Trimetallic Complexes with σ,σ,π-Bonded Thienylene Ligands

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*Summary: The reaction of dilithiated (η^5-thiophene)-$Cr(CO)_3$ with 2 equiv of $Mn(CO)_5X$ (X = Cl or Br) afforded $[(\eta^1:\eta^1:\eta^5\text{-}\overline{SC\{Mn(CO)_5\}CHCHC}\{Mn(CO)_5\})Cr(CO)_3]$ which irreversibly converts into the thermodynamically more stable $[(\eta^1:\eta^1:\eta^5\text{-}\overline{SC\{Mn(CO)_5\}CHCHC}\{Cr(CO)_5\})Mn(CO)_3]$. Insertion of a carbonyl unit in one of the thiophene–manganese σ-bonds, $[(\eta^1:\eta^1:\eta^5\text{-}\overline{SC\{C(O)Mn(CO)_5\}CHCHC}\text{-}\{Mn(CO)_5\})Cr(CO)_3]$, inhibits this ($\eta^1$-tnlMn, η^5-tnlCr) → (η^1-tnlCr, η^5-tnlMn (tnl = thienylene) metal exchange process. Crystals of **2**, $C_{17}H_2SO_{13}CrMn_2$, are monoclinic with $a = 8.101(2)$ Å, $b = 13.024(2)$ Å, $c = 21.771(4)$ Å, $\beta = 99.29(2)°$, space group $P2_1/c$, and $Z = 4$, and those of **3**, $C_{18}H_2SO_{14}CrMn_2$, are monoclinic with $a = 13.986(3)$ Å, $b = 14.053(3)$ Å, $c = 12.888(2)$ Å, $\beta = 112.42(1)°$, space group $P2_1/c$, and $Z = 4$. At convergence the refined structures yielded $R_w = 0.057$ and 0.025 for **2** and **3**, respectively, using reflections with $I \geq 3\sigma(I)$.*

The activation of thiophene (tp) by transition metals has recently been the topic of many investigations.[1] Some very interesting examples reported are the cleavage of the carbon–sulfur bond,[2] metal insertions into the carbon–sulfur bond,[3] the activation of thiophene ring protons,[4] silyl migrations,[5] $\eta^1(S) \rightleftarrows \eta^2(2,3C)$ isomerizations of benzo[*b*]thiophene,[6] and the homogeneous hydrogenolysis of thiophene by $ReH_7(PPh_3)_2$ in the presence of a hydrogen acceptor.[7]

We recently described the reaction of lithiated (η^5-tp)-$Cr(CO)_3$ and $Mn(CO)_5X$ (X = Br or Cl)[8] which afforded the novel compound $[(\eta^1:\eta^5\text{-}\overline{SC\{Cr(CO)_5\}CHCHCH})Mn(CO)_3]$. This reaction represents a facile metal exchange process whereby the η^1-manganese and the η^5-chromium irreversibly change places. This exciting new concept of site preference by transition metal fragments in heterobimetallic chemistry has prompted us to investigate the reaction of dilithiated (η^5-tp)$Cr(CO)_3$ with 2 equiv $Mn(CO)_5X$ (X = Br or Cl) under varied reaction conditions. The synthesis of complexes with different transition metal fragments in the 2- and 5-positions of a thienylene (tnl) ligand is a synthetic challenge and may lead to materials with interesting conducting or optical properties. Sonogashira and co-workers[9] prepared diplatinum complexes with the same metal substituent in the 2- and 5-positions of thienylene. Previously, the chloromercuration of the CH group in the 5-position of Fp-2-C_4H_3S (Fp = $CpFe(CO)_2$) afforded Fp-2-C_4H_2S-5-HgCl, which has different metal substituents in these positions.[10] During this study we also focused on the structural features of trimetallic complexes which are linked by a σ,σ,π-bridging tnl ligand.

