C NMR studies of the chromium-containing complexes were performed without ^1H decoupling using dimethyl ether (Me_2O) as the solvent, internal proton lock, and internal reference (δ 59.7 ppm) in a high-pressure 10-mm NMR tube. The low-temperature ^{13}C NMR studies of $[\text{Mn}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})]\text{OTf}$ were performed using CD_3NO_2 as the internal lock and internal reference.

$\text{Cr}(\text{CO})_6$ was used as purchased from Strem Chemicals. Gaseous Me_2O and ^{13}C (99.4 atom % ^{13}C) were used as purchased from Matheson. Thiophene was purified as described previously.¹⁶ Reagent grade CDCl_3 , CD_3NO_2 , 2-MeT, 2-EtT, 3-MeT, 2,5-Me₂T, and *cis*-cyclooctene were purchased from Aldrich and used without further purification. CD_2Cl_2 and CD_3OD were used as purchased from Cambridge Isotopes Laboratory. Me_4T ,¹⁷ Sel,¹⁸ 2-MeSel,¹⁹ 2,5-Me₂Sel,¹⁹ and $[\text{Mn}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})]\text{OTf}$ ^{19b} were prepared by literature methods.

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Preparation of the Cr(CO)₃(η⁵-Th) and Cr(CO)₃(η⁵-Seln) Complexes (1–9). To a solution of 0.22 g (1.0 mmol) of Cr(CO)₆ in 10 mL of *n*-Bu₂O and 1 mL of THF was added 5 mmol of the thiophene or selenophene ligand. The mixture was refluxed with stirring under nitrogen for 3.5 h, during which time the solution slowly changed from colorless to dark red. The volatile components, including Cr(CO)₆, were removed *in vacuo* for 10–15 min at room temperature and the resulting orange powder was extracted with hexanes–CH₂Cl₂ (10:1) and chromatographed on neutral alumina (2 cm × 20 cm). The orange band containing the product was eluted with 1:1 hexanes–CH₂Cl₂ and evaporated to dryness. The resulting solid was dissolved in a minimum amount of CH₂Cl₂ and layered with hexanes. This solution was allowed to slowly mix overnight at –20 °C. The yields for Cr(CO)₃(η⁵-3-MeT) (4) and Cr(CO)₃(η⁵-2,5-Me₂Sel) (9) were 18% and 58%, respectively; when corrected for recovered Cr(CO)₆, the yields based on reacted Cr(CO)₆ were 85% and 93%, respectively. These values are representative of the yields for the other alkyl-substituted thiophene and selenophene complexes. The Cr(CO)₃(η⁵-Th) and Cr(CO)₃(η⁵-Seln) complexes were positively identified by their ¹H NMR spectra in CDCl₃,^{5b,20} which are given in Table 1.

Preparation of ¹³CO-Enriched Cr(CO)₆. The ¹³CO-enriched Cr(CO)₆ was prepared by a modified literature method.²¹ A solution of Cr(CO)₅(COE) was prepared by UV irradiation of 0.223 g of Cr(CO)₆ in 20 mL of hexanes and 1 mL of *cis*-cyclooctene (COE) for 4 h at –16 °C. The solution was filtered and slowly cooled to –78 °C, which resulted in bright yellow crystals of Cr(CO)₅(COE) (0.20 g, 64%; ν(CO) in hexanes 2071 (w), 1954 (s, br) cm⁻¹). A solution of 0.20 g of Cr(CO)₅(COE) dissolved in 20 mL of hexanes was frozen in a liquid nitrogen bath and the flask was evacuated. The solution was thawed, and the ¹³C-enriched CO was bubbled in through a rubber septum using a metal needle connected via Tygon tubing to the lecture bottle. While stirring for 30 min at room temperature, the solution slowly turned from bright yellow to a colorless liquid. Filtering this solution and cooling it to –78 °C precipitated Cr(CO)₅(¹³CO) in essentially quantitative yield based on Cr(CO)₅(COE). A ¹³CO enrichment value (the percent of the total number of CO ligands that are ¹³CO) of 11.8% was calculated for the labeled Cr(CO)₆ from the relative intensities of the molecular ion peaks in the mass spectrum of the labeled complex. The ¹³CO-enriched Cr(CO)₃(η⁵-Th) and Cr(CO)₃(η⁵-Seln) complexes were produced as stated above, using equal weights of unlabeled Cr(CO)₆ and the ¹³CO-enriched Cr(CO)₆ as the starting material.

Preparation of ¹³CO-Enriched Mn(CO)₅Br. The ¹³CO-enriched Mn(CO)₅Br was prepared by a modification of a literature method.²² A solution of (CO)₄Mn(μ₂-Br)₂Mn(CO)₄ was prepared by refluxing a solution of 0.151 g of Mn(CO)₅Br in 20 mL of CHCl₃ under nitrogen for 4 h. Cooling the solution to 0 °C using an ice bath resulted in the formation of a red-brown powder of Mn₂(CO)₈Br₂ (0.121 g, 89%; ν(CO) in CHCl₃ 2102 (m), 2045 (vs), 2013 (s), 1977 (s) cm⁻¹). A solution of 0.121 g of Mn₂(CO)₈Br₂ in 20 mL of CHCl₃ was frozen in a liquid nitrogen bath, and the flask was evacuated. The ¹³C-enriched CO was condensed into the flask at –196 °C; the solution was thawed and allowed to stir at room temperature overnight. Cooling the solution to 0 °C in an ice bath gave a precipitate of Mn(CO)₄(¹³CO)Br in essentially quantitative yield. The ¹³CO-labeled [Mn(CO)₃(η⁵-2,5-Me₂Sel)]OTf was prepared according to a literature procedure using the labeled Mn(CO)₅Br.^{5b}

X-ray Diffraction Study of Cr(CO)₃(η⁵-2,5-Me₂T) (5). A single crystal of 5 suitable for X-ray diffraction was obtained by layering a CH₂Cl₂ solution of the complex with hexanes and

Table 4. Crystal and Data Collection Parameters for Cr(CO)₃(η⁵-2,5-Me₂T) (5)

formula	CrSC ₉ H ₈ O ₃
fw	248.22
space group	P2 ₁ /c
<i>a</i> , Å	6.725(2)
<i>b</i> , Å	12.348(1)
<i>c</i> , Å	12.485(4)
α, deg	90
β, deg	104.14(2)
γ, deg	90
<i>V</i> , Å ³	1005.3(5)
<i>Z</i>	4
<i>d</i> _{calc} , g/cm ³	1.64
cryst size, mm	0.35 × 0.30 × 0.25
μ(Mo Kα), cm ⁻¹	12.8
data colln instrument	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα(λ = 0.710 73 Å)
orientation reflns: no.; range (2θ), deg	25; 18.3 < 2θ < 31.6
temp, °C	–50(1)
scan method	θ–2θ
data colln range, 2θ, deg	4.0–50.0
no. of data collcd	3686
total no. of unique data with <i>F</i> _o ² > 3σ(<i>F</i> _o ²)	1758
no. of params refined	127
trans factors: max, min (ψ-scans)	0.998, 0.959
<i>R</i> ^a	0.022
<i>R</i> _w ^b	0.034
quality-of-fit indicator ^c	1.01
largest shift/esd, final cycle	0.00
largest peak, e/Å ³	0.23(3)

