Preferred Coordination Sites for Metal Fragments in σ,π-Bimetallic Complexes. Detailed Mechanistic Insight from Heteroatom, Bridging Ligand, Solvent, Temperature, and Pressure Effects on the Irreversible Exchange of Coordination Sites[1]

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New heterobimetallic complexes with σ,π-bridging thiophene and selenophene ligands, $(\eta^1:\eta^5\text{-XCRCHCHCMn(CO)}_5)\text{Cr(CO)}_3$ (X = S, R = H (**1**), R = Me (**2**); X = Se, R = H (**3**)), were synthesized from $(\eta^5\text{-XCRCHCHCLi})\text{Cr(CO)}_3$ and $\text{Mn(CO)}_5\text{Hal}$ (Hal = Cl⁻, Br⁻, CF₃SO₃⁻). The complexes **1**−**3** irreversibly convert at 0 °C in acetone into the complexes $(\eta^1:\eta^5\text{-XCRCHCHCCr(CO)}_5)\text{Mn(CO)}_3$ (X = S, R = H (**4**), R = Me (**5**); X = Se, R = H (**6**)) by exchanging coordination sites. The σ,π- exchange of coordination sites is a first-order process and rate constants for the reaction of **2** are $(3.8 \pm 0.1) \times 10^{-5}$ and $(1.1 \pm 0.1) \times 10^{-5}$ s⁻¹ in acetone and cyclohexane at 15 °C, respectively. This reaction shows no significant pressure dependence. The activation entropies for the exchange process are -16 ± 6 and -30 ± 11 J/(mol K) for **1** and **2**, respectively. The kinetic data suggest an intramolecular exchange mechanism involving bridging carbonyls without any direct involvement of the solvent. It is suggested that in the activated complex the metal centers are η^1-bonded to the C2 of the thienyl ligand and that the free coordination sites are occupied by two bridging carbonyls. The bimetallic complexes $(\eta^1:\eta^5\text{-XCRCHCHCC(O)Mn(CO)}_5)\text{Cr(CO)}_3$ (X = S, R = H (**7**), R = Me (**8**); X = Se, R = H (**9**)) were also isolated from the reaction mixtures and could be obtained in higher yields by working under a CO atmosphere. The inserted carbonyl in the bridging ligand inhibits the metal fragments from exchanging coordination positions. Excess BuLi leads to the formation of the trimetallic five-membered ring complexes $(\mu\text{-Hal})\{\mu\text{-}(\eta^1:\eta^1:\eta^5\text{-SCRCHCHCC(O)Mn(CO)}_4)\text{Cr(CO)}_3\}\text{Mn(CO)}_4$ (R = H, Hal = Cl (**10**); R = Me, Hal = Br (**11**)). The lithiated thiophene precursor exclusively attacks a carbonyl of Re(CO)₅Br to give a bimetallic acylate, which after subsequent alkylation with Et₃OBF₄ affords the bimetallic rhenium carbene complex $(\eta^1:\eta^5\text{-SCHCHCHCC(OEt)Re(CO)}_4\text{Cl})\text{Cr(CO)}_3$ (**12**). The target complex $(\eta^1:\eta^5\text{-SCHCHCHCRe(CO)}_5)\text{Cr(CO)}_3$ (**13**), which could not be converted and did not insert a carbonyl, was obtained from Re(CO)₅CF₃SO₃ and the lithiated precursor. The structures of **7** and **10** were confirmed by single-crystal X-ray diffraction studies.

Introduction

The activation of simple organic molecules by more than one transition metal constitutes an area of research which has increased in importance over the last few years.[2] Organometallic compounds that incorporate two or more metal sites in close proximity provide access to reaction pathways not available to mononuclear systems as a result of cooperative electronic and/or steric effects. Of particular interest in our laboratories are studies relating to the activation of organic substrates, such as benzene, thiophene, and their derivatives, linked by σ- and π-coordination to two or more different metal fragments.[3]

The coordination chemistry of thiophene and thiophene derivatives is of great importance not only for model studies of the adsorption processes involved during the catalytic hydrodesulfurization of petroleum products[4] but also because of the versatility of thiophene as a ligand[5] and the fascinating coordination chemistry[6] it displays. Recently we have added to this impressive list an irreversible exchange of coordination sites by metal fragments in bimetallic[7] and trimetallic[1] complexes with σ,π-bridged thiophene ligands (Scheme 1). We are now

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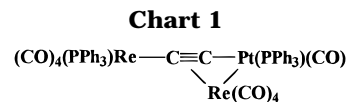
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Scheme 1

R=H, Mn(CO)$_5$
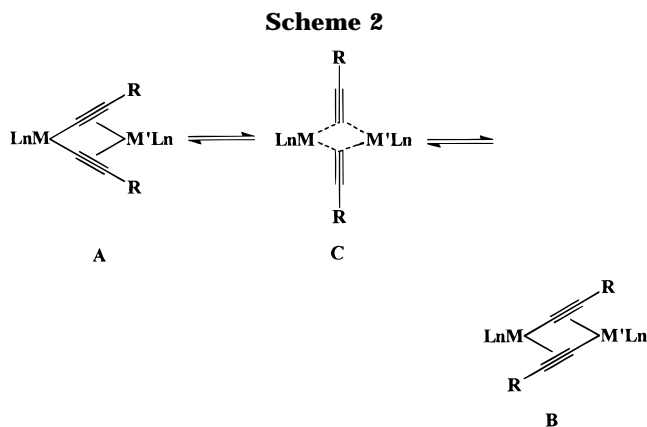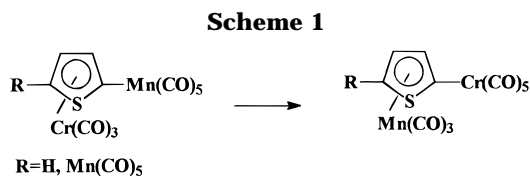
convinced that this result is far more general and demonstrates a new concept dealing with the presence of preferred coordination sites (σ vs π) around a common ligand in σ,π-heterobimetallic complexes.

Fluxional behavior in solution or the changing of coordination modes from σ to π by metal fragments, particularly for σ,π-bridged acetylide ligands, was previously observed by Erker[8] and Forniés[9] and their co-workers for σ,π-bridged acetylide ligands, (see **A** and **B** in Scheme 2). Erker showed that by reacting [M(R′Cp)$_2$-

Scheme 2

A   C

B

Chart 1

(CO)$_4$(PPh$_3$)Re—C≡C—Pt(PPh$_3$)(CO)
Re(CO)$_4$

(C≡CR)$_2$] (M = Zr, Hf, R = Ph, Me, R′ = H, Me, Bu^t) with zirconocenes "(RCp)$_2$Zr" (R = H, Me, Bu^t) bimetallic complexes were isolated with bridging σ,π-acetylide ligands, in which one σ-acetylide ligand had migrated from the one metal center to the other. Similarly, Forniés reported that dianionic complexes *cis*-[Pt(X)$_2$-(C≡CR)$_2$][10] (X = C$_6$F$_5$, CCR, R = Rh, Bu^t) reacted with *cis*-[Pt(C$_6$F$_6$)$_2$(THF)$_2$] to afford products of type **B**. It is also reasonable to assume that acetylide migrations proceed through the μ-η^1:η^1-C≡CR intermediate **C**. In fact, intermediates of this type can be stable and have been isolated. The X-ray structure determination of [Cp$_2$Ti(μ-C≡CBu^t)$_2$Pt(C$_6$F$_5$)$_2$] reveals that although the acetylide ligands were initially σ-bonded to the Ti-center, the asymmetric μ-σ-alkynyl ligands which bridge both metals are now tilted in such a way that the σ-bonding orbitals point more to the Pt atom in the final product.[10] In another example, the dimetalated ethyne (CO)$_5$Re—C≡C—Re(CO)$_5$ reacts with (PPh$_3$)$_2$PtC$_2$H$_4$ to give the σ,σ,π-bridged acetylide complex PtRe$_2$(μ-η^1:η^1:η^2-C≡C)(CO)$_9$(PPh$_3$)$_2$ with the Pt fragment not in a π-bonded but in a σ-bonded position (Chart 1).[11]

Substitution processes represented by the irreversible changing of σ- and π-coordination positions in bimetallic complexes with bridging acetylide ligands were described as acetylide migrations[8] or alkynyl transfer processes.[9] By comparison, we described the multiple substitution processes whereby two metal fragments exchange σ and π coordination sites around a thiophene ring as a metal exchange process.[1,7] In both cases the terminology was determined by the number of coordination positions involved during the conversion. As more examples are reported, irreversible metal exchange processes or irreversible acetylide migrations seems to be both the result of the same driving force, i.e. the existence of a kinetically favorable pathway for the changing of coordination sites leading to products of far greater thermodynamic stability. Therefore, we now refer to this observation as preferred coordination sites for metal fragments in σ,π-bimetallic complexes.

In preliminary communications[1,7] we reported the first examples of σ,π-complexes exhibiting metal ex-

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change processes. This unusual reaction, where six bonds are broken and six new bonds are formed, prompted us to perform a detailed kinetic investigation of the metal exchange process as a function of several chemical and physical variables in order to gain insight into the underlying reaction mechanism. In this paper, the synthesis and characterization of several new heterobimetallic complexes with σ,π-bridged thienyl and selenyl ligands are reported and the metal exchange process is investigated. Aspects associated with the metalation of (π-selenophene)Cr(CO)$_3$ and the reactivity of the metalated precursors used in the synthesis of novel σ,π-bimetallic compounds are also discussed. The insertion of a carbonyl ligand into the σ-bond of σ,π-complexes and reaction conditions utilizing 3 equiv of butyllithium and excess Mn(CO)$_5$Hal gave stable σ,π-complexes with modified bridging ligands and trimetallic complexes with novel five-membered rings consisting of a 1,2-bridging CO unit, two manganese fragments, and a μ-halogen ligand. The X-ray structures of (η^1:η^5-SCRCHCHCC(O)Mn(CO)$_5$)Cr(CO)$_3$ and {μ-Cl}{μ-(η^1:η^5:η^1-SCRCHCHCC(O)Mn(CO)$_4$)Cr(CO)$_3$}-Mn(CO)$_4$ are described and give insight into structural properties of these carbonyl-inserted products.

Experimental Section

I. General Procedures. Unless otherwise stated, all reactions and manipulations were conducted under a nitrogen atmosphere by using standard Schlenk and vacuum line techniques.[12] Thiophene was purified as described previously.[13] Literature procedures[14] were used for the preparation of (π-thiophene)Cr(CO)$_3$ and complexes with π-bonded thiophene derivatives (2-methylthiophene, 3-bromothiophene, 2,2′-bithiophene, 2-lithiothiophene). A modified version of the reported procedure[15] was used for the synthesis of (π-selenophene)Cr(CO)$_3$. Literature preparations were used for Mn-(CO)$_5$Hal (Hal = Br$^-$, Cl$^-$),[16] Mn(CO)$_5$CF$_3$SO$_3$,[17] Re(CO)$_5$CF$_3$SO$_3$,[17] and Cr(NH$_3$)$_3$(CO)$_3$.[18] Solvents were freshly distilled from the appropriate drying agents prior to use.[19] Column chromatography was performed on silica gel (0.063−0.200 mm) and the column cooled by recycling (−20 °C) 2-propanol through the column jacket. For the kinetic measurements acetone, THF, acetonitrile (all Roth, HPLC grade), cyclohexane (Aldrich, water free), and ^{13}CO (Aldrich) were used as received.

NMR spectra were recorded at various temperatures from −20 to +20 °C on a Bruker AC-300 spectrometer with reference to the deuterium signal of the solvent employed. ^{1}H NMR and ^{13}C NMR spectra were measured at 300.135 and 75.469 MHz, respectively, unless specified otherwise. NMR solvents were degassed by several freeze−pump−thaw cycles, and NMR sample tubes were sealed under nitrogen. Infrared spectra were recorded as liquid solutions on a Bomem Michelson-100 FT spectrophotometer, and frequencies (cm^{-1}) were assigned relative to a polystyrene standard. Mass spectra were recorded on a Perkin-Elmer RMU-6H instrument operat-

ing at 70 eV. Elemental analyses were obtained from the Analytical Division (PCMT) of the Council for Scientific and Industrial Research, Pretoria, South Africa.

The kinetics of the metal fragment exchange reactions were followed at ambient pressure in the thermostated cell compartment (quartz sample cell) of a Shimadzu 2100 spectrophotometer and on a Bruker Avance DRX 400 MHz WB spectrometer. For kinetic experiments at elevated pressure (up to 150 MPa), a thermostated (±0.1 °C) high-pressure cell[20] built into the cell compartment of the spectrophotometer and a specially designed optical cell equipped with a Teflon pressure transmitting tube[21] was employed. Reported rate constants are the average of at least three kinetic runs.

II. Synthesis of (π-Thiophene)Cr(CO)$_3$ and (π-Selenophene)Cr(CO)$_3$. The synthesis of the tricarbonyl complexes of chromium is illustrated by the general method described below.