Experimental Section

Unless otherwise stated, all reactions were conducted under a nitrogen atmosphere by using standard Schlenk and vacuum line techniques.[11] Literature procedures were used for the preparation of (π-thiophene)$Cr(CO)_3$[12] and the dilithiation thereof.[13] Solvents were freshly distilled from the appropriate drying agents prior to use.[14] Column chromatography was performed on silica gel (0.063-0.200 mm) and the column cooled by recycling cold (−20 °C) methanol through the column jacket.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-300 spectrometer with reference to the deuterium signal of the solvent employed. ^1H 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 operating at 70 eV. Elemental analyses were obtained from the Analytical Division (PCMT) of the council for Scientific and Industrial Research, Pretoria, South Africa. Melting points were recorded in capillaries on a Gallenkamp hot-stage apparatus and are uncorrected.

Reaction of Dilithiothienylenetricarbonylchromium(0) with Bromopentacarbonylmanganese(I). A THF solution (50 mL, −50 °C) of $[(\eta^5\text{-tp})Cr(CO)_3]$ (0.55 mmol), was treated with 3 equiv of *n*BuLi and subsequently with a solution of $[Mn(CO)_5Br]$ at −70 °C. The reaction mixture was stirred for 2 h, the solvent was removed under vacuum, and the soluble fraction of the residue was subjected to column chromatography (SiO_2), eluting with hexane/dichloromethane (1:1) mixtures. The major band, the trimetallic complex $[(\eta^1:\eta^1:\eta^5\text{-}\overline{SC\{Cr(CO)_5\}CHCHC}\{Mn(CO)_5\})Mn(CO)_3]$ (**2**), was collected from the column and crystallized from a dichloromethane/hexane mixture (12% yield). The reaction mixture also yielded $Mn_2(CO)_{10}$, (η^5-tp)$Cr(CO)_3$, and other intractable products. Changing the eluent to ether/hexane (1:1) gave $[(\eta^1:\eta^1:\eta^5\text{-}\overline{SC\{Mn(CO)_5\}CHCHC}\{Mn(CO)_5\})Cr(CO)_3]$ (**1**) (3%) and $[(\eta^1:\eta^1:\eta^5\text{-}\overline{SC\{C(O)Mn(CO)_5\}CHCHC}\{Mn\text{-}$

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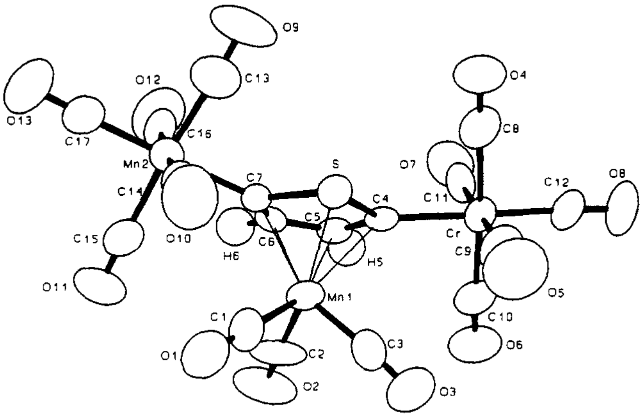

Figure 1. Perspective view of 2.

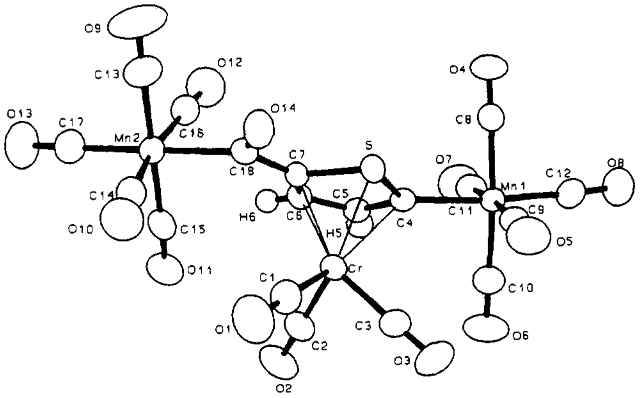

Figure 2. Perspective view of 3.

$(CO)_5\})Cr(CO)_3]$ (**3**) (5%). The complexes were fully characterized by elemental analysis and IR, ^1H NMR, ^{13}C NMR, and mass spectra.