^a *R* = Σ|*F*_o – |*F*_c||/Σ|*F*_o|. ^b *R*_w = [Σw(|*F*_o – |*F*_c||)²/Σw|*F*_o|²]^{1/2}; w = 1/σ²(|*F*_o|). ^c Quality-of-fit = [Σw(|*F*_o – |*F*_c||)²/(*N*_{obs} – *N*_{params})]^{1/2}.

allowing the solution to mix at –20 °C; the crystal was mounted on a glass fiber. The cell constants for data collection were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information are given in Table 4. Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections of 1.9% was applied to the data. An absorption correction based on a series of ψ-scans was applied. The agreement factor for the averaging of observed reflections was 1.1% based on *F*. The centric space group P2₁/c was unambiguously determined by the systematic absences. The positions of all non-hydrogen atoms were determined by direct methods.²³ All non-hydrogen atoms were refined with anisotropic thermal parameters. After the least squares converged, all hydrogen atoms were found in a difference Fourier map. These were placed into the model with isotropic temperature factors set equal to 1.0 times the isotropic equivalent of the attached atom. The hydrogen atom positions were not refined in the final least-squares cycle. Bond distances, selected angles, and atomic positional parameters for 5 are presented in Tables 5 and 6. An ORTEP drawing of 5 is given in Figure 1.

Extended Hückel Molecular Orbital (EHMO) Calculations. The molecular structures of the Th and Seln ligands and selected Cr(CO)₃(η⁵-Th) complexes were calculated using the extended Hückel method.²⁴ The orbital exponents were obtained from standard tables,²⁵ and the orbital energies for the atoms were evaluated from atomic spectral tables.²⁶ It should be noted that valence 3d orbitals were not included for the sulfur atom. The bond distances and angles for the free thiophene and

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Table 5. Bond Distances (Å)^a and Selected Angles (deg)^a for Cr(CO)₃(η⁵-2,5-Me₂T) (5)

Distances			
Cr-S	2.3757(6)	S-C(5)	1.758(2)
Cr-C(2)	2.210(2)	C(1)-C(2)	1.496(3)
Cr-C(3)	2.206(2)	C(2)-C(3)	1.383(3)
Cr-C(4)	2.213(2)	C(3)-C(4)	1.422(3)
Cr-C(5)	2.213(2)	C(4)-C(5)	1.385(3)
Cr-C(7)	1.837(2)	C(5)-C(6)	1.499(3)
Cr-C(8)	1.837(2)	C(7)-O(1)	1.152(2)
Cr-C(9)	1.832(2)	C(8)-O(2)	1.144(3)
S-C(2)	1.754(2)	C(9)-O(3)	1.157(2)

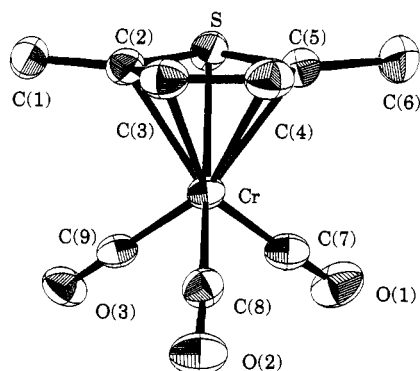
Angles			
C(7)-Cr-C(8)	90.15(8)	C(1)-C(2)-C(3)	128.7(2)
C(7)-Cr-C(9)	92.11(9)	C(2)-C(3)-C(4)	113.4(2)
C(8)-Cr-C(9)	86.35(8)	C(3)-C(4)-C(5)	113.5(2)
Cr-C(7)-O(1)	177.5(2)	C(4)-C(5)-C(6)	129.1(2)
Cr-C(8)-O(2)	178.2(2)	C(4)-C(5)-S	110.3(1)
Cr-C(9)-O(3)	177.0(1)	C(6)-C(5)-S	120.2(2)
S-C(2)-C(1)	120.3(1)	C(2)-S-C(5)	91.9(1)
S-C(2)-C(3)	110.6(1)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 6. Positional Parameters for Cr(CO)₃(η⁵-2,5-Me₂T) (5)

atom	x	y	z	B, Å ²
Cr	0.50427(4)	0.19908(2)	0.32686(2)	2.253(6)
S	0.85713(7)	0.18768(3)	0.41913(4)	2.833(9)
C(1)	0.7918(3)	-0.0221(2)	0.3275(2)	3.39(4)
C(2)	0.7652(3)	0.0974(1)	0.3098(1)	2.68(3)
C(3)	0.6927(3)	0.1532(2)	0.2120(1)	2.92(4)
C(4)	0.7010(3)	0.2676(2)	0.2252(2)	3.06(4)
C(5)	0.7783(3)	0.3005(1)	0.3334(2)	2.96(4)
C(6)	0.8206(3)	0.4129(2)	0.3787(2)	3.96(5)
C(7)	0.4014(3)	0.2996(2)	0.4075(2)	3.05(4)
C(8)	0.2684(3)	0.2078(1)	0.2159(2)	2.69(3)
C(9)	0.3797(3)	0.0873(2)	0.3816(2)	2.86(4)
O(1)	0.3411(2)	0.3655(1)	0.4569(1)	4.58(3)
O(2)	0.1196(2)	0.2108(1)	0.1480(1)	3.91(3)
O(3)	0.2957(2)	0.0159(1)	0.4116(1)	3.94(3)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

**Figure 1.** ORTEP drawing of Cr(CO)₃(η⁵-2,5-Me₂T) (5).

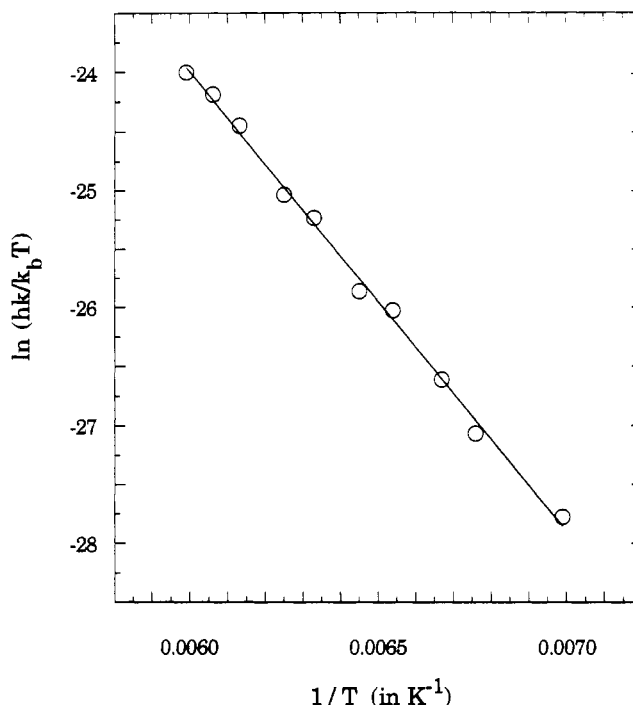
selenophene ligands were taken from the structures of free T²⁷ and Sel.²⁸ The bond distances and angles for the Cr(CO)₃(η⁵-Th) complexes were taken from the molecular structure (Table 5) of Cr(CO)₃(η⁵-2,5-Me₂T).