A suspension of 7.37 g (39.4 mmol) of Cr(NH$_3$)$_3$(CO)$_3$, 197 mmol of ligand (thiophene, selenophene, and thiophene derivatives), and 130 mmol of BF$_3$·Et$_2$O (40 mL) was stirred at room temperature for 14 h, during which time the solution slowly changed color from yellow to red. A further 80 mL of ether was added (for selenophene, dichloromethane was used instead of ether), the mixture was cooled to −40 °C, and 50 mL of deoxygenated water was added dropwise over a period of 30 min. The reaction flask was removed from the cold and stirred at room temperature until all the ice had melted. The ether phase was decanted; the water phase was extracted with 30 mL portions of ether until the ether was almost colorless. The combined ether fractions were filtered through silica gel and evaporated to dryness. The residue was dried for 2 h under vacuum. The solid was washed 13 times with 30 mL of petroleum ether, dissolved in 120 mL of dichloromethane, and filtered through silica gel. The solution was concentrated to 30 mL, whereupon some precipitate separated. The addition of 60 mL of petroleum ether and the subsequent concentration of the mixture to 30 mL afforded red crystals of the desired compound. The solution was decanted, the crystals washed with petroleum ether (2 × 30 mL), and the product dried under reduced pressure. Yields were higher than 70% based on the mass of Cr(NH$_3$)$_3$(CO)$_3$. This method avoids separation by column chromatography. When 3-bromothiophene was used, however, a mixture of (η^5-3-bromothiophene)Cr(CO)$_3$ and (η^5-thiophene)Cr(CO)$_3$ was obtained and the desired product could be isolated after separation by column chromatography (1/1 dichloromethane/petroleum ether mixture) in 40% yield.

III. Preparation of a THF Solution of Lithiated (π-Thiophene)Cr(CO)$_3$. A THF solution (30 mL) of 0.60 g (2.7 mmol) of (π-thiophene)Cr(CO)$_3$ was cooled to −90 °C and treated with 1.8 mL (2.88 mmol) of n-BuLi (1.6 M solution in hexane). During the addition the color changed from orange to yellow. The mixture was stirred at −70 °C for 10 min, cooled to −90 °C, and used for subsequent reactions.

IV. Reaction of Lithiated (π-Thiophene)Cr(CO)$_3$ with Mn(CO)$_5$Hal (Hal = Cl, Br). (a) A solution of 2.7 mmol of (η^5-LiC$_4$H$_3$S)Cr(CO)$_3$ in 30 mL of THF was cooled to −90 °C and treated with a cold (−90 °C) THF solution (50 mL) of 2.7 of mmol Mn(CO)$_5$Hal. The brown solution was stirred and warmed to room temperature after 2 h. After the mixture was stirred at room temperature for a further 1 h, the solvent was removed under vacuum and the remaining residue chromatographed on silica gel (3 cm × 30 cm). A number of bands developed on elution with a 1/1 dichloromethane/petroleum ether solution and were collected. The first yellow band gave Mn$_2$(CO)$_{10}$ (2%), the following yellow fraction gave (η^5-SCHCHCHCCr(CO)$_5$)Mn(CO)$_3$ (**4**; (118 mg, 10.5%), a red

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fraction yielded (π-thiophene)Cr(CO)$_3$, and the next darker fraction afforded (η^5-SCHCHCHCC(O)Mn(CO)$_5$)Cr(CO)$_3$ (**7**; 60 mg, 5.1%).

4: C$_{12}$H$_3$O$_8$SCrMn (414.12). Anal. Found (calcd): C, 34.71 (34.80); H, 0.72 (0.74). MS (*m/z* (fragment, *I* %)): 414 (M$^+$, 17), 386 (M$^+$ − CO, 4), 358 (M$^+$ − 2CO, 8), 330 (M$^+$ − 3CO, 10), 302 (M$^+$ − 4CO, 21), 274 (M$^+$ − 5CO, 59), 246 (M$^+$ − 6CO, 31), 218 (M$^+$ − 7CO, 61), 190 (M$^+$ − 8CO, 79).

7: C$_{13}$H$_3$O$_9$SCrMn (442.13). Anal. Found (calcd): C, 35.27 (35.32); H, 0.66 (0.68). MS (*m/z* (fragment, *I* %)): 414 (M$^+$ − CO, 4), 386 (M$^+$ − 2CO, 1), 358 (M$^+$ − 3CO, 3), 330 (M$^+$ − 4CO, 3), 302 (M$^+$ − 5CO, 4), 274 (M$^+$ − 6CO, 13), 246 (M$^+$ − 7CO, 9), 218 (M$^+$ − 8CO, 17), 190 (M$^+$ − 9CO, 27).

(b) The same method was used as described in (a) with the only exception being that the temperature of the reaction solution was slowly raised to −10 °C, after which volatiles were immediately removed. Chromatography of the residue again yielded the products described in (a) with an additional orange band which eluted immediately after (π-thiophene)Cr(CO)$_3$ and afforded (η^5-SCHCHCHCMn(CO)$_5$)Cr(CO)$_3$ (**1**; 101 mg, 9.0%).

1: C$_{12}$H$_3$O$_8$SMnCr (414.12). Anal. Found (calcd): C, 34.65 (34.80); H, 0.71 (0.74). MS (*m/z* (fragment, *I* %)): 413 (M$^+$ − H, 35), 385 (M$^+$ − H − CO, 7), 357 (M$^+$ − H − 2CO, 15), 329 (M$^+$ − H − 3CO, 14), 301 (M$^+$ − H − 4CO, 25), 273 (M$^+$ − H − 5CO, 66), 245 (M$^+$ − H − 6CO, 31), 217 (M$^+$ − H − 7CO, 55), 190 (M$^+$ − 8CO, 75).

(c) Higher yields of **1** were obtained with the same method as in (b) with the exception that the Mn(CO)$_5$CF$_3$SO$_3$ complex was dissolved at −90 °C in 40 mL of THF (cooled before to −90 °C). Yields of **1** increased by more than 100%.

(d) Improved yields of **7** (134 mg, 11.1%) were obtained by repeating the method described in (a) under a CO atmosphere. Yields increased by *ca.* 120% for **7** but were much lower for **1** and **4**.

(e) To a cooled (−90 °C) THF solution (30 mL) of 2.7 mmol of (η^5-LiC$_4$H$_3$S)Cr(CO)$_3$ was added, in small portions, 0.52 g (2.7 mmol) of CuI. The suspension was warmed slowly to −50 °C and stirred for 10 min. The mixture darkened and was cooled to −90 °C, after which it was treated with 0.63 g (2.7 mmol) of Mn(CO)$_5$Cl, which was dissolved in 50 mL of THF. After removal of volatile materials the residue was chromatographed as above and gave Mn$_2$(CO)$_{10}$, 2,2′-bithiophene, (π-thiophene)Cr(CO)$_3$, and **1** (68 mg, 6%).

(f) A 0.60 g (2.7 mmol) amount of (π-thiophene)Cr(CO)$_3$ was dissolved in 30 mL of THF; this solution was cooled to −90 °C and treated with excess 5.1 mL (8.2 mmol) of *n*-BuLi (1.6 M solution in hexane). The mixture turned yellow and was stirred for 10 min at −70 °C. The mixture was cooled to −90 °C and a THF solution (150 mL) of 1.26 g (8.2 mmol) Mn(CO)$_5$Cl was added dropwise. The mixture turned red-brown, and the temperature was slowly raised to −10 °C. The solvent was removed under vacuum and the residue chromatographed on silica gel as before. The fractions were collected and yielded Mn$_2$(CO)$_{10}$, the black compound (μ-Cl)-{μ-(η^1:η^1:η^5-SCRCHCHCC(O)Mn(CO)$_4$)Cr(CO)$_3$}Mn(CO)$_4$ (**10**; 123 mg, 7.3%), which was recrystallized from dichloromethane and hexane, and unreacted (π-thiophene)Cr(CO)$_3$.

10: C$_{16}$H$_3$ClO$_{12}$SMn$_2$Cr (616.58). Anal. Found (calcd): C, 31.29 (31.17); H, 0.50 (0.48).

V. Reaction of (η^5-SC(Me)CHCHCLi)Cr(CO)$_5$ with Mn-(CO)$_5$Br. To a solution of 0.50 g (2.1 mmol) of (η^5-SC(Me)-CHCHCH)Cr(CO)$_3$ in 30 mL of THF at −90 °C was added 1.47 mL (2.5 mmol) of *n*-BuLi dropwise. The mixture was warmed to −80 °C, stirred for 10 min, and cooled to −90 °C, and a cold (−90 °C) THF solution (40 mL) of 0.37 g (1.3 mmol) of Mn-(CO)$_5$Br was added. The temperature of the mixture was slowly brought to −10 °C and the solvent removed under reduced pressure. The residue was chromatographed on silica gel, and the fractions were collected. Products obtained from the reaction were Mn$_2$(CO)$_{10}$, (μ-Br){μ-(η^1:η^1:η^5-SC(Me)-CHCHCC(O)Mn(CO)$_4$)Cr(CO)$_3$}Mn(CO)$_4$ (**11**; 7 mg, 0.5%), some unreacted precursor, (η^5-SC(Me)CHCHCH)Cr(CO)$_3$, (η^5-

SC(Me)CHCHCMn(CO)$_5$)Cr(CO)$_3$ (**2**; 60 mg, 6.5%), and (η^5-SC-(Me)CHCHCC(O)Mn(CO)$_5$)Cr(CO)$_3$ (**8**; 20 mg, 2.1%).

2: C$_{13}$H$_5$O$_8$SMnCr (428.15). Anal. Found (calcd): C, 36.39 (36.47); H, 1.16 (1.18).

8: C$_{14}$H$_5$O$_9$SMnCr (456.19). Anal. Found (calcd): C, 36.69 (36.86); H, 1.05 (1.09).

11: C$_{17}$H$_5$BrO$_{12}$SMn$_2$Cr (675.06). Properties and spectroscopic data were comparable to those of **10**.

VI. Preparation of (η^5:η^5-Bithiophene)Cr$_2$(CO)$_6$ (14). A 7.37 g (39.4 mmol) amount of Cr(NH$_3$)$_3$(CO)$_3$, 3.24 g (19.5 mmol) of 2,2′-bithiophene, and 130 mmol of BF$_3$·Et$_2$O were mixed in 40 mL of ether. The suspension was stirred for 14 h at room temperature, and the solution changed color from yellow to red with the precipitation of a red solid. An additional 80 mL of ether was added to the mixture, which was cooled over to −40 °C. Deoxygenated water (50 mL) was added dropwise over 30 min. The reaction flask was removed from the cold and stirred at room temperature until all the ice melted. The mixture was filtered, and the filtrate, which yielded (η^5-bithiophene)Cr(CO)$_3$, was handled according to the procedures described in section II. The precipitate was washed (4 × 30 mL) with water, ethanol, and ether before it was dissolved in acetone and filtered through silica gel. The solvent was removed from the filtrate under vacuum to give the red-brown product (η^5:η^5-bithiophene)Cr$_2$(CO)$_6$ (**14**; 3.33 g, 39%). Analytically pure crystals of **14** could be obtained by recrystallization from dichloromethane.

14: C$_{14}$H$_6$S$_2$O$_6$Cr$_2$ (438.31). Anal. Found (calcd): C, 37.97 (38.36); H, 1.32 (1.38). MS (*m/z* (fragment, *I* %)): 437 (M$^+$ − H, 9), 409 (M$^+$ − H − CO, 1), 381 (M$^+$ − H − 2CO, 1), 353 (M$^+$ − H − 3CO, 5), 325 (M$^+$ − H − 4CO, 4), 297 (M$^+$ − H − 5CO, 9), 269 (M$^+$ − H − 6CO, 39), 166 (C$_8$H$_6$S$_2$$^+$, 27).

VII. Reaction of (η^5-SCHCHCHCLi)Cr(CO)$_3$ with Re-(CO)$_5$Cl and Re(CO)$_5$O$_3$SCF$_3$. (a) To a cooled (−90 °C) solution containing 2.7 mmol of (η^5-SCHCHCHCLi)Cr(CO)$_3$, prepared according to section III, a THF solution containing 0.98 g (2.7 mmol) of Re(CO)$_5$Cl was added. The color of the solution immediately changed from yellow to black. The temperature of the solution was slowly raised to 0 °C and the volatile material removed under vacuum. The remaining black residue contained a salt which was dissolved in 40 mL of dichloromethane. The solution was cooled to −60 °C and treated with 0.54 g of Et$_3$OBF$_4$ in 20 mL of dichloromethane. The color of the solution changed from brown to violet when the temperature was raised to room temperature. The solvent was removed by reduced pressure and the residue chromatographed by using a 1:1 mixture of hexane and dichloromethane as eluant. The product isolated from the column gave (η^5-SCHCHCHCC(OEt)Re(CO)$_4$Cl)Cr(CO)$_3$ (**12**; 2.05 g, 75%).