Reaction of Dilithiothienylenetricarbonylchromium(0) with Bromopentacarbonylmanganese(I) under CO Atmosphere. The same procedure as above was followed, but after lithiation the nitrogen atmosphere in the reaction tube was replaced with CO. The main product from this reaction was **3** (15%) which was purified by column chromatography.

Spectral data for 1: IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2126 (m), 2074 (w), 2041 (vs), 2015 (s, sh), 1931 (s), 1839 (s, br); ^1H NMR (300 MHz, $CD_3C(O)CD_3$, −20 °C, δ 6.03 (s, H5 and H6); ^{13}C NMR (75.43 MHz, $CD_3C(O)CD_3$, −20 °C) δ 236 ($Cr(CO)_3$), 208 ($Mn(CO)_5$), 117 (C7 and C6), 112 (C5 and C4).

Spectral data for 2: IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2133 (m), 2057 (s, sh), 2043 (vs), 1977 (s), 1957 (s), 1923 (vs, br); ^1H NMR (300 MHz, $CD_3C(O)CD_3$, 10 °C) δ 6.75 (d, $^3J = 2.67$ Hz, 1H, H5 or H6), 6.46 (d, $^3J = 2.67$ Hz, 1H, H_5 or H_6); ^{13}C NMR (75.43 MHz, $CD_3C(O)CD_3$, 10 °C) δ 218 (*cis* $Cr(CO)_5$), 222 (*trans* $Cr(CO)_5$), 221 ($Mn(CO)_3$), 208 ($Mn(CO)_5$), 165 (C7), 132 (C4), 114, 111 (C5 and C6); MS (70 eV) *m/z* (%) 608 (7) [M^+]. Anal. Calc for $CrMn_2C_{17}H_2SO_{13}$: C, 33.57; H, 0.33. Found: C, 33.9; H, 0.36.

Spectral data for 3: IR (CH_2Cl_2) ν(CO) (cm^{-1}) ([M]CO) 2132 (w), 2123 (m), 2067 (w), 2040 (vs), 2025 (s, sh), 1953 (s), 1882 (s), 1868 (s); IR (CH_2Cl_2) ν(CO) (cm^{-1} ([M]C(O)tnl) 1564; ^1H NMR (300 MHz, $CD_3C(O)CD_3$, −20 °C) δ 6.51 (d, $^3J = 3.43$ Hz, 1H, H5 or H6), 6.13 (d, $^3J = 3.39$ Hz, 1H, H5 or H6); ^{13}C NMR (75.43 MHz, $CD_3C(O)CD_3$, 10 °C) δ 243 (−C(O)−, uncertainty in assignment due to a high signal to noise ratio), 235 ($Cr(CO)_3$), 209 ($-C(O)Mn(CO)_5$), 208 ($Mn(CO)_5$), 124, 118, 109, 97 (C4–C7); MS (70 eV) *m/z* (%) 608 (4) (M^+ − CO). Anal. Calc for $CrMn_2C_{18}H_2SO_{14}$: C, 33.98; H, 0.32. Found: C, 34.4; H, 0.37.

X-ray Crystallographic Analyses. Crystallographic data for $[(\eta^1{:}\eta^1{:}\eta^5\text{-}\overline{\mathrm{SC\{Cr(CO)_5\}CHCHC}}\{Mn(CO)_5\})Mn(CO)_3]$ (**2**) and $[(\eta^1{:}\eta^1{:}\eta^5\text{-}\overline{\mathrm{SC\{C(O)Mn(CO)_5\}CHCHC}}\{Mn(CO)_5\})Cr(CO)_3]$ (**3**), measured at 294 K, appear in Table I. Accurate unit cell parameters were obtained by least-squares methods from the position of 25 carefully selected centered reflections ($12<\theta<18°$ for **2**, $15<\theta<20°$ for **3**) on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (λ = 0.7107 Å), graphite monochromator, aperture 1.3 × 4.0 mm. There was no significant crystal decay, as indicated by the intensities of three standard reflections measured every 200 throughout the data collections, and intensities were corrected for absorption (empirical, based on the azimuthal scans for nine reflections of each crystal), as well as for Lorentz–polarization effects.