Band Shape Analysis. Rate constants for the Th and Seln ring rotations were calculated using the DNMR5²⁹ subroutine

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**Figure 2.** Eyring plot for Cr(CO)₃(η⁵-2,5-Me₂T) (5).

(QCPE³⁰ No. 365) of NMRi³¹ which uses an iterative nonlinear least-squares regression analysis to obtain the best fit of the experimental spectra. The reliability of the program was determined by calculating the activation parameters of neat *N,N*-dimethylformamide, which was distilled over CaH₂ before use. The resulting activation parameters ($\Delta H^* = 22.3(4)$ kcal/mol and $\Delta S^* = 6.6(11)$ cal/(mol K)) are in good agreement with the reported values of 23.8(2) kcal/mol for ΔH^* and 6.6(4) cal/(mol K) for ΔS^* .³² The ¹³C NMR spectra of the carbonyl ligands were analyzed as A₃ = B₂C for the metal complexes with symmetric Th and Seln ligands (T, 2,5-Me₂T, Me₄T, Sel, and 2,5-Me₂Sel) and as A₃ = BCD for the metal complexes with asymmetric Th and Seln ligands (2-MeT, 2-EtT, 3-MeT, and 2-MeSel). The line widths were measured at several slow exchange temperatures and are independent of temperature. The band shape calculations were performed on extracted spectra from δ 232 to 240 ppm. The chemical shifts, rate constant (*k*), baseline increment, and baseline tilt were optimized in the iterative calculations.

Activation parameters were obtained from the slope and intercept of Eyring plots (eq 1)³³ of $\ln(hk/\kappa k_b T)$ versus $1/T$, where *h* is Planck's constant, *k_b* is Boltzmann's constant, and *R* is the

$$\ln\left(\frac{hk}{\kappa k_b T}\right) = -\frac{\Delta G^*}{RT} = -\frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R} \quad (1)$$

gas constant. A transmission coefficient (κ) of 1 was used in these calculations. The errors reported for ΔH^* and ΔS^* are the estimated standard deviations from the linear least-squares analysis of the Eyring plots. An Eyring plot of the rate constants for Cr(CO)₃(η⁵-2,5-Me₂T) is given in Figure 2.

Results and Discussion

Synthesis and Characterization of the Cr(CO)₃(η⁵-Th) and Cr(CO)₃(η⁵-Seln) Complexes. Chromium tricarbonyl thiophene and selenophene complexes, Cr(CO)₃(η⁵-Th) and Cr(CO)₃(η⁵-Seln), have been prepared by a variety of methods.^{20,34} The synthetic route used in

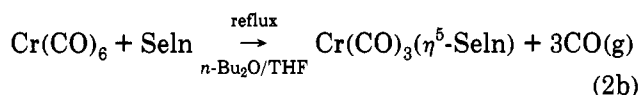
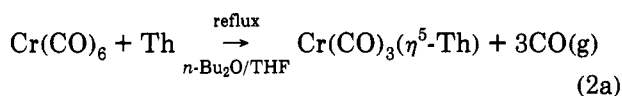
(30) Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.

(31) New Methods Research, Inc., Syracuse, NY.

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this study (eq 2) is a modification of one used for the



preparation of chromium tricarbonyl arene complexes.³⁵ This method is useful for the synthesis of the chromium tricarbonyl complexes of thiophene, selenophene, and their alkyl-substituted derivatives. The advantage of this method is that the complexes can be made in one step without the need to isolate air-sensitive intermediates such as $\text{Cr}(\text{CO})_3(\text{NCMe})_3$ or $\text{Cr}(\text{CO})_3(\text{NC}_5\text{H}_5)_3$.^{34b,d} However, the yields for these complexes are only moderate to poor (58% for Seln = 2,5-Me₂Sel and 18% for Th = 3-MeT); attempts to increase the yield by additional heating resulted in substantial decomposition due to the thermal instability of these complexes. The $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes exhibit moderate thermal and air sensitivity, especially in solution, and should be handled under nitrogen; however, they are stable for prolonged periods of time (greater than 2 years) in the solid state when stored under nitrogen at reduced temperatures (-20 °C). All of the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ complexes were previously reported²⁰ and were positively identified in this study by their ¹H NMR spectra in CDCl₃. The ¹H NMR assignments for the $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes^{5b} were made by comparison to the analogous $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ complexes and were aided by the fact that the 2- and 5-hydrogen (α protons) peaks in the Seln complexes show ⁷⁷Se satellites but the 3- and 4-hydrogen (β protons) peaks do not.

The ¹H NMR spectra for the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes are given in Table 1 and show a dramatic upfield shift of the aromatic protons upon metal complexation (1.2–2.1 ppm). It has been suggested previously³⁶ for $\text{Cr}(\text{CO})_3(\eta^6\text{-arene})$ complexes that this upfield shift is based on a reduction of π -electron density and ring current in the aromatic ring or on a magnetic anisotropy effect of the electric field arising from the metal–ring dipole. Dipole moments measured for $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ complexes are larger than those of the $\text{Cr}(\text{CO})_3(\eta^6\text{-arene})$ complexes;³⁷ this has been attributed to the large dipole moment of the Cr–S bond. In the case of $[\text{Mn}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})\text{OTf}]$ and other cationic metal–arene complexes, the positive charge on the metal increases the downfield shift and this results in a smaller total upfield shift of the aromatic protons upon metal complexation;^{16,38} in dicationic metal–arene complexes, the downfield shift

caused by the positive charge is large enough to overcome the upfield shift and these complexes show proton shifts downfield from the free ligands.³⁹

The upfield shift of the aromatic protons in the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes shows several trends with respect to alkyl and heteroatom substitution. It has been noted previously²⁰ for $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ complexes that within the same complex, aromatic protons in the α positions are shifted upfield to a larger degree than protons in the β positions. The α protons in these complexes are shifted from 1.7 to 2.1 ppm upfield from the free ligands, whereas the upfield shift of the β protons ranges from 1.2 to 1.6 ppm. Jackson *et al.*⁴⁰ have suggested that aromatic protons that are eclipsed with CO ligands are deshielded relative to those that are not. Octahedral coordination in $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ or $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ results in a structure (Chart 1) in which the α protons are eclipsed to the metal carbonyls; consequently, the α protons should be deshielded to a larger extent than the β protons. However, this is inconsistent with the experimental evidence.

The addition of alkyl groups to the thiophene ring reduces the upfield shift of the aromatic protons upon complexation. This is evidenced by the decreasing shift of the H(4) proton relative to the free ligands in $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ for Th = T (1.51 ppm), 2-MeT (1.35 ppm), and 2,5-Me₂T (1.24 ppm). Similar trends for the proton shifts are seen in the methyl-substituted selenophene complexes. Substitution of the S heteroatom by Se does not greatly affect the β proton upfield shifts, as noted in the H(4) shifts upon complexation in the T and Sel (1.55 ppm) complexes. The upfield shifts in the α protons, however, are somewhat affected by heteroatom substitution. Substitution of S with Se leads to a 0.12 ppm increase in the upfield shift, as seen for H(2) protons in the T (1.94 ppm) and Sel (2.06 ppm) complexes.