12: C$_{14}$H$_8$O$_8$SReCr (609.92). Anal. Found (calcd): C, 27.70 (27.57); H, 1.28 (1.32). IR (hexane, cm^{-1}): Cr(CO)$_3$, 1949 (A$_1$, s), 1938, 1931 (E, vs); Re(CO)$_4$, 2104 (A$_1$, m), 2027 (B$_1$, s), 2007 (B$_2$, s), 1995 (A$_1$, m). ^{1}H NMR (−20 °C, CDCl$_3$): δ 6.89 (d, *J* = 3.13, 1H), 6.20 (d, *J* = 3.21, 1H) 5.83 (s, 1H), 5.04 (q, 2H), 1.53 (t, 3H). ^{13}C NMR (−20 °C, CDCl$_3$): δ Cr(CO)$_3$ 232, Re(CO)$_4$ 183, 185, and 189, thienyl 89, 93, 99, and 107, OEt 78 (CH$_2$) and 15 (CH$_3$). See Tables 3−5 for more data.

(b) To a cooled (−90 °C) THF solution (60 mL) of 1.2 g (2.5 mmol) of Re(CO)$_5$CF$_3$SO$_3$ was added a cold solution of 2.5 mmol of (η^5-SCHCHCHCLi)Cr(CO)$_3$ (see section III). The mixture was slowly heated to room temperature and stirred for an additional 1 h. The solvent was removed under reduced pressure and the residue chromatographed using a 1:1 mixture of hexane and dichloromethane as eluant. Fractions were collected, affording (η^5-thiophene)Cr(CO)$_3$ and the orange compound (η^5-SCHCHCHCRe(CO)$_5$)Cr(CO)$_3$ (**13**; 50 mg, 3.6%).

13: C$_{12}$H$_3$CrO$_8$SReCr (545.41) Anal. Found (calcd): C, 25.55 (26.13); H, 0.60 (0.56).

VIII. Metalation of (η^5-SeCHCHCHCH)Cr(CO)$_3$ and Subsequent Reactions with Mn(CO)$_5$Br. (a) A 100 mg (0.37 mmol) amount of (π-selenophene)Cr(CO)$_3$ was dissolved in 20 mL of THF and the solution cooled to −90 °C. A hexane

solution (10 mL) containing 0.23 mL (0.37 mmol) of *n*-BuLi was added, whereupon the solution immediately changed from red to dark brown. After the mixture was stirred in the cold for 10 min, 1.0 mL (7.9 mmol) of Me₃SiCl was added dropwise and the solution was removed from the cold and stirred for 2 h; the residue was chromatographed, but no silylated product or starting compound could be collected.

(b) A solution of 100 mg (0.37 mmol), (π-selenophene)Cr-(CO)₃ was prepared as before and slowly added to a cold (−90 °C) THF solution (15 mL) containing 0.37 mmol of lithium diisopropylamide (LDA). The mixture was stirred at −50 °C for 10 min and cooled again to −90 °C, and 1 mL of Me₃SiCl was added. The mixture was removed from the cold and stirred until it reached room temperature, after which the solvent was removed under vacuum. The solvent was removed under vacuum, the residue was chromatographed, and the fractions that were collected gave (η^5-SeCHCHCHCSiMe₃)-Cr(CO)₃ (**15**; 95.2 mg, 75%) and unreacted (η^5-SeCHCHCH-CH)Cr(CO)₃.

15: C₁₀H₁₂O₃SeSiCr (339.25). Anal. Found (calcd): C, 35.20 (35.40); H, 3.47 (3.57).

(c) A solution of 500 mg (1.87 mmol) of (π-selenophene)Cr-(CO)₃ in 50 mL of THF was slowly added to a THF solution (20 mL) containing 1.9 mmol of LDA at −90 °C. The mixture was warmed to −50 °C, stirred for 10 min, and cooled to −90 °C. First 3.50 mL (5.6 mmol) of *n*-BuLi was added, the same temperature changes as above were repeated, and 3.0 mL (23.6 mmol) of Me₃SiCl was added slowly. The mixture was stirred until it reached room temperature, after which the solvent was removed under vacuum. Chromatography of the residue afforded a red fraction, which after recrystallization from dichloromethane and hexane gave red metallic crystals of (η^5-2,3,5-*tris*(trimethylsilyl)selenophene)Cr(CO)₃ (**16**; 606.7 mg, 70%).

16: C₁₆H₂₈O₃Si₃SeCr (463.47). Anal. Found (calcd): C, 41.19 (41.47); H, 6.21 (6.13).

(d) A solution of 620 mg (2.25 mmol) of (π-selenophene)Cr-(CO)₃ in 50 mL of THF was added slowly to a solution of 2.5 mmol of LDA in 20 mL of THF at −90 °C. The mixture was warmed to −50 °C and stirred for 10 min. before it was again cooled to −90 °C, and a cold (−90 °C) THF solution (50 mL) of 617 mg of Mn(CO)₅Br was added. The temperature of the mixture was slowly raised to −20 °C, and the solvent was removed under reduced pressure. Chromatography of the residue and collection of the different fractions afforded Mn₂-(CO)₁₀, unreacted (π-selenophene)Cr(CO)₃, the orange compound (η^5-SeCHCHCHCMn(CO)₅)Cr(CO)₃ **3**; 60 mg, 5.2%), and the black compound (η^5-SeCHCHCHCC(O)Mn(CO)₅)Cr(CO)₃ **9**; 20 mg, 1.8%).

3: C₁₂H₃O₈SeMnCr (461.05) Anal. Found (calcd): C, 31.11 (31.26); H, 0.55 (0.59).

9: C₁₃H₃O₉SeMnCr (489.06) Anal. Found (calcd): C, 31.78 (31.93); H, 0.58 (0.61).

(e) A solution of 6.75 mmol of LDA in 20 mL of THF was treated with a solution of 600 mg (2.25 mmol) of (π-selenophene)Cr(CO)₃ in 50 mL of THF at −90 °C. The mixture was warmed to −50 °C, stirred for 10 min. and again cooled to −90 °C before a cold (−90 °C) THF solution (70 mL) of Mn-(CO)₅Br was added. The temperature of the mixture was raised to −20 °C and the solvent removed under vacuum. Chromatography on silica gel and the collection of fractions afforded Mn₂(CO)₁₀, unreacted (π-selenophene)Cr(CO)₃, **3**, and an impure mixture that contained **9**.

(f) A solution of 600 mg (2.25 mmol) of (π-selenophene)Cr-(CO)₃ in 50 mL of THF was slowly added to 2.5 mmol of LDA in 20 mL of THF at −90 °C. The mixture was warmed to −50 °C, stirred for 10 min, and cooled to −90 °C again before 4.21 mL (6.7 mmol) of *n*-BuLi was added. The temperature of the mixture was raised to −50 °C, the mixture was stirred for 10 min and again cooled to −90 °C, and a cold THF solution (−90 °C) of 1.23 g (4.5 mmol) of Mn(CO)₅Br in 70 mL of THF was

added. The mixture was warmed slowly until −20 °C, after which the solvent was removed under vacuum. Separation by column chromatography on silica gel gave Mn₂(CO)₁₀, unreacted (−-selenophene)Cr(CO)₃, and **9**.

IX. Conversion of 1, 2, and 3 into 4, 5, and 6, Respectively. The conversion of **1**−**3** into **4**−**6**, respectively, was studied under controlled reaction conditions. The complexes **1**−**3** (10−20 mg) were dissolved at −20 °C in *d₆*-acetone and sealed under nitrogen in a NMR tube. The ¹H and ¹³C NMR spectra were recorded at −20 °C once a week, and the mixture was stored at 0 °C for a period of 3 weeks. During this time the solution gradually changed from orange to yellow and the conversions from **1**−**3** into **4**−**6** were completed quantitatively with little decomposition.

X. Attempted Conversion of 13. A sample of **13** prepared and treated the same as under section X changed color from orange to yellowish green. The NMR spectra of this product indicated that no conversion took place. Instead, the Cr(CO)₃ fragment was displaced from the σ,π-heterobimetallic complex, affording Re(2-thienyl)(CO)₅ (**17**).

17: C₉H₃O₅SRe (409.4). Anal. Found (calcd): C, 26.88 (26.40); H, 0.85 (0.73). IR (CH₂Cl₂, cm⁻¹): 2138 (A₁, m), 2079 (B, vw), 2028 (E, vs), 1993(A₁, s). ¹H NMR (−20 °C, CDCl₃): δ (ppm) 7.44 (d, H5, 1H, ^3J = 5.0 Hz), 7.15 (d, H3, 1H, ^3J = 2.9 Hz), 6.98 (dd, H4, 1H, ^3J = 3.2, ^4J = 0.8 Hz). ¹³C NMR (−20 °C, CD₃C(O)CD₃): δ (ppm) Re(CO)₅ 183 (*cis*), 182 (*trans*); thienyl 124, 128, 129, 139.

XI. Kinetic Measurements. Solutions of **1** and **2**, whether prepared from either dried or nondried solvents such as acetone and dichloromethane, revealed no significant difference in the observed kinetics, and solvents were therefore used as received. In essence, no differences in the general kinetic behavior were observed when the metal exchange processes of **1** and **2** into **4** and **5**, respectively, were studied. Since complex **2** was found to be more stable than **1**, our kinetic investigations focused on **2** and its converted product **5**. A typical kinetic run involved the following procedure. Stock solutions of a fixed concentration of **1** or **2** were prepared in different solvents. The progress of the reaction was monitored by the increase and decrease of characteristic MLCT bands in the UV−vis spectra over the range 325−600 nm. The temperature dependence of the conversion was studied in acetone over the range 10−30 °C and the concentration (20 °C) and pressure dependence (18.7 °C) of **2** in acetone over the ranges (2−42) × 10⁻⁵ M and 10−150 MPa, respectively. OLIS KINFIT²² software was employed to calculate k_{obs} values from absorbance vs time traces by fitting single- or double-exponential functions through the data points.

In a control experiment the ¹³C NMR spectrum of **2** in *d₆*-acetone was recorded repeatedly over the period required for complete site exchange.

XII. X-ray Structure Determination of (η^1:η^5-SCHCHCHCC(O)Mn(CO)₅)Cr(CO)₃ (7) and (μ-Cl){μ-(η^1:η^1:η^5-SCRCHCHCC(O)Mn(CO)₄)Cr(CO)₃}Mn(CO)₄ (10). Data Collection and Processing. Crystal parameters and experimental conditions are listed in Table 1. All data were collected on an Enraf-Nonius CAD4 diffractometer by using graphite-monochromatized Mo Kα (λ = 0.7107 Å) radiation at room temperature. Accurate unit cell parameters were obtained by least-squares methods from the position of 25 centered reflections for each crystal (θ > 14° for **7**, θ > 15° for **10**). The zone collected for **7** was *h* (0, +7), *k* (−8, +8) and *l* (−21, 21) and for **10** was *h* (−10, +10), *k* (−12, +12), and *l* (0, 20). Both data sets were collected in the ω−2θ mode. Three standard reflections were monitored every 200 reflections. Reflections were corrected for Lorentz−polarization and absorption effects.

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(22) OLIS KINFIT, Bogart, GA.

Table 1. Crystal and Data Collection Parameters for 7 and 10

	7	10
formula	$C_{13}H_3O_9SCrMn$	$C_{16}H_3O_{12}ClSCrMn_2$
fw	442.16	616.58
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	6.162(1)	8.006(1)
b, Å	7.017(1)	9.651(2)
c, Å	18.194(2)	16.062(3)
α, deg	83.67(1)	72.74(2)
β, deg	86.32(1)	83.57(2)
γ, deg	85.75(1)	68.06(1)
V, Å^3	778.5(2)	1099.4(3)
Z	2	2
d_{calcd}, g/cm^3	1.89	1.77
cryst size, mm	$0.07 \times 0.25 \times 0.50$	$0.12 \times 0.25 \times 0.37$
appearance (parallelepiped)	purple	dark red
μ(Mo Kα), cm^{-1}	16.1	18.1
scan angle (ω + 0.34 tan θ), deg	0.66	0.52
data collection range, 2θ, deg	3−25	3−27
no. of data collected	2744	4034
total no. of unique data with $I > 2\sigma(I)$	1860	2971
no. of params refined	217	299
transmission factors: max, min (ψ scans)	1.000, 0.836	1.000, 0.961
R^a	0.1036	0.0592
$R_w{}^b$	0.0701	0.0431
largest positional shift/esd, final cycle	0.03	0.02
largest peak, e/Å^3	1.57^c	0.52

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c} 1.1 Å from Mn.

Structural Analysis and Refinement. The structures were solved by standard Patterson methods.[23] Refinement was by full-matrix least-squares methods.[24] The non-hydrogen atoms were refined anisotropically (excluding C2 and O8 in **7**), and the hydrogen atoms were placed in idealized positions with common isotropic thermal parameters, which were also refined. Atomic scattering factors were taken from the literature.[25] Perspective views of the molecules were prepared with ORTEP.[26]

Results and Discussion

Synthesis and Characterization. The complexes **1**−**17** were characterized by elemental analysis, mass spectra, and IR spectra (Tables 2 and 3) and ^{1}H and ^{13}C NMR spectroscopy (Tables 2, 4, and 5). Spectral assignments are based on fixed numbers assigned to ring protons and carbon atoms of the heteroaromatic ring with the lower number 2 allocated to the substituent containing the metal fragment.