Table I. Crystallographic Data Acquisition and Refinement Details for Compounds 2 and 3

empirical formula	$CrMn_2C_{17}H_2SO_{13}$	$CrMn_2C_{18}H_2SO_{14}$
mol wt	608.13	636.14
cryst dimens, mm	0.17 × 0.20 × 0.20	0.20 × 0.40 × 0.42
space group	$P2_1/c$	$P2_1/c$
cell dimens		
a, Å	8.101(2)	13.986(3)
b, Å	13.024(2)	14.053(3)
c, Å	21.771(4)	12.888(2)
α, deg	90	90
β, deg	99.29(2)	112.42(1)
γ, deg	90	90
Z	4	4
vol, Å^3	2266.9(9)	2341.7(8)
D(calc), g·cm^{-3}	1.78	1.80
μ, cm^{-1}	16.48	16.00
F(000)	1192	1248
scan type (ω:2θ)	1:1	1:1
scan range (θ), deg	$3 < \theta < 30$	$3 < \theta < 30$
zone collcd		
h	0, +11	−19, +19
k	−18, 0	0, +19
l	−30, +30	0, +18
max scan speed, deg·min^{-1}	3.30	5.48
max scan time, s	60	60
scan angle (ω + 0.34 tan θ), deg	0.59	0.58
no. of reflns collcd	7288	7328
decay, % (uncorrected)	1.1	1.2
EAC correction factor		
max	1.000	1.000
min	0.898	0.935
av	0.945	0.965
no. of unique reflns used ($>3\sigma(I)$)	2514	4898
R_{int}	0.03	0.02
no. of params refined	308	333
max positional shift/esd	<0.01	<0.04
residual electron density, e Å^{-3}		
max	0.90	0.33
min	−0.79	−0.46
U_{iso}(H), Å^2	0.07(3)	refined
R	0.083	0.038
R_w	0.057	0.025

Both structures were solved by Patterson and Fourier methods.[15] Refinement was by full-matrix least-squares methods,[16] using $\sigma^{-2}(F_o)$ weights. The non-hydrogen atoms were refined anisotropically, and for **2** the hydrogen atoms were included in idealized positions for refinement with a common thermal parameter that was also refined. The two hydrogen atoms in **3** were refined in experimentally determined positions. Perspective drawings of the molecules are shown in Figures 1 and 2 illustrating the crystallographic numbering scheme used, and were prepared with ORTEP.[17] Atomic scattering factors were taken from the literature.[18]

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Table II. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Thermal Factors ($Å^2 \times 10^3$) for 2

atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Mn(1)	2754(2)	3688(1)	2797(1)	49(1)
C(1)	2293(19)	4078(10)	3533(6)	72(4)
O(1)	1968(13)	4337(8)	4014(4)	89(3)
C(2)	3646(22)	4931(10)	2699(8)	89(5)
O(2)	4188(16)	5688(7)	2599(6)	115(4)
C(3)	810(19)	4078(10)	2403(6)	70(4)
O(3)	–486(14)	4383(9)	2151(5)	111(4)
S	2589(4)	1912(2)	2822(1)	44(1)
C(4)	2758(13)	2394(8)	2076(5)	36(3)
C(5)	4272(14)	2963(8)	2197(5)	44(3)
C(6)	5141(14)	2979(8)	2821(5)	44(3)
C(7)	4407(13)	2449(8)	3258(5)	38(3)
Cr	1333(2)	1966(2)	1240(1)	47(1)
C(8)	1622(17)	572(11)	1485(6)	59(4)
O(4)	1834(13)	–239(7)	1609(5)	84(3)
C(9)	–707(18)	2060(13)	1578(7)	80(5)
O(5)	–1893(13)	2065(10)	1784(6)	120(4)
C(10)	1189(17)	3385(10)	1013(6)	63(4)
O(6)	1105(14)	4200(8)	848(5)	95(3)
C(11)	3373(18)	1854(11)	913(5)	62(4)
O(7)	4574(13)	1772(8)	717(4)	90(3)
C(12)	128(15)	1579(10)	485(5)	58(4)
O(8)	–629(11)	1370(8)	3(4)	95(3)
Mn(2)	5466(2)	2022(2)	4148(1)	49(1)
C(13)	5091(19)	686(12)	3898(6)	74(4)
O(9)	4867(16)	–161(7)	3774(5)	115(4)
C(14)	3352(17)	2006(11)	4401(6)	59(4)
O(10)	2109(12)	1958(10)	4547(5)	99(4)
C(15)	5747(17)	3451(10)	4352(6)	58(4)
O(11)	5852(14)	4280(7)	4465(5)	86(3)
C(16)	7503(17)	1989(12)	3857(6)	70(4)
O(12)	8712(12)	1976(10)	3661(5)	112(4)
C(17)	6506(16)	1659(10)	4917(6)	60(4)
O(13)	7162(12)	1391(8)	5407(4)	95(3)
H(5)	4748(14)	3369(8)	1830(5)	69(27)[b]
H(6)	6311(14)	3383(8)	2946(5)	69(27)[b]