Upon metal complexation, the proton–proton coupling constants (³J_{HH} and ⁴J_{HH}) show a marked decrease from values found for the free ligands (Table 1). This decrease is dependent upon the position of the protons in question: the decrease in J values is larger for α than for β protons. This is demonstrated by the fact that $J_{2,5}$, the coupling constant between two α protons, for Th = 3-MeT decreases to 1.6 Hz, a value that is 53% of that seen for the free ligand (3.0 Hz); however, the values for $J_{3,4}$, the coupling constant between the two β protons, decreases to only 80–85% of the value seen for the free ligand (Th, Seln = 2-MeT, 2-EtT, and 2-MeSel). $J_{4,5}$, which represents the coupling of an α and β proton, shows a decrease from the value in the free ligand of 65–70% (Th, Seln = 2-MeT, 2-EtT, 3-MeT, and 2-MeSel) which is intermediate between the two values listed above. It has been previously suggested³⁶ for chromium tricarbonyl arene complexes that this decrease in proton–proton coupling constants can be related to a slight decrease in the electron density at the aromatic protons which results in smaller proton–proton coupling constants. The larger decrease in J values for the α protons suggests that the α carbons in the thiophene

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and selenophene rings interact more strongly with the metal atom than the β carbons. This is consistent with the fact that the α protons are shifted upfield to a larger extent than the β protons in these complexes.

Upon coordination to the metal, the methyl protons on the thiophene and selenophene rings show rather small shifts (0.02–0.22 ppm). It is interesting to note that methyl groups in the α positions are shifted upfield whereas methyl groups in the β positions are shifted downfield.

The $^{13}\text{C}\{^1\text{H}\}$ peaks for the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes are given in Table 2 and have not been previously reported. The ^{13}C peak assignments for the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ (Th = T, 2-MeT, 2-EtT, and 3-MeT) and the $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ (Seln = Sel and 2-MeSel) complexes were made using HETCOR experiments. Since a HETCOR spectrum correlates peaks of the ^1H NMR spectrum to the peaks in the ^{13}C spectrum, these studies allow the assignment of all ^{13}C NMR peaks to specific carbon atoms in the complexes. As in the ^1H NMR studies, the ^{13}C NMR spectra of the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes show a dramatic upfield shift of the aromatic carbons upon metal complexation (24–39 ppm). Similar upfield shifts in chromium tricarbonyl arene complexes have been rationalized in terms of a change in the mobile bond order of the C–C bonds,⁴¹ a change in the hybridization of the carbon atoms from sp^2 to sp^3 upon metal coordination,⁴² or the presence of a net negative charge on the carbon atoms.⁴³ Calculations for $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)$ using self-consistent charge and configuration molecular orbital theory (SCCCMO) and the Pople–Karplus equation correctly predicted an upfield shift of the aromatic carbons and a downfield shift of the carbonyl ligands with respect to free CO upon metal complexation.⁴⁴

For a given Th or Seln ligand, the α carbons are shifted upfield to a larger extent than the β carbons upon complexation. This can be seen in the upfield shifts of the α carbons (39.26 ppm) versus the β carbons (35.63 ppm) in $\text{Cr}(\text{CO})_3(\eta^5\text{-T})$. Addition of methyl groups to the thiophene ring results in a smaller upfield shift of the aromatic carbons, as evidenced by the smaller shifts of C(4) in $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ for Th = T, 2-MeT (34.70 ppm) and 2,5-Me₂T (32.61 ppm). It is interesting to note that the upfield shift of an aromatic carbon is smaller when its hydrogen is replaced by a methyl group. Consequently, the upfield shift for 2-MeT in $\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeT})$ is larger for the C(5) atom (38.26 ppm) than it is for C(2) (33.02 ppm). Similar trends are seen in the methyl-substituted selenophene complexes. Substitution of the heteroatom from S to Se leads to a larger upfield shift on the β carbons and a smaller upfield shift in the α carbons. This trend is demonstrated by comparison of the upfield shifts of C(4) (36.66 ppm) and C(5) (37.41 ppm) in $\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeSel})$ with those values (34.70 and 38.26 ppm, respectively) in $\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeT})$.

The ^{13}C NMR chemical shift of the carbonyl peaks in $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ demonstrate a definite trend with methyl and heteroatom substitution. The CO peak in these complexes shows a downfield shift upon addition of alkyl groups to the thiophene or

selenophene rings. A similar trend was observed⁴⁵ in the substituted $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6\text{-}x\text{R}_x)$ complexes in which the CO resonance is shifted upfield with respect to the benzene complex when electron-withdrawing and π -acceptor groups such as Cl, F, CO_2Me , or CF_3 are bound to the ring; similarly, the carbonyl resonances are shifted downfield with respect to $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)$ with the addition of electron-donating and π -donor groups such as Me, OMe, or NMe_2 . A comparison of Th and Seln complexes shows that substitution of the S heteroatom by Se results in a 0.2 ppm downfield shift of the CO resonance. This downfield shift suggests that the selenophenes donate more electron density to the metal than the analogous thiophenes. This is consistent with the larger upfield shift of the α protons in selenophene versus the thiophene complexes.

The aromatic carbons of the $[\text{Mn}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})]\text{-OTf}$ complex are shifted upfield from the free ligand, but these shifts are still downfield with respect to $\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})$. The β carbons show an upfield shift of 27 ppm; the α carbons, which have a methyl group attached instead of a hydrogen, are only shifted upfield by about 15 ppm. Similar upfield shifts in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum were seen in the methyl-substituted derivatives of $[\text{Mn}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)]\text{I}_3$.^{38a}

The infrared spectra of the η^5 -thiophene and -selenophene complexes were measured in CH_2Cl_2 and are given in Table 3. Each spectrum contains three bands in the metal–carbonyl region, which is indicative of slow metal–ring rotation on the IR time scale. The peak at highest energy is very sharp and intense; the other two peaks are strong, but broadened with respect to the first peak, and are close in energy. In concentrated or impure samples, it is not uncommon for the two lower energy peaks to appear as one, very broad peak. The IR bands in the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes shift to lower energy with increasing alkyl substitution. This is consistent with a previous IR study^{34d} of $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ complexes in which a correlation was observed between the decreasing carbonyl frequencies and the electron-donating power of the substituents as measured by the Hammett parameter σ_p . Comparison of $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ shows that their ν_{CO} values are very similar, which suggests that thiophene and selenophene donate comparable electron density to the metal. As noted above, trends in the ^{13}CO chemical shifts suggest that a Seln ligand donates slightly more electron density to the metal than the analogous Th ligand. A correlation was observed in this study between the ^{13}C NMR chemical shift of the CO ligands (δ_{CO}) and the ν_{CO} band at highest energy for the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes ($\nu_{\text{CO}} = 4079 - 9.068\delta_{\text{CO}}$, $R = 0.974$). A similar correlation was noted for the δ_{CO} and ν_{CO} values in the series of $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{X})$ complexes ($R = 0.964$ and 0.976 for the two ν_{CO} bands).^{45a} The ν_{CO} bands of $[\text{Mn}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})]\text{OTf}$ are shifted to higher energy by 110–140 cm^{-1} from the neutral $\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})$. This is consistent with the cationic manganese complex having less electron density at the metal for back-donation to the CO ligands than the chromium complex.