η^5-Heteroatom-Ring Complexes. Chromium tricarbonyl thiophene and selenophene complexes were prepared in a two-step procedure first by converting Cr-(CO)$_6$ into Cr(CO)$_3$(NH$_3$)$_3$ and second by treating the latter with BF$_3$·Et$_2$O in the presence of excess thiophene or selenophene. Unlike Angelici and Sanger,[27] we favor

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Table 2. Spectroscopic Data for (π-ring)Cr(CO)$_3$ Complexes

complex	IR^a ν(CO) (cm^{-1}) assign		^{1}H NMR^b (δ, ppm; J, Hz) assign	
14^c	A$_1$	1964 (s)	H5, H5′	6.14 (d, 2H, ^3J 3.5)
	E	1882 (vs)	H3, H3′	6.09 (d, 2H, ^3J 3.7)
			H4, H4′	5.99 (t, 2H)
15	A$_1$	1961 (s)	H5	6.70 (dd, 1H, ^3J 3.5, ^4J 0.6, $^2J_{H,Se}$ 38.4)
	E	1864, 1884 (vs)	H3	6.23 (d, 1H, ^3J 3.2)
			H4	6.20 (t, 1H, ^3J 3.5)
16	A$_1$	1952 (s)	SiMe	0.27 (s, 9H)
	E	1856, 1879 (vs)	H4	6.26 (s, 1H)
			SiMe	0.28 (s, 9H)
				0.36 (s, 9H)
				0.40 (s, 9H)

^{a} CH$_2$Cl$_2$. ^{b} CD$_3$COCD$_3$, −10 °C. ^{c} CD$_3$COCD$_3$, −20 °C.

this method which was developed by Öfele,[14e] as no column separation is necessary and yields of final products are high (over 70%). Hermann et al.[28] were successful in isolating only (η^5-2,2′-bithiophene)Cr(CO)$_3$, whereas we succeeded in isolating (η^5:η^5-2,2′-bithiophene)-{Cr(CO)$_3$}$_2$ (**14**) from Cr(NH$_3$)$_3$(CO)$_3$. Complex **14** is poorly soluble in dichloromethane and precipitates as a red solid in ether. Purification of **14**, mainly from unreacted Cr(NH$_3$)$_3$(CO)$_3$, was achieved by extraction with cold acetone and column chromatography with dichloromethane. The Cr(CO)$_3$ fragment is very labile and is easily displaced to give (η^5-bithiophene)Cr(CO)$_3$ and ultimately bithiophene. In the ^{1}H NMR spectrum of **14** three resonances are observed for the six protons, and in the ^{13}C NMR spectrum four resonances for the eight carbon atoms are observed, indicating both rings to be electronically equivalent. The chemical shifts of the resonances are shifted upfield compared to free bithiophene, as is expected for π-bonded heteroatom ring systems.[29]

Metalation. Deprotonation of the thiophene complexes at the 2-position is achieved with *n*-BuLi in THF at low (−70 °C) temperatures.[14d] The metalation of (η^5-selenophene)Cr(CO)$_3$ under similar reaction conditions with *n*-BuLi, however, led to decomposition. When we employed the less nucleophilic LDA, a clear orange solution was obtained, which, on the addition of Me$_3$-SiCl, changed to red. The NMR and IR spectral data of the red product conformed to a formulation of (η^5-SeCHCHCHC(SiMe$_3$))Cr(CO)$_3$ (**15**) for the product, proving that the monolithiation of the chromium tricarbonyl selenophene complex was achieved. The reaction of the π-selenophene complex with 1 equiv of LDA, followed by 3 equiv of *n*-BuLi and subsequent treatment with excess Me$_3$SiCl, afforded the trisubstituted trimethylsilyl complex (η^5-2,3,5-SeC(SiMe$_3$)CHC(SiMe$_3$)C(SiMe$_3$))-Cr(CO)$_3$ (**16**). A progressive increase of electron density on the selenyl ring when protons were substituted by trimethylsilyl groups was evident from the lowering of carbonyl frequencies for the two bands of the Cr(CO)$_3$ unit in the infrared spectra on going from (π-thiophene)-Cr(CO)$_3$ to **15** to **16**. The coupling of the proton at the 5-position to the ^{77}Se nucleus gives the two-bond coupling constant $^2J_{H,Se}$ = 38.4 Hz for **15** and makes the assignment of the resonance of the doublet of doublets at δ 6.70 ppm for H(5) unambiguous. This value is smaller than $^2J_{H,Se}$ = 47 Hz found for free

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Table 3. Infrared Absorptions (cm^{-1}) for the Complexes in CH$_2$Cl$_2$

		ν(CO)					
		M(CO)$_3$ fragment		M(CO)$_5$ fragment			
complex	Mn−C(O)	A$_1$	E	A$_1^{(1)}$	B$_2$	E	A$_1^{(2)}$
1		1947 (m)	1859 (s)	2131 (w)	2075 (vw)	2040 (vs)	2021 (s)
2		1943 (m)	1854 (s)	2131 (w)	2075 (vw)	2040 (vs)	2020 (s)
3		1947 (m)	1858 (s)	2130 (w)	2074 (vw)	2039 (vs)	2019 (s)
7	1563 (vw)	1974 (m)	1884 (s) 1908 (s)	2125 (w)	2069 (vw)	2031 (vs)	2026 (s)
8	1566 (vw)	1970 (m)	1880 (s) 1903 (s)	2124 (w)	2069 (vw)	2031 (vs)	2025 (s)
9	1560 (vw)	1975 (m)	1881 (s) 1910 (s)	2124 (w)	2069 (vw)	2031 (vs)	2026 (s)
13		1946 (m)	1856 (s)	2146 (w)	2078 (vw)	2036 (vs)	2011 (s)

		ν(CO)					
		M(CO)$_3$ fragment		cis-M(CO)$_4$ fragment			
complex	Mn−C(O)	A$_1$	E	A$_1^{(1)}$	B$_1$	B$_2$	A$_1^{(2)}$
12[a]		1942 (m) (1949) (m)	1910 (s) (1938, 1931) (s)	2106 (m) (2104) (m)	2005 (vs) (2027) (s)	2005 (vs) (2007) (s)	1990 (s) (1995) (s)
10[b]	n.o.	1974 (m)	1890 (s) 1913	2117 (w), 2091 (m), 2042 (vs), 2013 (s), 1946 (s)			
11[b]	n.o.	1972 (m)	1886 (s) 1909	2114 (w), 2087 (m), 2040 (vs), 2031 (s), 1947 (s)			
4[b]		2066 (m), 2045 (s), 1993 (s), 1978 (s), 1929 (vs)					
5[b]		2064 (m), 2043 (s), 1990 (s), 1973 (s), 1927 (vs)					
6[b]		2064 (m), 2042 (s), 1991 (s), 1973 (s), 1928 (vs)					

[a] Values in parentheses are for data recorded in hexane. [b] Assignments not possible due to overlapping of bands.

Table 4. ^{1}H NMR[a] Chemical Shifts (δ) and Coupling Constants (Hz) for the Complexes in CD$_3$C(O)CD$_3$

complex	thiophene			other
1	6.16 (dd, H5) ^3J 3.5, ^4J 0.7	5.94 (dd, H3) ^3J 3.1, ^4J 0.8	5.98 (dd, H4) ^3J 3.5, ^3J 3.1	
2	5.87 (d, H3 or H4) ^3J 3.0	5.80 (d, H3 or H4) ^3J 3.0		2.31 (s, CH$_3$)
3	6.63 (dd, H5) ^3J 3.6, ^4J 0.9, $^2J_{\text{H,Se}}$ 33.5	6.23 (dd, H3) ^3J 3.5, ^4J 0.9	6.22 (t, H4) ^3J 3.3	
4[b]	7.11 (d, H5) ^3J 3.6	6.50 (d, H3) ^3J 2.9	6.78 (t, H4) ^3J 3.2	
5[b]	6.54 (d, H3 or H4) ^3J 2.8	6.36 (d, H3 or H4) ^3J 2.8		2.54 (s, CH$_3$)
6[b]	7.52 (d, H5) ^3J 3.8, $^2J_{\text{H,Se}}$ 28.3	6.83 (d, H3) ^3J 3.1	7.05 (t, H4) ^3J 3.4	
7[c]	6.51 (d, H3 or H5) ^3J 3.7	6.16 (d, H3 or H5) ^3J 3.1	6.07 (t, H4) ^3J 3.6	
8[d]	6.47 (sbr, H3 or H4)	5.91 (d, H3 or H4) ^3J 3.2		2.31 (s, CH$_3$)
9[b]	6.65 (d, H3 or H5) ^3J 3.7	6.54 (d, H3 or H5) ^3J 3.9	6.32 (t, H4) ^3J 3.9	
10[e]	6.46 (d, H3 or H5) ^3J 3.6	5.84 (d, H3 or H5) ^3J 3.5	5.58 (t, H4) ^3J 3.7	
12	7.11 (d, H3 or H5) ^3J 3.1	6.97 (d, H3 or H5) ^3J 3.2	6.32 (t, H4) br	5.32 (m, CH$_2$) 1.51 (t, CH$_3$)
13	6.11 (dd, H3 or H5) ^3J 3.6, ^4J 0.5	6.09 (dd, H3 or H5) ^3J 3.1, ^4J 0.5	5.89 (dd, H4) ^3J 3.1, ^3J 3.6	

[a] Assignments for H5 of **1** and **4** were made by comparison with **3** and **6**, respectively. All data were recorded at −20 °C unless otherwise noted. [b] 10 °C. [c] 5 °C. [d] 0 °C. [e] 0 °C (CDCl$_3$).

selenophene[30] but larger than the reported value of 18.8 Hz for (π-selenophene)Cr(CO)$_3$.[15] Three single resonances were observed for the SiMe$_3$ substituents in **16**. The chemical shifts of the selenyl carbons in the ^{13}C NMR spectra move downfield with decreasing positive charge on the ring, owing to the higher degree of substitution with SiMe$_3$ but the carbonyl carbon resonances stay unaffected.

The reaction of monolithiated (η^5:η^5-bithiophene){Cr-(CO)$_3$}$_2$ (**14**) from n-BuLi or LDA with Mn(CO)$_5$Hal leads to excessive decomposition.

Synthesis of σ,π-Heterobimetallic Complexes. Although π-coordinated thiophene complexes with two or more metal fragments bonded to the sulfur atom have been reported,[31] we are aware of only two other types of synthesized heterobimetallic σ,π-complexes with η^1:η^5-bridging thiophene ligands, one class having thienyl ligands, (η^1:η^5-SCHCHCHCFeCp(CO)$_2$)Cr(CO)$_3$[32] and (η^1:η^5-SCHCHCHCPt(L$_2$)(C$_4$H$_3$S))Cr(CO)$_3$ (L$_2$ = diphos,

(30) Simonin, M. P.; Pouet, M. J.; Cense, J. M.; Paulmier, C. *Org. Magn. Reson.* **1976**, *8*, 508.
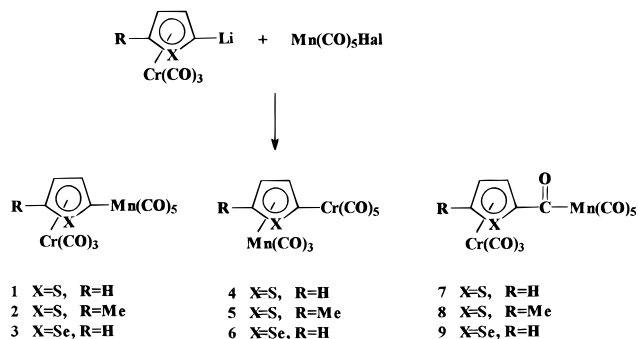
(31) (a) Chen, J.; Angelici, R. J. *Organometallics* **1990**, *9*, 879. (b) Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436. (c) Chen, J.; Angelici, R. J. *Appl. Organomet. Chem.* **1992**, *6*, 479. (d) Chen, J.; Young, V. G.; Angelici, R. J. *Organometallics* **1996**, *15*, 2727.

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Table 5. ^{13}C NMR Chemical Shifts (δ) for the Complexes in CD$_3$C(O)CD$_3$ at -20 °C

complex	thiophene	M(CO)$_5$	Cr(CO)$_3$	Mn(CO)$_3$	MnC(O)	other
1	96, 97, 109, 113	208	236			
2	98, 109, 111, 116	208	236			15 (CH$_3$)
3	98, 101, 109, 121	208	236			
4[a]	102, 103, 109, 164	218 (*cis*), 222 (*trans*)		220		
5[b]	101, 109, 124, 159	218 (*cis*), 222 (*trans*)		220		15 (CH$_3$)
6[a]	103, 108, 110, 177	218 (*cis*), 222 (*trans*)		220		
7[c]	91, 94, 95, 118	208	234		245	
8[b]	90, 95, 110, 117	209	234		245	16 (CH$_3$)
9[a]	93, 95, 96, 126	209	234		246	
10[d]	89, 91, 94, 113		232		n.o.	n.o.
12	94, 96, 102		233			79.9 (OCH$_2$), 15 (CH$_3$), 187, 186 (Re(CO)$_4$)
13	91, 96, 98, 109	218 (*cis*), 222 (*trans*)	236			

[a] 10 °C. [b] 0 °C. [c] 5 °C. [d] 5 °C (CDCl$_3$).