Structure of $\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{T})$ (5). The structure (Figure 1) of $\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{T})$ (5) indicates that the thiophene ring binds to the chromium tricarbonyl fragment

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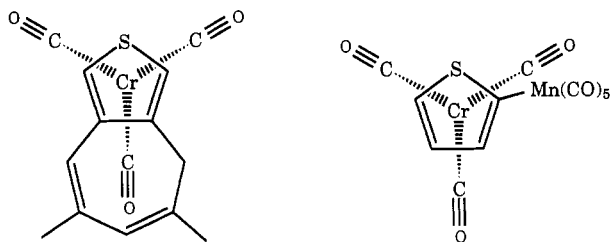
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with the sulfur atom *trans* to one of the CO ligands. This conformation is the same as those found in $\text{Cr}(\text{CO})_3(\eta^5\text{-T})^{10a}$ (a structure that is complicated by a 3-fold disorder of the thiophene ring), in the 5,7-dimethyl-4*H*-cyclohepta-[*c*]thiophene (5,7-Me₂-4*H*-H[*c*]T) complex $\text{Cr}(\text{CO})_3(\eta^5\text{-5,7-Me}_2\text{-4H-H[*c*]T})^{10b}$ and in the (2-thienyl)manganese



$\text{Cr}(\text{CO})_3(\eta^5\text{-5,7-Me}_2\text{-4H-H[*c*]T})$

$\text{Cr}(\text{CO})_3(\eta^5\text{-2-Mn}(\text{CO})_5\text{T})$

pentacarbonyl (2-Mn(CO)₅T) complex $\text{Cr}(\text{CO})_3(\eta^5\text{-2-Mn}(\text{CO})_5\text{T})^{10c}$. Thus, the three coordination sites of the ligand (the two double bonds and the sulfur) and the three carbonyls occupy approximately octahedral coordination sites around the d⁶ Cr(0) metal atom in 5. The crystal structure of the *endo* complex of chromium tricarbonyl angular-terphenylene,⁴⁶ an arene that exhibits a distinct localization of the double bonds in the central ring,⁴⁷ also contains an octahedrally coordinated chromium(0) atom. The thiophene ligand in 5 is best described as a planar diene unit (± 0.002 Å) with the sulfur atom slightly (0.0959(5) Å) above that plane. The dihedral angle defined by the diene plane and the plane containing S, C(2), and C(5) is 4.5(4)°. The distortion of the planar ligand upon complexation to the chromium atom is probably due more to the fact that the Cr–S bond length is longer than that of a Cr–C bond than to any loss of thiophene aromaticity. The Cr–S bond length of 2.3757(6) Å in 5 is comparable to Cr–S distances of 2.355(2) Å in $\text{Cr}(\text{CO})_2(\eta^1(\text{S})\text{-1,3-dithiane}(\eta^6\text{-C}_6\text{H}_6))^{48}$ and 2.331(1) Å in $\text{Cr}(\text{CO})_5(\eta^1(\text{S})\text{-2,5-dihydrothiophene 1-oxide})^{49}$. Similarly, the average Cr–C(Th) bond length of 2.211(2) Å in 5 is comparable to the average Cr–C(C₆H₆) distance of 2.229(2) Å in $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)$.⁵⁰ The C(2)–S and C(5)–S bond lengths of 1.754(2) and 1.758(2) Å in 5 are longer than that of 1.714(1) Å in free thiophene.²⁷ Similarly, the C(2)–C(3) (1.383(3) Å) and C(4)–C(5) (1.385(3) Å) distances are longer than the corresponding distance in free thiophene (1.370(2) Å); the C(3)–C(4) distances in 5 (1.422(3) Å) and free thiophene (1.424(2) Å) are the same within experimental error. Lengthening of the C–S and the C–C double bonds in thiophene upon metal coordination is consistent with either electron donation from the π -orbitals of the ring to the metal or an increased population of the π^* antibonding orbitals on the thiophene ligand due to back-bonding interactions with the metal atom.⁵¹ The idea that the chromium tricarbonyl fragment is capable of π^* back-donation to arene rings is supported by the molecular structures of $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{Et}_6)$, $[\text{Cr}(\text{CO})_2(\text{NO})(\eta^6\text{-C}_6\text{-$

$\text{Et}_6)]\text{BF}_4$, and $[\text{Cr}(\text{CO})(\text{CS})(\text{NO})(\eta^6\text{-C}_6\text{Et}_6)]\text{BF}_4$ in which the substitution of CO by NO⁺ and CS results in increased arene centroid–chromium distances (1.725, 1.795, and 1.803 Å, respectively).^{13f} This bond lengthening implies that the chromium–arene interaction has a substantial π^* metal-to-ligand back-bonding contribution that is weakened by strong π -accepting ligands. Similarly, SCF MS–X α calculations of the $\text{CpFe}(\eta^6\text{-C}_6\text{H}_6)^+$ cation (where Cp = $\eta^5\text{-C}_5\text{H}_5$) suggested that the filled 3d orbitals on the iron atom interact to a much larger extent with the empty π^* -orbitals on benzene than those on the cyclopentadienyl ligand.⁵²

Comparison of 5 with $[(\eta^4\text{-COD})\text{Rh}(\eta^5\text{-2,5-Me}_2\text{T})]\text{BF}_4^{53}$ (where COD is 1,5-cyclooctadiene) allows us to comment on relative distortions of the 2,5-Me₂T ligand upon complexation to chromium and rhodium. In contrast to 5, the C(2)–C(3) and C(4)–C(5) bonds that are formally double bonds in the free ligand are now longer than the formal C–C single bond (C(3)–C(4)) in the Rh complex (1.400(8) and 1.377(8) Å, respectively). The C–S bond lengths of 1.764(6) and 1.743(6) Å in the Rh complex are the same within experimental error to the C–S bond lengths in 5. From this comparison, it is obvious that the 2,5-Me₂T ligand is distorted from the structure of free thiophene to a greater extent in the Rh complex than in 5.

EHMO Calculations. The total energies of the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ complexes where Th = T, 2-MeT, and 3-MeT were calculated using the extended Hückel method, assuming perfect 3-fold symmetry of the $\text{Cr}(\text{CO})_3$ fragment using the Cr–C and C–O distances (Table 5) from 5. In order to estimate the energy barrier for thiophene ring rotation, the total energy of $\text{Cr}(\text{CO})_3(\eta^5\text{-T})$ was optimized with respect to the orientation of the thiophene ring relative to the $\text{Cr}(\text{CO})_3$ fragment. The conformation of lowest energy occurs when the S atom is *trans* to a carbonyl ligand and is consistent with the molecular structure of 5; the highest energy conformer contains a chromium atom in an approximately trigonal prismatic coordination site (S eclipsed with a CO ligand). The energy difference between these two conformers is 0.174 eV (4.01 kcal/mol), which is similar to the experimental value of ΔH^\ddagger (6.2 kcal/mol). Similar calculations performed for $\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeT})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-3-MeT})$ predict a low energy conformer with octahedral coordination that is 0.225 eV (5.18 kcal/mol) and 0.227 eV (5.24 kcal/mol), respectively, more stable than the trigonal prismatic conformer. The $\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{T})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Me}_4\text{T})$ complexes are also calculated to have an octahedral low energy conformer; however, the calculated rotational barrier for both of these complexes is 0.224 eV (5.16 kcal/mol), which is the same as that for the 2-MeT and 3-MeT complexes. The fact that the EHMO results show no difference in the rotational barriers for the 2-MeT, 3-MeT, 2,5-Me₂T, and Me₄T complexes indicates that these calculations are not useful in explaining trends in the activation parameters for thiophene ring rotation in these complexes.