Scheme 3

1 X=S, R=H
2 X=S, R=Me
3 X=Se, R=H

4 X=S, R=H
5 X=S, R=Me
6 X=Se, R=H

7 X=S, R=H
8 X=S, R=Me
9 X=Se, R=H

2 PMe$_3$, 2 CO),[33] and the other having bridging thienylcarbene ligands, (η^1:η^5-SCHCHCHCC(OR)M(CO)$_5$)-Cr(CO)$_3$ (M = W, Cr; R = Et, O(CH$_2$)$_4$OEt).[33] Beck and co-workers[34] synthesized the bimetallic complex (η^1:η^4-SCHCHCHCH{Re(CO)$_5$})Mn(CO)$_3$ from [Re(CO)$_5$]$^-$ and [(η^5-SCHCHCHCH)Mn(CO)$_3$]$^+$ and the trimetallic complex {(η^1:η^4-SCHCHCHCH)Mn(CO)$_3$}$_2$Os(CO)$_4$ from [Os(CO)$_4$]$^{2-}$ and the cationic manganese precursors.

The utilization of lithiated arene complexes of chromium in reactions of complexes with halogen ligands has been well-established in our laboratories and was successfully employed to synthesize a large range of σ,π-bimetallic arene complexes.[3] The reaction of equimolar solutions of the lithiated thiophene and selenophene precursors with Mn(CO)$_5$Hal (Hal = Br$^-$, Cl$^-$) afforded Mn$_2$(CO)$_{10}$, **4**–**6**, and **7**–**9** in low yields.

Careful repetition of the synthesis without raising temperature over -10 °C and swift chromatography enabled the isolation and characterization of **1**–**3** in low yields. When crystals of **1**–**3** were dissolved in polar solvents such as THF and acetone and the temperature raised to 0 °C, they spontaneously and irreversibly underwent a metal exchange process (eq 1) to afford the

$$\{Cr(\eta^5\text{-}XC_4H_3), Mn(\eta^1\text{-}XC_4H_3)\} \rightarrow$$
$$\{Cr(\eta^1\text{-}XC_4H_3), Mn(\eta^5\text{-}XC_4H_3)\} \quad (1)$$
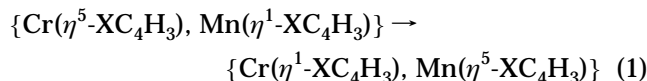
thermodynamically favored products **4**–**6**. The site exchange was practically quantitative, with only some minor decomposition occurring during the conversion. Two minor side products, (2-methyl-5-thienyl)Mn(CO)$_5$ and Cr(CO)$_6$, could be identified more clearly in the ^{13}CO experiment (see further discussion).

Whereas the utilization of phenylcopper instead of phenyllithium was very successful in increasing the yield of (η^5-C$_5$H$_5$)Re(CO)(NO)Ph,[35] the reaction of the lithiated precursor with CuI and Mn(CO)$_5$Cl afforded 2,2′-bithiophene, (η^5-2,2′-bithiophene)Cr(CO)$_3$, and (in a very low yield) **1**. Yields of **1** could be doubled by treating Mn(CO)$_5$Br with silver triflate prior to the reaction with the lithiated precursors. Irrespective of whether the reactions were carried out under normal conditions or in the dark, the yield of Mn$_2$(CO)$_{10}$ was unaffected. Furthermore, the fact that no products containing bithiophene or biselenophene were found in the reactions seems to exclude a radical mechanism for the metal exchange.

The conversions of **1**–**3** into **4**–**6** are accompanied by dramatic spectral changes as shown by the UV–vis, IR, and NMR spectra. The IR spectra display two totally different patterns for the ν(CO) bands in the IR spectra on exchanging the metal carbonyl fragments from σ- to π-environments. Typically, π-bonded thienyl or selenyl complexes of chromium reported in the literature[27] display two bands for the asymmetric vibrations (E) of the Cr(CO)$_3$ fragment. This was also observed in the spectra of **4**–**9** recorded in dichloromethane, but not for **1**–**3**, where these bands overlap. Uncertainty exists in the assignment of some of the bands to the vibrational modes of the Cr(CO)$_5$ and Mn(CO)$_3$ moieties of **4**–**6**. Replacing a π-bonded thienyl by a selenyl ring or a Mn-(CO)$_5$ by a Re(CO)$_5$ fragment does not affect the positions of the Cr(CO)$_3$ frequencies. A small but significant lowering of these carbonyl frequencies is observed in **2** compared to **1** by the introduction of a methyl substituent in the 5-position. In contrast, a pronounced lowering of ν(CO) bands of the Cr(CO)$_3$ fragment occurs on replacing the electron-withdrawing substituent R = C(O)Mn(CO)$_5$ in **7** and **9** by R = H as found in the reference complexes. This trend of a lowering in the ν(CO) value of the Cr(CO)$_3$ vibrations (ca. 20 cm^{-1}) is continued by replacement of R = H by Mn(CO)$_5$ in **1** and **3**. Therefore, the σ-bond is polarized by the metal fragment to the extent that the positive pole of the bond resides on the metal and the negative charge on the carbon atom of the ring.

The ν(CO) bands of the acyl groups of **7**–**9** are observed between 1560 and 1570 cm^{-1}, indicating a lowering of the C–O bond order of the acyl group when compared to values of 1593 and 1607 cm^{-1} recorded for the analogous benzene complexes {η^1:η^6-C$_6$H$_4$RC(O)Mn-(CO)$_5$}Cr(CO)$_3$ (R = H, F).[3a] This is consistent with the

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delocalization of π-electron density from either the heteroatom ring or the σ-bonded metal fragment to the acyl oxygen. Support of less electron density on the rings of **7**–**9** compared to the case for the (π-ring)Cr-(CO)$_3$ precursors[27] is manifested in the higher wavenumbers (frequencies for the A$_1$ and E bands increased by ca. 8 and 20 cm^{-1}, respectively) for the Cr(CO)$_3$ fragment.

Both the patterns and positions of the chemical shifts of the thienyl and selenyl protons in the ^{1}H NMR spectra of the unconverted complexes **1**, **3**, and **13** and the converted complexes **4** and **6** are totally different and represent two characteristic sets of signals. The spectra exhibit resonances for **1**, **3**, and **13** over a much narrower range (0.20–0.40 ppm), which are shifted upfield by ca. 1 ppm compared to **4** and **6**. The chemical shifts of H(4) and H(3) occur close together with H(5) shifted downfield by 0.20–0.40 ppm for **1** and **3** and resemble those displayed by Cp$_2$M(2-thienyl)$_2$ (M = Zr, Ti),[36] (η^1:η^5-SCHCHCHC{FeCp(CO)$_2$})Cr(CO)$_3$,[32] and Cp(NO)(Ph$_3$P)Re(2-thienyl).[6f] The resonances of **1** are shifted upfield compared to those of Cp$_2$M(2-thienyl)$_2$ (M = Zr, δ 7.45, 7.01, and 6.99) but downfield compared to those of (η^1:η^5-SCHCHCHC{FeCp(CO)$_2$})Cr(CO)$_3$ (δ 5.73, 5.45, and 5.34). However, the thienyl resonances of **4** and **6** are more evenly spread, with features similar to those recorded for the allylic compound (η^1:η^4-SCHCHCHCH{Re(CO)$_5$})Mn(CO)$_3$,[34a] for which the resonances of H(5)–H(3) (δ 5.28, 4.77, and 4.22) are shifted upfield. The chemical shifts for H(5) of **3** and **6** are clearly identifiable from the two-bond coupling with selenium, and the corresponding resonances for H(5) of **1** and **4** have been assigned accordingly by comparison with values reported in the literature.[15,30] In the ^{1}H NMR spectra of **1**, **3**, and **13** the H(3) and H(5) resonances appear as doublets of doublets by displaying in addition to the three-bond coupling a four-bond coupling with a constant of ^4J = 0.7–0.9 Hz. The two three-bond coupling constants for H(4) of the thienyl and selenyl rings are the same, with the exception of those observed for **1** and **13**, and appear as a triplet in the spectra. The chemical shifts in the ^{1}H NMR spectra of **7** and **9** are further downfield, revealing less electron density on the thienyl and selenyl rings when compared to **1** and **3**, which can be ascribed to the electron-withdrawing properties of the acyl substituent. The same is found when **5** is compared with **2**. The broad signals of lower intensity are associated with Mn(CO)$_5$ at δ 208 ppm, and the chemical shifts for Cr(CO)$_3$ at δ 236 in **1**–**3** are absent in the ^{13}C NMR spectra of **4**–**6**. Instead, a broad signal for Mn(CO)$_3$ at δ 220 and two resonances of different intensity at δ 218 (*cis*-CO) and 222 (*trans*-CO) are observed. The positions of these signals are consistent with values reported for complexes which contain the same metal carbonyl fragments.[37] Notable is the relatively high value for the *ipso* carbon of the thienyl and selenyl ring σ-bonded to chromium (δ (ppm) 164 (**4**), 159 (**5**), and 177 (**6**)), which is indicative of some carbene character in the σ-bond. Initially the spectrum of **6** was recorded at −20 °C , but only resonances of Mn(CO)$_3$, Cr(CO)$_5$, and the C(2) carbon of the selenyl ring were observed. When the measurement was repeated at higher temperature (10

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Scheme 4

Scheme 5

Scheme 6[a]

10 R=H, X=Cl
11 R=Me, X=Br
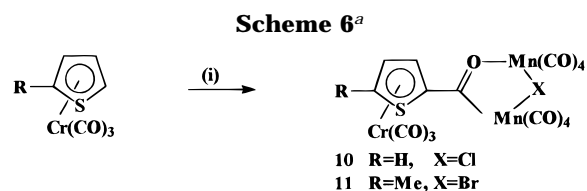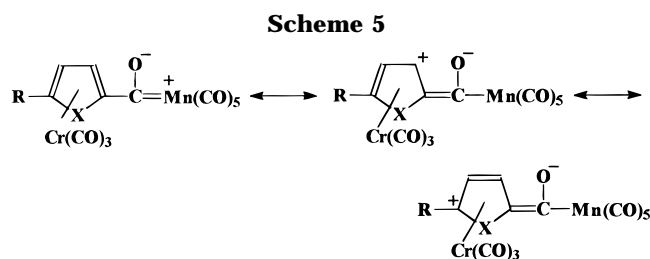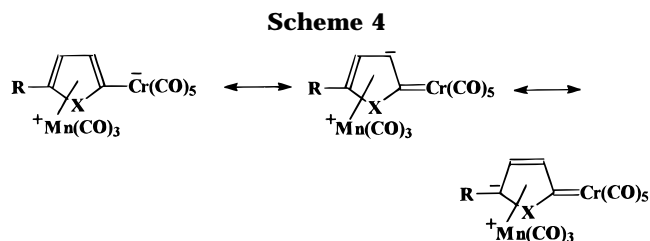
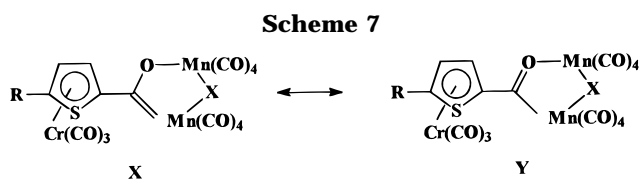[a] Legend: (i) 3 equiv of BuLi and excess Mn(CO)$_5$Hal.

°C), all the signals were resolved. Resonances for **7**–**9** observed at δ 245 ppm were assigned to the chemical shift of the carbonyl-carbon of the acyl group. From the spectroscopic data it was evident that the complexes had planar η^1:η^5 rings and that irreversible conversions of **1**–**3** into **4**–**6** occurred whereby the metal fragments exchanged coordination positions. It was also clear that, whereas the Mn(CO)$_5$ substituents increased the charge on the heterocyclic ring, the charge was decreased by acyl–metal fragments.

Conclusions drawn from the NMR data of the electronic properties of the thienyl and selenyl rings of **1**–**9** as affected by the nature of the σ-bonded substituents were supported by the IR data and are illustrated by the different resonance structures in Schemes 4 and 5.

Carbonyl-inserted products **7**–**9** were observed in all of the reactions but did not form during the metal exchange processes. Thus, the formation of carbonyl-inserted products **7**–**9** presented an alternative, competitive pathway. The yields of **7**–**9** were markedly improved when the synthesis was carried out under a CO atmosphere. Stabilization of complexes with metal–alkyl σ-bonds by carbonyl insertion to afford σ-bonded acyl analogs is well-known in the chemistry of alkyl complexes of cobalt and manganese carbonyls[38] and was also reported for (η^1:η^6-C$_6$H$_4$RC(O)Mn(CO)$_3$L$_2$)Cr(CO)$_3$ (L = CO, P(OMe)$_3$, L$_2$ = diphos, tmeda).[3a,c] The complexes **4**–**9** are stable in solution under an inert atmosphere.