EHMO calculations of the free Th and Seln ligands, however, appear to be more useful. The bond distances and angles for the heteroatom skeleton of the free Th and Seln ligands were taken from the microwave structures of T²⁷ and Sel.²⁸ The C–C and C–H bond lengths for the

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Table 7. Orbital Populations (e) for the π Orbitals in the Th and Seln Ligands

ligand	C2	C3	C4	C5	E	ΣC^a	$E + \Sigma C^b$	$E - \Sigma C^c$
T	1.059	1.127	1.127	1.059	1.628	4.372	6.000	-2.744
2-MeT	0.996	1.170	1.126	1.081	1.644	4.373	6.017	-2.729
2-EtT	0.987	1.180	1.126	1.086	1.648	4.379	6.027	-2.731
3-MeT	1.105	1.071	1.143	1.058	1.637	4.377	6.014	-2.740
2,5-Me ₂ T	1.017	1.171	1.171	1.017	1.659	4.376	6.035	-2.717
Me ₄ T	1.062	1.129	1.129	1.062	1.675	4.382	6.057	-2.707
Sel	1.022	1.101	1.101	1.022	1.755	4.246	6.001	-2.491
2-MeSel	0.957	1.150	1.099	1.050	1.765	4.256	6.021	-2.491
2,5-Me ₂ Sel	0.983	1.149	1.149	0.983	1.774	4.264	6.038	-2.490

^a Total orbital population for the four aromatic carbons. ^b Total orbital population for the aromatic ring. ^c Difference in orbital populations of the heteroatom (E) and the four carbons.

alkyl substituents were taken from a table of distances determined by X-ray and neutron diffraction studies of organic compounds.⁵⁴ Table 7 contains the orbital populations for the p_z (π) orbitals of the heterocyclic rings as well as the total π -electron density in the ring ($E + \Sigma C$) and the difference in the electron populations of the heteroatom and the diene ($E - \Sigma C$). The total π -electron densities on T (6.000e) and Sel (6.001e) demonstrate that the protons do not donate any electron density to the metal. Addition of alkyl groups to the T and Sel ligands, however, increases the electron density in the ring. These calculations suggest that a methyl group donates comparable electron density to the ring in either the 2- or 3-position (0.017 and 0.014 e, respectively). This is consistent with IR studies (Table 3 and ref 34d) of the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ complexes which demonstrate that the energy of the ν_{CO} bands is essentially unaffected by the position of the substituents (α versus β) on the Th ring. The calculations also suggest that an ethyl group donates more electron density to the ring than a methyl group, which is also supported by the ν_{CO} data (Table 3). The orbital populations of the carbon atoms show two distinct trends: β carbons tend to have more π -electron density than α carbons (1.059 and 1.127 e, respectively, in T), and replacement of a hydrogen with a methyl group results in a lower electron density at that carbon, as evidenced by the populations at C(2) (0.996 e) and C(5) (1.081 e) in 2-MeT. The orbital population of the heteroatom also increases with increasing alkyl substitution. Comparison of the electron densities at S in 2-MeT (1.644 e) and 3-MeT (1.637 e) supports the conclusions made previously⁵⁵ that methyl substitution at the 2-position donates more electron density to the sulfur than a methyl in the 3-position and is consistent with the fact that dissociative substitution of Th by PPh_3 in $\text{CpRe}(\text{CO})_2(\eta^1\text{-S})\text{-Th}$ ⁵⁵ and $[\text{CpRu}(\text{CO})_2(\eta^1\text{-S})\text{-Th}]\text{BF}_4$ ⁵⁶ occurs at a slower rate for Th = 2-MeT than for Th = 3-MeT.

Activation Parameters for the Restricted Th and Seln Rotation. The ^{13}C NMR spectra of the ^{13}CO -labeled $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes were measured using dimethyl ether (mp = -141 °C, bp = -25 °C) as the solvent, internal proton lock, and internal reference. The spectra were measured in 2–5 K increments from just above the melting point of the solvent (132 K) to the point where the CO signal appeared as a sharp singlet (typically, 10–20 K above the coalescence temperature). At low temperatures, the carbonyl spectra of $\text{Cr}(\text{CO})_3$ -

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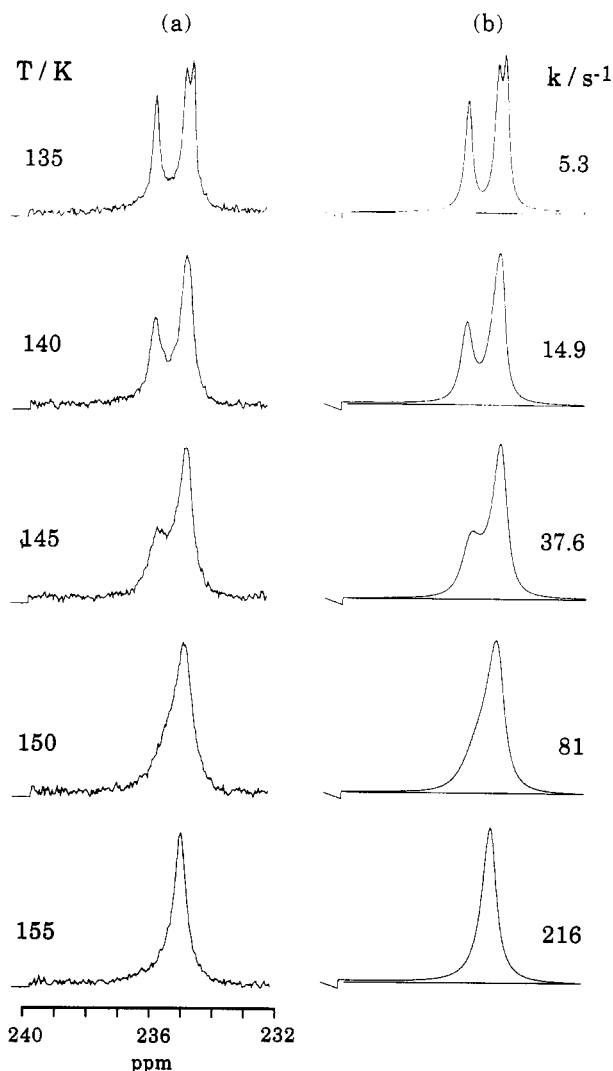


Figure 3. Variable-temperature ^{13}C NMR of $\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeT})$ (2): (a) observed; (b) calculated.

($\eta^5\text{-Th}$) and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ appear as two singlets of relative intensity 2:1 for the symmetric heterocycles (Th = T, 2,5-Me₂T, Me₄T; Seln = Sel, 2,5-Me₂Sel) and as three singlets of equal relative intensity for the asymmetric heterocycles (Th = 2-MeT, 2-EtT, 3-MeT; Seln = 2-MeSel). The experimental and theoretical band shapes for the $\text{Cr}(\text{CO})_3(\eta^5\text{-2-MeT})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{T})$ complexes are given in Figures 3 and 4, respectively. The enthalpy of activation (ΔH^\ddagger), the entropy of activation (ΔS^\ddagger), the coalescence temperature (T_c), and the free energy of activation at coalescence (ΔG_c^\ddagger) determined from Eyring plots are given in Table 8. Values of ΔG_c^\ddagger at T_c for the coalescence of an unequally populated doublet measured by NMR can be calculated⁵⁷ from the expression in eq 3, where $\delta\nu$ is the NMR chemical shift difference of

$$\Delta G_c^\ddagger (\text{eq 3}) = RT_c \ln \left(\frac{k_b T_c X}{h \pi \delta \nu (1 - \Delta P)} \right) \quad (3)$$

the two peaks at slow exchange in hertz, and X is a parameter which depends on the value of the population difference ΔP . For the symmetric Th and Seln ligands, ΔP is 0.33 and the corresponding value of X is 2.0823. For the case of an equally populated doublet, ΔP is zero, X is

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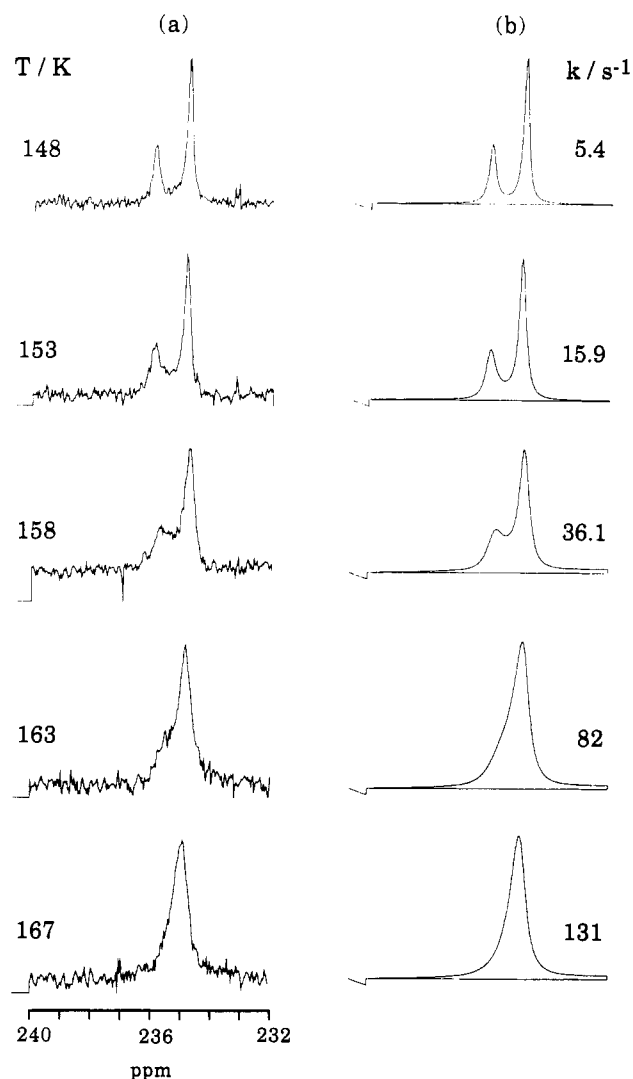


Figure 4. Variable-temperature ^{13}C NMR of $\text{Cr}(\text{CO})_3(\eta^5\text{-}2,5\text{-Me}_2\text{T})$ (5): (a) observed; (b) calculated.

Table 8. Activation Parameters for Restricted Rotation in the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ Complexes

ligand	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/(mol K)	T_c , K	ΔG_c^\ddagger , kcal/mol	ΔG_c^\ddagger (eq 3), ^a kcal/mol
T	6.2(2)	-1.6(12)	132	6.42(5)	6.40
2-MeT	7.1(3)	-1.1(19)	147	7.25(5)	
2-EtT	6.9(3)	-1.4(19)	145	7.08(5)	
3-MeT	6.5(3)	-1.2(23)	138	6.66(5)	
2,5-Me ₂ T	7.7(2)	-1.3(10)	161	7.94(5)	7.90
Me ₄ T	7.4(4)	-1.7(30)	158	7.63(5)	7.67
Sel	7.8(2)	-1.5(14)	163	7.99(5)	7.92
2-MeSel	8.4(2)	-1.2(11)	178	8.64(5)	
2,5-Me ₂ Sel	9.0(3)	-1.3(15)	185	9.20(5)	9.13

^a From eq 3 and ref 57.

equal to $\sqrt{2}$, and eq 3 reduces to the widely used equation to estimate ΔG_c^\ddagger .³³ Unfortunately, there is no simple equation to calculate ΔG_c^\ddagger for the asymmetric Th and Seln complexes that give a 1:1:1 set of singlets. Comparison of the measured ΔG_c^\ddagger values and the values calculated from eq 3, ΔG_c^\ddagger (eq 3) (Table 8) reveals that the two ΔG_c^\ddagger values are the same within experimental error.

The ΔS^\ddagger values for these complexes are all very similar to each other (from -1.9 to -1.1 cal/(mol K)) and show no real trends with respect to heteroatom or alkyl substitution. Although the ΔS^\ddagger values are all slightly negative, which is indicative of a more ordered transition state, almost all

of them are equal to zero within experimental error. The errors reported for ΔH^\ddagger and ΔS^\ddagger are conservative estimates given by the linear least-squares fit to the Eyring equation (eq 1). Because the ΔS^\ddagger values in the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes are similar to each other, both ΔH^\ddagger and ΔG_c^\ddagger follow the same trends.

The ΔH^\ddagger values for the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ complexes, where Th = T (6.2(2) kcal/mol), 2-MeT (7.1(3) kcal/mol), and 2,5-Me₂T (7.7(2) kcal/mol), demonstrate that the addition of a methyl group to the α -position of the thiophene ring increases ΔH^\ddagger by 0.6–0.9 kcal/mol. EHMO calculations presented in this work imply that the addition of methyl groups to the thiophene ring increases the π -electron density in the ring which, in turn, donates more electron density to the metal. This has been supported by the ^{13}C NMR and IR results discussed above. The increased electron density shared by the metal and the ring results in the larger ΔH^\ddagger values upon methyl substitution. The calculations also suggest that the increased electron density appears mainly on the S atom, as evidenced by an increase of 0.031 e in the S π -electron density but only 0.004 e in the diene π -electron density in 2,5-Me₂T with respect to T. These results suggest that the ΔH^\ddagger values are primarily dependent on the π -electron density on the heteroatom. The $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes show a similar trend in ΔH^\ddagger upon α -methyl substitution.