Temperature plays an important role during the lithiation of π-coordinated thiophene. Treatment of the chromium thiophene precursor with 3 equiv of *n*-BuLi at −70 °C afforded the monolithiated intermediates, which subsequently reacted with 3 equiv of Mn(CO)$_5$Hal to give the novel complexes **10** and **11**. The complexes **1**, **2**, **4**, and **5** did not form under these conditions. The black crystals of **10** and **11** are less polar than (π-

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Scheme 7

Scheme 8[a]

[a] Legend: (i) $Re(CO)_5Cl$, Et_3OBF_4; (ii) $Re(CO)_5OTf$.

thiophene)$Cr(CO)_3$ and are very soluble in dichloromethane. To explore a foundation for understanding the formation of **10** and **11**, two possible reaction pathways were considered. The trimetallic carbene moiety **X** can be regarded as a resonance form of an O-metalated acylate accompanied by a halogen elimination and subsequent carbonyl substitution at a second $Mn(CO)_5Hal$. Heterobimetallic Fischer carbene complexes are readily synthesized by metalation of acylate intermediates at the oxygen and have been reported in the literature.[39] The resonance form **Y** is the result of the acyl group of **7** or **8** and the halo ligand of a second $Mn(CO)_5Hal$ group substituting carbonyl ligands. Whereas assignments of bands to ν(CO) vibrations of the $Cr(CO)_3$ unit were made, it was impossible to assign bands for the vibrations of the two different $Mn(CO)_4$ units, which displayed only five bands due to overlapping. The vibration associated with the bridging acyl carbonyl was not observed. The ν(CO) vibrations for $Cr(CO)_3$ are unaffected by the formation of a five-membered ring with a second $Mn(CO)_4$ moiety and are practically the same as those observed for **7** and **8**. Furthermore, this also applies for the chemical shifts of the protons of the thienyl ring, which are shifted slightly downfield compared to those for **7** and **8**. Final confirmation of the structures of **10** and **11** was obtained from a single-crystal X-ray diffraction study of **10**. Even though the structural units Mn–Hal–Mn, *cis*-Mn-$(CO)_4L_2$, M–O=C, and (π-thiophene)$Cr(CO)_3$ are well-represented in the literature,[40] we are unaware of any reported examples of all of them present in a single compound. The mechanism for the formation of **10** and **11** is complex in nature, and among the factors to be considered in proposing such a mechanism are the large excess of butyllithium required, the lithiated thienyl chromium precursor not affording the target compound when reacted consecutively with 2 equiv of $Mn(CO)_5Hal$, and the fact that no substitution reaction was observed when **7** or **8** was treated with $Mn(CO)_5Hal$, even under forcing reaction conditions.

In contrast, nucleophilic attack of (η^5-SCHCHCHC-Li)$Cr(CO)_3$ occurs at a *cis* carbonyl of $Re(CO)_5Cl$, which is consistent with reactions of organolithium reagents with $Re(CO)_5Cl$.[41] The resulting salt was alkylated to the corresponding bimetallic carbene complex **12**, which is stable in air for short periods of time but loses the $Cr(CO)_3$ fragment in polar solvents. Protonation of the acetyl anion *cis*-$[Re(CO)_4\{C(O)Me\}Cl]^-$ afforded the
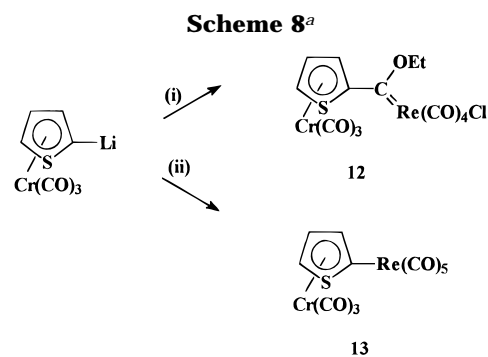
corresponding hydroxy(methyl)carbene complex.[42] Angelici and co-workers[43] synthesized a series of carbene complexes of rhenium, $[Re(carbene)(CO)_4X]$, which contain five-membered cyclic carbene ligands by a halide-catalyzed reaction of coordinated carbonyls and thiocarbonyls with three-membered heterocycles. The conversion of anionic $[Re(CO)_5]^-$ by alkyl halides or the decarboxylation of the acyl complexes $RC(O)Re(CO)_5$ (R = alkyl, aryl) are general methods[44] for the synthesis of alkyl complexes of rhenium carbonyls. Therefore, it is anticipated that the reaction of $Na[Re(CO)_5]$ with (η^5-2-bromothiophene)$Cr(CO)_3$ should lead to the target compound (η^5-SCHCHCHC$\{Re(CO)_5\}$)$Cr(CO)_3$ (**13**). The electrophilicity of Re was increased by exchanging the chloro ligand for a triflate ion, and subsequent reaction with the lithiated precursor afforded **13** in low yield. Experiments to facilitate the metal exchange process $\{\eta^1$-Re, η^5-Cr$\} \to \{\eta^1$-Cr, η^5-Re$\}$ according to conditions used for the corresponding Mn–Cr conversions failed, and no metal exchange was observed. Instead, the labile Re–thienyl ligand was substituted by solvent molecules, giving Re$\{$thienyl$\}(CO)_5$ (**17**), which was isolated and identified by IR and ^{1}H and ^{13}C NMR spectra. The Re results focused our attention on the importance of relative bond strengths of metal–thienyl σ-bonds and the lability of metal carbonyl ligands of Re compared to Mn. A carbonyl ligand is more easily displaced by PPh_3 in $MeMn(CO)_5$ compared to MeRe-$(CO)_5$,[45] and the energy for the Mn-Me σ-bond dissociation is lower compared to the Re–Me bond.[46] Therefore, a stronger Re–thienyl σ-bond and less labile carbonyl ligands could account for the bimetallic complex, with the Re fragment being inert toward a metal site exchange. However, Angelici and co-workers[47] synthesized $[(\eta^5$-thiophene)$Mn(CO)_3]^+$ from $Mn(CO)_5CF_3SO_3$

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Scheme 9[a]
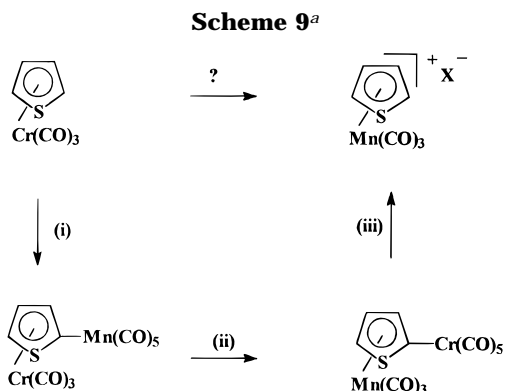
[a] Legend: (i) BuLi, Mn(CO)$_5$Hal; (ii) THF; (iii) HX, L.

and thiophene, but the analogous Re complex has not yet been reported.

Ligand exchange reactions from the coordination sphere of a metal are the most common of all reaction types. In contrast, the displacement of one metal atom by another in a fixed arrangement of ligands is unprecedented in the literature for simple organometallic compounds. The exchange of metal atoms, each from their own ligand environment to the site of the other, involves the breaking and making of many bonds. After the irreversible metal exchange conversion was realized, the substitution of the chromium metal atom in (π-thiophene)Cr(CO)$_3$ by a manganese metal atom to give [(π-thiophene)Mn(CO)$_3$]$^+$ became an attractive possibility. The stability of **4**, however, is remarkable, and initial efforts to displace the σ-bonded Cr(CO)$_5$ fragment by protonation of the thienyl group failed. Treatment of **4** with HBF$_4$ under a CO atmosphere and at elevated temperatures afforded an unstable intermediate which displayed an additional carbonyl frequency (1658 cm^{-1}) in the infrared spectrum but immediately converted back to **4** during workup procedures. Further work in this area has been initiated.

Kinetic Studies. The metal exchange reaction of **1**−**3** into **4**−**6** can be studied by several spectroscopic techniques, as conversions are associated with major spectral changes. The UV−vis spectra of **1** or **2** in acetone display maxima at 402 and 338 nm or 404 and 338 nm and a minimum at 365 or 363 nm, respectively. Typical examples are given in Figure 1. The exchange of coordination sites during the conversion of **1**−**3** into **4**−**6** are accompanied by characteristic changes in the spectra, as is indicated by a decrease in the intensity of the band at 402 nm and a small increase of the intensity of the band at 338 nm for **1** and increases at 338 and 363 nm with a decrease at 404 nm for **2**. The spectra exhibit two isosbestic points at 507 and 377 nm for **1** and at 533 and 397 nm for **2**. The largest spectroscopic change was found at 402 nm, and kinetic measurements were performed at this wavelength. The absorbance−time traces could be fitted to a single-exponential function, i.e. a first-order process, under all experimental conditions.

Table 6 lists rate constants for the metal exchange process of **2** in different solvents, and Table 7 lists data for acetone at different concentrations of **2**. Measurements for the conversion of **2** in THF or dichloromethane result practically in no change in the position of the bands, whereas a bathochromic shift is observed for the spectrum in cyclohexane compared to that in acetone.
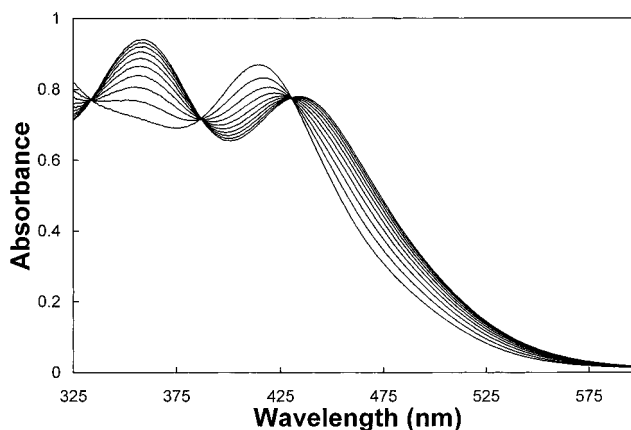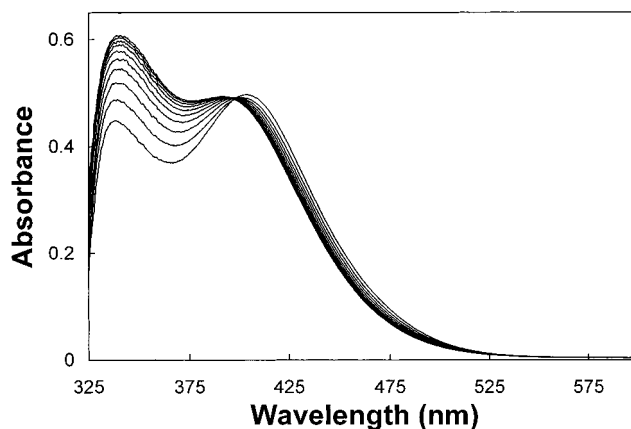
Figure 1. Repetitive scan spectra recorded for the conversion of **2** at 15 °C: (a, top) experimental conditions [**2**] = 2.8×10^{-4} M, Δt = 1500 s, solvent acetone; (b, bottom) experimental conditions [**2**] = 2.4×10^{-4} M, Δt = 3600 s, solvent cyclohexane.

Table 6. Rate Parameters for the Exchange Reaction of 2 in Various Solvents at 15 °C[a]

solvent	DN	ϵ	$10^6 \, k_{obs}$, s^{-1}
dioxane	14.8	2.21	dec
tetrahydrofuran		7.32	36.3 ± 0.6
acetonitrile	14.1	36.2	dec
dimethyl sulfoxide	29.8	49	dec
dichloromethane		8.9	25.9 ± 0.8
cyclohexane		2.02	11 ± 1
acetone	17	20.7	37.6 ± 0.5

[a] DN = donor number; ϵ = solvent dielectric constant.

Table 7. Kinetic Data for the Influence of the Concentration of 2 on the Exchange Reaction in Acetone at 20 °C

10^5[**2**], M	$10^5 k_{obs}$, s^{-1}	10^5[**2**], M	$10^5 k_{obs}$, s^{-1}
3.2	8.65 ± 0.13	29.8	7.55 ± 0.03
6.8	7.16 ± 0.04	41.8	7.20 ± 0.03
13.7	7.67 ± 0.04		

The changes in absorbance in the spectrum of **2** during the conversion in cyclohexane at 413 nm (decrease) and 359 nm (increase) are sufficient in magnitude to allow the determination of k_{obs} at the two different wavelengths. In cyclohexane, however, the reaction is accompanied by a slower decomposition process, which affected the final absorbance value and the calculated rate constants. At 359 nm the infinity absorbance was reached too soon and the rate constant (1.24×10^{-5} s^{-1}) was too high as compared to the data at 413 nm, where the infinity value was not reached and the rate constant (1.02×10^{-5} s^{-1}) was too low. Therefore, the true value

Table 8. Temperature Dependence for the Metal Fragment Exchange Reactions of 1 and 2 in Acetone

temp, °C	$10^6 k_{obs}$ (**1**), s^{-1}	$10^5 k_{obs}$ (**2**), s^{-1}
10	5.48 ± 0.04	2.20 ± 0.02
15	11.30 ± 0.01	3.76 ± 0.03
20	22.90 ± 0.01	7.53 ± 0.05
25	41.90 ± 0.09	12.83 ± 0.06
30		26.48 ± 0.16
$\Delta H^{\ddagger}$, kJ/mol	93 ± 2	86 ± 3
$\Delta S^{\ddagger}$, J/Kmol	−16 ± 6	−30 ± 11

must lie somewhere in between. Fortunately, the decomposition reaction is an order of magnitude slower than the metal exchange process, such that for a given time scale the data could be fitted to a first-order process. The rate constants in Table 6 indicate that solvent polarity plays no important role in the metal exchange reaction, such that changes in electrostriction or the direct participation of coordinated solvent molecules in the transition state can be ruled out. Furthermore, the observed first-order rate constant is independent of the employed complex concentration. The reaction of **2** was also followed kinetically with ^{1}H NMR in d_6-acetone ($k_{obs} = (1.06 \pm 0.06) \times 10^{-5}$ s^{-1} at 10 °C) and in d_2-dichloromethane ($k_{obs} = (1.46 \pm 0.09) \times 10^{-5}$ s^{-1} at 20 °C). The formation of any intermediate species could not be observed; the spectra only showed the formation of small quantities of side products such as (2-methyl-5-thienyl)Mn(CO)$_5$ and Cr(CO)$_6$.
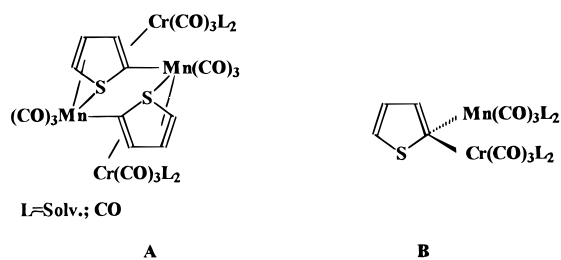
The temperature dependence of the rate constants for the conversions of **1** and **2** was used to determine the thermal activation parameters (see Table 8). Only a narrow temperature range could be used, as excessive decomposition occurred at 30 °C for **1** and 35 °C for **2**, and temperatures lower than 10 °C did not lead to experimentally significant amounts of converted products **4** and **5**, respectively. Activation enthalpies for the site-exchange reactions of **1** and **2** were found to be 93 ± 2 and 86 ± 3 kJ/mol, respectively, which are characteristic for the cleavage of covalent bonds. The activation entropies are small and negative, almost zero within the experimental error limits, in both cases and point to an intramolecular exchange process.

Further investigations into the reaction mechanism were conducted on **2** because of its greater stability as compared to **1**. In order to establish whether an addition or dissociation of ligands is important in the rate-determining step of the reaction, the volume of activation for the exchange reaction of **2** in acetone was determined. The measurements showed an increased deviation from the isosbestic point with increasing pressure during the conversion of **2** to **5**, which could be attributed to an acceleration of the decomposition reaction at higher pressures. The kinetic data showed that the reaction in acetone is independent of pressure within the experimental error limits and that the activation volume is approximately zero (−0.6 ± 0.5 cm^3 mol^{-1}) for the site-exchange process (Figure 2). In light of this observation and the fact that the metal exchange process is independent of concentration, we can exclude the possibility of an intermolecular arene displacement route, for the reaction of which an intermediate of the type A in Chart 2 is representative. Since the kinetic data reveal no significant actvation entropy and activation volume, it is concluded that an intramolecular mechanism is operative. Furthermore, the reactions
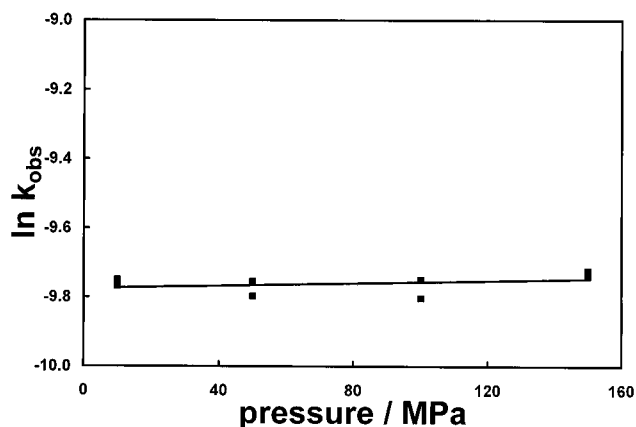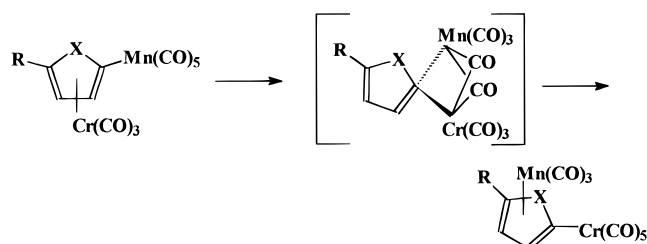
Figure 2. Effect of pressure on the reaction of **2**. Experimental conditions: [**2**] = (1.5–1.7) × 10^{-4} M; solvent acetone; temperature 18.7 °C.
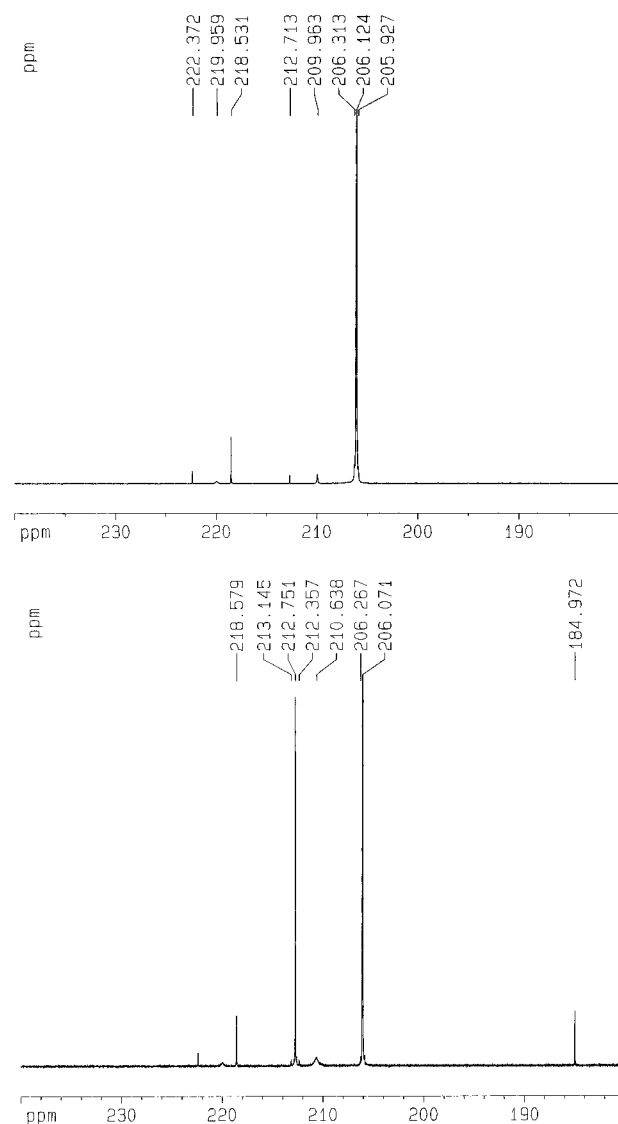
Figure 3. ^{13}C NMR spectra recorded after the completion of the metal exchange reaction of **2** in d_6-acetone in the presence of ^{13}CO (a) and in the absence of ^{13}CO (b) (see Results and Discussion). Experimental conditions: [**2**] = 4.0 × 10^{-2} M; temperature 20 °C.

afford first-order rate constants and are practically solvent-independent, thus excluding a dominant role by coordinating solvent molecules during the site-exchange process. A solvent-dependent rollover type of mecha-

Chart 2

L=Solv.; CO

A   B

Scheme 10

Table 9. Selected Bond Distances (Å) and Angles (deg) for 7 and 10

	7	10
Distances		
Cr−C(O)[a]	1.83(2)	1.853(8)
Cr−C(7)	2.16(1)	2.168(6)
Cr−C(6)	2.18(1)	2.188(7)
Cr−C(5)	2.23(2)	2.223(8)
Cr−C(4)	2.14(2)	2.154(7)
Cr−S	2.369(5)	2.354(2)
S−C(7)	1.75(1)	1.790(7)
S−C(4)	1.73(1)	1.750(7)
C(7)−C(6)	1.37(2)	1.403(8)
C(7)−C(8)	1.54(2)	1.450(8)
C(6)−C(5)	1.42(2)	1.399(9)
C(5)−C(4)	1.37(2)	1.365(10)
C(8)−O(4)	1.25(2)	1.275(7)
C(8)−Mn	2.07(1)	2.058(7)
Mn−C(O)[b]	1.91(2)	1.867(9)
Mn−C(11)	1.84(2)	1.856(8)
Mn(1)−C(9)		1.784(8)
Mn(1)−Cl		2.391(2)
Mn(2)−C(O)[b]		1.893(8)
Mn(2)−C(15)		1.802(8)
Mn(2)−Cl		2.360(2)
Mn(2)−O(4)		2.020(4)
Angles		
S−C(7)−C(6)	114.3(10)	109.2(5)
S−C(7)−C(8)	114.6(9)	117.3(5)
S−C(4)−C(5)	113.2(10)	112.7(6)
C(7)−C(6)−C(5)	110.6(12)	114.2(7)
C(7)−C(8)−Mn	124.2(8)	125.5(5)
C(7)−C(8)−O(4)	112.9(10)	112.3(6)
C(6)−C(7)−C(8)	131.1(14)	133.0(7)
C(6)−C(5)−C(4)	112.5(12)	113.0(7)
O(4)−C(8)−Mn	122.6(9)	122.2(5)
C(4)−S−C(7)	88.5(6)	90.2(3)
C(8)−Mn(1)−Cl		89.6(2)
C(8)−O(4)−Mn(2)		134.7(4)
Mn(1)−Cl−Mn(2)		106.4(1)
O(4)−Mn(2)−Cl		86.9(1)

[a] Average of M−C(carbonyl) distances. [b] Average of M−C(carbonyl) distances for carbonyls trans to other carbonyls.

nism, of which an important intermediate B is shown in Chart 2, is therefore unlikely. On the basis of the kinetic data, the formation of an intermediate with bridging carbonyls in the transition state and with both metal centers attached to the carbon in the 2-position in a $\eta^1:\eta^1$ manner, similar to the bridging carbon of the acetylide ligands in $[Cp_2Ti(\mu\text{-CCBu}^t)_2Pt(C_6F_5)_2]$,[10] is proposed (Scheme 10). A planar thienyl ligand will imply coordinative unsaturated metal fragments, whereas coordination of the thienyl sulfur will probably result in the destruction of the ring aromaticity and cause a deviation in the planarity of the ring. Coordination to the sulfur atom of π-coordinated thiophene by a second metal fragment invariably leads to the distortion of the ring and the formal changing of the coordination mode from η^5 to $\mu_2\text{-}\eta^4(S)$.[31b]

A control experiment was set up to monitor the progress of the site-exchange process of **2** by ^{13}C NMR spectroscopy and to determine whether free CO is formed at some stage during the reaction. For this purpose a solution of **2** in acetone was treated with ^{13}CO and ^{1}H and ^{13}C NMR spectra were recorded at the start and end of the site-exchange process (Figure 3a). The experiment was also repeated under identical conditions in the absence of ^{13}CO (Figure 3b). The ^{13}C NMR spectra in the presence of ^{13}CO showed, in addition to the signals associated with the formation of **8**, signals at 212, 210, 185, 139, 128, 127, 126, and 15 ppm. The signal at 185 ppm can be assigned to ^{13}C-labeled CO,[48] whereas those between 15 and 139 ppm can be assigned to the 2-methyl-5-thienyl fragment. The broad signal at 210 ppm and the signal at 212 ppm can be assigned to the $Mn(CO)_5$ and $Cr(CO)_6$ moieties, respectively.[49] The presence of $Cr(CO)_6$ and $Mn(CO)_5$ is supported by the IR spectra recorded in hexane following the experiment: the bands at 2000 cm^{-1} and between 2100 and 2130 cm^{-1} are associated with these fractions, respectively. The bands between 2100 and 2130 cm^{-1} for the $Mn(CO)_5$ fragment suggest the incorporation of ^{13}CO. Important to note is that no evidence for the formation of (2-methyl-5-acylthienyl)-

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$Mn(CO)_5$, a possible product in the presence of free CO, was found. The inclusion of ^{13}CO in $Cr(CO)_6$ is probably responsible for the interesting coupling observed at 212 ppm. The additional quartet of signals could be due to $^{13}C-^{53}Cr$ coupling ($J = 26.5$ Hz), which to our knowledge has not been reported in the literature. From a comparison of the spectra (Figure 3) it can be seen that in the presence of ^{13}CO both of the side products (2-methyl-5-thienyl)$Mn(CO)_5$ and $Cr(CO)_6$ are formed to a larger extent than in the absence of ^{13}CO. The intensity ratio of the signals for $Mn(^{13}CO)$, $Cr(cis^{13}CO)$, and $Cr(trans\ ^{13}CO)$ is, however, within the experimental error limits (10−20%) the same in both NMR spectra. If free CO is formed during the site-exchange process, ^{13}CO should in the described experiments bind to the Cr fragment and cause a significant change in the signal ratio. Since this is not the case, we conclude that no significant release of coordinated CO occurs during the exchange process, which is in line with all the other arguments presented in favor of an intramolecular process.