Although the EHMO calculations imply that 2-MeT and the isomeric 3-MeT ligands have comparable total π -electron densities, the ΔH^\ddagger value for the $\text{Cr}(\text{CO})_3(\eta^5\text{-}2\text{-MeT})$ complex is 0.6 kcal/mol higher than that of $\text{Cr}(\text{CO})_3(\eta^5\text{-}3\text{-MeT})$. These values imply that ΔH^\ddagger is dependent not only on the total π -electron density but also on the relative electron densities on the S and the diene fragment in the ring. Comparison of the ΔH^\ddagger values for $\text{Cr}(\text{CO})_3(\eta^5\text{-T})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-}2\text{-MeT})$ demonstrates that increasing the π -electron density on the sulfur without changing the diene electron density leads to an increased activation barrier in these complexes. On the other hand, an increase in the electron density on the diene fragment, which presumably occurs to a greater extent in $\text{Cr}(\text{CO})_3(\eta^5\text{-}3\text{-MeT})$, would strengthen the metal–diene interaction and reduce the dominating influence of the Cr–S bond; this would be expected to give a smaller activation barrier, as is observed for $\text{Cr}(\text{CO})_3(\eta^5\text{-}3\text{-MeT})$ as compared with $\text{Cr}(\text{CO})_3(\eta^5\text{-}2\text{-MeT})$.

Substitution of the methyl group with an ethyl group results in comparable ΔH^\ddagger values for $\text{Cr}(\text{CO})_3(\eta^5\text{-}2\text{-MeT})$ (7.1(3) kcal/mol) and $\text{Cr}(\text{CO})_3(\eta^5\text{-}2\text{-EtT})$ (6.9(3) kcal/mol). EHMO calculations suggest that 2-EtT has a greater total π -electron density than 2-MeT; however, the differences in the orbital populations of the sulfur atom and the four carbons ($E - \sum C$) for 2-MeT and 2-EtT are very similar. In general, there is a very good linear correlation ($\Delta H^\ddagger = 156 + 54.6(E - \sum C)$, $R = 0.997$) between the ΔH^\ddagger values and the difference ($E - \sum C$) in the π -electron density on the sulfur and the diene fragment for the $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ complexes, where Th = T, 2-MeT, 2-EtT, 3-MeT, and 2,5-Me₂T (all Th except Me₄T). The ΔH^\ddagger value of 7.4(4) kcal/mol for $\text{Cr}(\text{CO})_3(\eta^5\text{-Me}_4\text{T})$ is much lower than expected; in fact, the ΔH^\ddagger value for the Me₄T complex is lower than that for the 2,5-Me₂T complex. This suggests that the addition of two methyl groups to the ring lowers the activation barrier and is inconsistent with the trend seen in every other complex upon alkyl substitution in

this study. In fact, extrapolation of the correlation between ΔH^\ddagger and $(E - \sum C)$ mentioned previously for the Th complexes to Me_4T results in a theoretical ΔH^\ddagger value of 8.3 kcal/mol for $\text{Cr}(\text{CO})_3(\eta^5\text{-Me}_4\text{T})$, a value that is 0.9 kcal/mol larger than that experimentally measured.

A comparison of the activation barriers for $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes demonstrates that the substitution of S by Se increases the ΔH^\ddagger values by 1.3–1.6 kcal/mol. EHMO calculations for the free ligands suggest that the Seln ligands have slightly higher π -electron densities than the analogous Th ligands; this is supported by the ^{13}C NMR data for the CO ligands. The difference between activation barriers for $\text{Cr}(\text{CO})_3(\eta^5\text{-T})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Sel})$ is, as expected, reflected in a large difference in the relative electron densities of the heteroatom and the diene fragment ($E - \sum C$) in the T (−2.744 e) and Sel (−2.491 e) ligands. This is also true for the other $\text{Cr}(\text{CO})_3(\eta^5\text{-Th})$ and $\text{Cr}(\text{CO})_3(\eta^5\text{-Seln})$ complexes. Studies that have measured the aromaticities of the T and Sel ligands generally agree that T is more aromatic than Sel.⁸ In particular, it has been reported that the π bonding in Sel is more localized on the heteroatom and the two double bonds than in the case of the T ligand.^{6a} EHMO calculations of the Th and Seln ligands (Table 7) demonstrate that there is an increased electron density on the Se heteroatom and a decreased electron density on the diene fragment of the Seln ligands with respect to the analogous Th ligands. This is in agreement with our assumption that increasing the electron density on the heteroatom and decreasing the electron density on the diene fragment raises the activation barrier.

It should be noted that in the case of the Seln ligands, methyl substitution increases the electron density on the Se atom and the diene fragment equally, as evidenced by the constant $E - \sum C$ values in the Seln ligands. Thus, the activation barriers in the Seln complexes should increase to a smaller extent upon methyl substitution than in the analogous Th complexes, as observed. The addition of two methyl groups at the α -position in $\text{Cr}(\text{CO})_3(\eta^5\text{-T})$ increases the ΔH^\ddagger value by 1.5 kcal/mol; similar substitution of the $\text{Cr}(\text{CO})_3(\eta^5\text{-Sel})$ complex increases the ΔH^\ddagger value by only 1.2 kcal/mol.

Attempts to measure the activation barrier of the cationic $[\text{Mn}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})]\text{OTf}$ complex were limited because the complex, while rather soluble in CD_2Cl_2 (mp = −95 °C) at room temperature, becomes only

sparingly soluble at temperatures approaching −95 °C and precipitates out of solution as yellow needles. Consequently, we were unable to measure the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **10** in CD_2Cl_2 at low temperatures. The solvents CD_3OD , CD_3COCD_3 , and CD_3CN could not be used because these coordinating solvents are known to rapidly displace $\eta^5\text{-Th}$ and $\eta^5\text{-Seln}$ ligands from metal complexes^{4b,16,38c,d} including **10**.^{5b} The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **10** was measured in CD_3NO_2 down to the solvent melting point (mp = −29 °C). At this temperature, the ^{13}C NMR resonance for the carbonyl ligands was still a very sharp singlet. Assuming that the $\delta\nu$ value for **10** is similar to that (63 Hz) for the isoelectronic $\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})$ complex, the maximum ΔG_c^\ddagger value can be estimated from eq 3 to be 11.77 kcal/mol. This estimate, however, does not establish whether the activation barrier for $[\text{Mn}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})]\text{OTf}$ is higher or lower than that of $\text{Cr}(\text{CO})_3(\eta^5\text{-2,5-Me}_2\text{Sel})$. On the basis of our conclusion that a strong metal–selenium bond would lead to a higher barrier to rotation, we expected that the cationic (+1) d^6 Mn(I) complex would yield a stronger M–Se bond than that in the neutral d^6 Cr(0) complex. Although it has not been possible to determine this, the relatively high coalescence temperature ($T_c = 20$ °C) for $(\eta^5\text{-Me}_4\text{T})\text{RuCl}_2(\text{PPh}_3)$ may be an indication that the more positive oxidation state of Ru(II) leads to stronger sulfur to Ru(II) bonding, which leads to the higher rotational barrier.

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Supplementary Material Available: Textual description of data collection and structure solution and tables of additional positional and thermal parameters, bond angles, torsion angles, and least-squares planes for **5** and rate constants for the complexes at each temperature (11 pages). Ordering information is given on any current masthead page.

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