Structural Characterization of 7 and 10. The structures of complexes **7** and **10** are represented in parts a and b of Figure 4, respectively, and selected bond distances and angles are given in Table 9. The atom-numbering schemes for the molecular structures **7** and **10** differ from those used in the assignments of the

Table 10. Summary of Selected X-ray Data for Complexes with σ,π-Bridged Thiophene Ligands

complex				bond distance (Å)									bond angle (deg)[b]					
no.	M^1	X	R^1	R^2	C2C3	C3C4	C4C5	C2S	C5S	M^1C2	M^1C3	M^1C4	M^1C5	a	b	c	d	e	ref
T^a					1.370	1.424	1.370	1.714	1.714					111.5	112.5	112.5	111.5	92.2	47
1	Cr		H	Mn(CO)$_5$	1.390	1.428	1.371	1.764	1.723	2.289	2.228	2.218	2.198	107.6	115.5	111.8	111.7	93.3	7
4	Mn		H	Cr(CO)$_5$	1.485	1.472	1.399	1.768	1.729	2.299	2.252	2.150	2.131	109.7	109.4	115.3	111.0	94.5	7
7	Cr	CO	H	Mn(CO)$_5$	1.37	1.42	1.37	1.748	1.735	2.164	2.183	2.23	2.14	114.3	110.6	112.5	113.2	88.5	
10	Cr	CO	H	Mn$_2$(CO)$_8$Cl	1.403	1.399	1.365	1.790	1.750	2.168	2.188	2.223	2.154	109.2	114.2	113.0	112.7	90.2	
	Cr	CO	Mn(CO)$_5$	Mn(CO)$_5$	1.391	1.427	1.388	1.768	1.767	2.168	2.178	2.227	2.299	109.1	113.3	115.7	107.9	93.8	1
	Mn		Mn(CO)$_5$	Cr(CO)$_5$	1.421	1.425	1.385	1.768	1.763	2.304	2.151	2.136	2.23	101.9	117.6	116.6	103.9	99.9	1

^{a} T = thiophene. ^{b} Bond angles a–e are defined as follows:
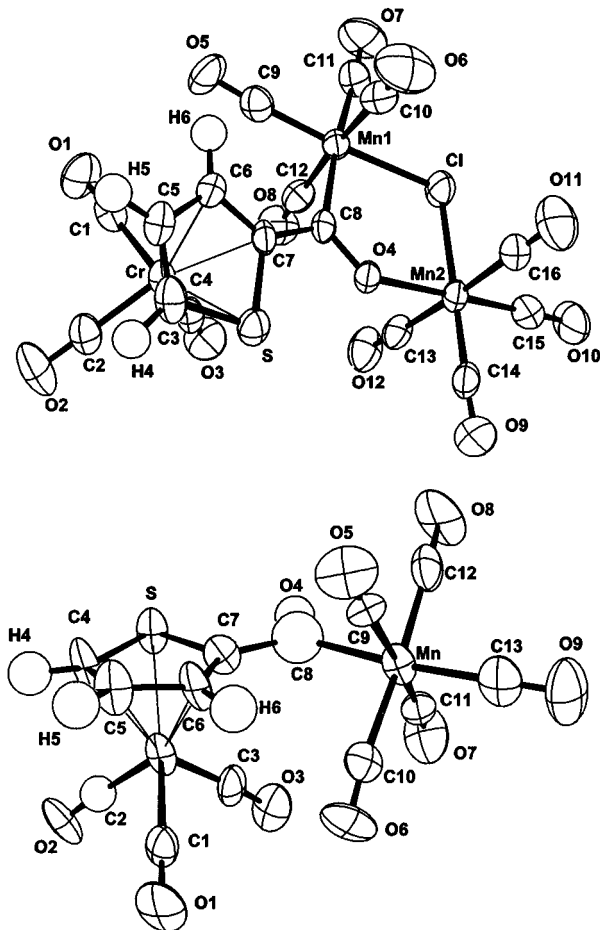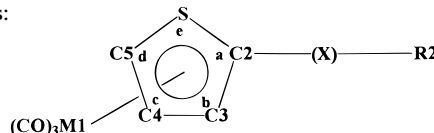
Figure 4. ORTEP drawings of **7** (a, top) and **10** (b, bottom).

carbon atoms and protons in the NMR data. The Cr–C distances are practically the same and together with the Cr–S distances of 2.369(5) Å for **7** and 2.354(2) Å for **10**, which are significantly shorter than the typical Cr–S single bond (ca. 2.50 Å; the Cr–S distance in [Cr-{S(Et)CH$_2$CH$_2$Ph}(CO)$_5$] is 2.459(2) Å[50]), are comparable to or slightly longer than the average value of 2.32(2) Å reported for Cr(η^5-thiophene)(CO)$_3$.[51] The data clearly indicate that all five atoms of the thiophene ring are bonded to the chromium in an η^5 fashion. As is expected for η^5-bonded thiophene ligands, the rings in **7** and **10**

are not entirely planar and the larger sulfur lies above the C(7)–C(6)–C(5)–C(4) plane and away from the chromium by 0.14(3) Å for **7** and 0.16(1) Å for **10**. The bond lengths of the bridging thiophene ligands in **7** and **10** display shorter C(7)–C(6) and C(5)–C(4) distances compared to the C(6)–C(5) distance and C–S distances which are longer than those of free thiophene.[52] The sulfur atom of the ring is *trans* to one of the carbonyl ligands, which is a common feature of η^5-bonded thiophene carbonyl systems and was also observed for the disorderly structure of (π-thiophene)Cr(CO)$_5$.[51] The most remarkable feature of structures **7** and, to a lesser extent, **10** is an acyl unit which is in the same plane as the thiophene ring. This is manifested in C(6)–C(7)–C(8)–O(4) torsion angles of 0.6 (**7**), 18.6 (**10**), and 3.7° for the trimetallic complex (η^1:η^1:η^5-C$_4$H$_2${Mn(CO)$_5$}-C(O)Mn(CO)$_5$)Cr(CO)$_3$.[1] The planar acyl unit is also shown by the angles between the planes described by the thiophene ring and C(7)–C(8)–O(4)–Mn are only 4.3° for **7**, 14.4 and 14.7° for **10**, and 1.5° for the trimetallic complex. In contrast, the acyl deviates by 34° for (η^1:η^6-C$_6$H$_5$C(O)Mn(CO)$_5$)Cr(CO)$_3$,[3a] 39° for *cis*-[(η^1:η^6-C$_6$H$_5$C(O)Mn{P(OMe)$_3$}(CO)$_4$)Cr(CO)$_3$],[3c] and 89° for [NEt$_4$][(η^1:η^6-o-C$_6$H$_4$(Cl)C(O)Fe(CO)$_4$)Cr(CO)$_3$].[53] The planar nature of the bridging ligand facilitates π-electron distribution from the thiophene ring and the manganese to the oxygen of the inserted carbonyl. Spectroscopic data support the removal of electron density from the thienyl ring, as was illustrated by the resonance structure shown in Scheme 5. The C–O bond distance of the acyl group is 1.254 Å for **7**, which is 0.051 Å longer than the C–O distance of MeC(O)Mn{P(OPh)$_3$}$_2$-(CO)$_2$[54] but 0.061 Å shorter than the C–O(carbene) bond in MnCp(CO)$_2$(C(OEt)Ph).[55] The Mn–C(acyl) distances of 2.066 Å for **7** and 2.058 Å for **10** are shorter than the corresponding distance of 2.103 Å for (η^1:η^6-C$_6$H$_5$C(O)-Mn(CO)$_5$)Cr(CO)$_3$,[3a] and 2.080 Å for *cis*-[η^1:η^6-C$_6$H$_5$C-(O)Mn{P(OMe)$_3$}(CO)$_4$)Cr(CO)$_3$][3c] and significantly shorter than the value of 2.207 Å recorded for the Mn–C(sp^2) distance in Mn{C(O)CH$_2$CH$_2$Ph}(dppm)(CO)$_2$.[56] By comparison, the Mn–C(O) bond length of **10** is shorter than the corresponding distance for **7**, indicating

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more carbene character, but is significantly longer than the Mn−C bond length of 1.96 Å for the carbene complex *cis*-[Mn{COCH$_2$CH$_2$O}(CO)$_4$Cl].[57] The C−O distance of the bridging acyl group of **10** is longer than the corresponding distance in **7** due to the coordination of the oxygen to a second manganese fragment. Whereas the Mn−Hal−Mn distances are the same for Mn$_2$(CO)$_8$Br$_2$,[58] a significant difference of 0.031 Å was found for the Mn−Cl distances in the chloro bridge of **10**. Again the structural data support the spectroscopic data, and contributions of both resonance structures **X** and **Y** in Scheme 7 are evident. Selected bond distances and angles relating to σ,π-bridged thiophenic ligands in bimetallic and trimetallic complexes are summarized in Table 10. Comparison of all bond distances in the frame of the bridging thiophene ring, which, if added and taken as a qualitative measure for the electron density on the ring, indicates the shortest distance (highest density) for free thiophene,[52] which increases (lower density) after π-coordination to Cr(CO)$_3$,[51] decreases only slightly for a metal fragment in the 2-position (**1**),[7] and gives the longest overall distance for an allylic-type thienyl ring (**4**).[7] This trend supports conclusions drawn from the NMR and infrared data. The structures of both free thiophene[52] and **1**[7] (where the thienyl ring is bonded to Cr(CO)$_3$ in a η^5 fashion) afford C−C bond distances in the thiophene ring that follow the sequence of short (C(2)−C(3) = 1.370 and 1.390 Å, respectively)−long (C(3)−C(4) = 1.424 and 1,428 Å, respectively)−short (C(4)−C(5) = 1.370 and 1.371 Å, respectively). This ordering changes to long (1.485 Å)−long (1.472 Å)−short (1.399 Å) from C(2) to C(5) for **4**,[7] displaying allylic character for the ring of the converted products on bonding to Mn(CO)$_3$ in an η^5 fashion. The latter is supported by some carbene character in the σ-bond, as is illustrated by the last two resonance structures in Scheme 4. Given the standard deviations of **7**, there are no significant differences in the C−C distances of the thiophene ring. Interestingly, an inductive effect is also evident in the σ-bond of the bimetallic complexes, where the largest angle of the ring is displayed at the *ipso* carbon with an electron-withdrawing acyl substituent in the 2-position and the smallest angle with an electron-donating metal fragment. However, this observation is more difficult to apply to the trimetallic complexes.

Conclusions. Two metal fragments, bonded directly to an aromatic ring in a σ,π-fashion, are in electronic contact via π-resonance effects. It was found that Cr and Mn fragments bonded to thiophene and selenophene in this manner can exchange coordination sites. Some analogy exists with the behavior of certain bimetallic acetylide complexes reported in the literature.[8,9] Kinetic studies showed that the exchange process follows first-order kinetics, is independent of the solvent, exhibits an almost zero activation entropy, and is characterized by a zero volume of activation. On the basis of these and other observations on the site-exchange reaction, an intramolecular metal exchange mechanism is postulated in which the first step is rate-determining and involves bridging carbonyl ligands. Furthermore, the metal exchange process is a clean, almost quantitative process and no side, competitive reactions, such as a carbonyl insertion into the metal−2-methyl-5-thienyl σ-bond, were observed. From our results and results reported for site occupation by metal fragments in bimetallic acetylide chemistry,[8−11] it seems reasonable to conclude that these are but the first examples of a far more general concept dealing with preferred coordination sites for metal fragments in σ,π-bimetallic complexes. In such compounds preferred coordination sites may exist and, when a favorable reaction pathway is present, a new type of reaction, i.e. an irreversible site exchange of metal fragments, occurs. In the process coordination sites are exchanged to give a converted thermodynamically favored bimetallic complex with the previously σ-bonded metal in the π-position and the π-bonded metal fragment in the σ-position in the converted product. In all the examples of metal exchange reactions observed so far, the product is always less polar than the starting material, as observed in the chromatographic separation. The metal exchange reaction was only observed in systems where an sp^2- or sp-hybridized carbon atom is simultaneously involved in σ and π metal−carbon bonding.

Supporting Information Available: Figures giving infrared and ^{1}H and ^{13}C NMR spectra for **1** and **4** and X-ray structural information, including tables of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and coordinates of hydrogen atoms for **7** and **10** and ORTEP drawings of the structures (12 pages). Ordering information is given on any current masthead page.

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