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j(\mathbf{a}_i\cdot\mathbf{a}_j)$. [b] $U_{isotropic}$.

Final atomic coordinates and equivalent isotropic thermal parameters, selected bond lengths, and selected bond angles appear in Tables II–V, respectively.

Table III. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Thermal Factors ($Å^2 \times 10^3$) for 3

atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Cr	6719(1)	–267(1)	3344(1)	33(1)
C(1)	7732(2)	–1068(2)	3277(3)	49(1)
O(1)	8374(2)	–1576(2)	3275(2)	81(1)
C(2)	7385(2)	–300(2)	4868(2)	48(1)
O(2)	7807(2)	–317(2)	5836(2)	73(1)
C(3)	5972(2)	–1321(2)	3438(3)	45(1)
O(3)	5508(2)	–1988(1)	3468(2)	73(1)
C(4)	5231(2)	584(2)	2424(2)	30(1)
C(5)	5920(2)	1112(2)	3303(2)	32(1)
C(6)	6914(2)	1266(2)	3264(2)	35(1)
C(7)	7029(2)	841(2)	2342(2)	31(1)
S	5846(1)	301(1)	1495(1)	34(1)
Mn(1)	3655(1)	352(1)	1954(1)	33(1)
C(8)	3490(2)	1052(2)	648(2)	37(1)
O(4)	3402(2)	1481(1)	–117(2)	58(1)
C(9)	3752(2)	–806(2)	1262(3)	42(1)
O(5)	3810(2)	–1517(2)	899(2)	68(1)
C(10)	3916(2)	–316(2)	3278(3)	46(1)
O(6)	4087(2)	–721(2)	4085(2)	75(1)
C(11)	3629(2)	1454(2)	2747(3)	48(1)
O(7)	3624(2)	2101(2)	3266(2)	78(1)
C(12)	2246(2)	244(2)	1472(3)	52(1)
O(8)	1367(2)	213(2)	1152(2)	86(1)
C(18)	7886(2)	814(2)	1925(2)	35(1)
O(14)	7691(1)	401(2)	1035(2)	50(1)
Mn(2)	9310(1)	1463(1)	2742(1)	38(1)
C(13)	9247(3)	1758(2)	1314(3)	61(1)
O(9)	9197(2)	1925(2)	435(2)	105(1)
C(15)	9359(2)	1118(2)	4144(3)	42(1)
O(11)	9427(2)	917(2)	5022(2)	64(1)
C(14)	9814(2)	257(2)	2597(2)	48(1)
O(10)	10048(2)	–486(2)	2449(2)	67(1)
C(17)	10591(2)	2048(2)	3423(3)	62(1)
O(13)	11352(2)	2430(2)	3865(2)	105(1)
C(16)	8572(2)	2554(2)	2718(3)	50(1)
O(12)	8085(2)	3210(2)	2678(2)	81(1)
H(5)	5802(18)	1356(17)	3884(20)	42(8)[b]
H(6)	7437(16)	1593(16)	3780(18)	29(7)[b]

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j(\mathbf{a}_i\cdot\mathbf{a}_j)$. [b] $U_{isotropic}$.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for 2

	Bond Distances		
Mn1–center	1.797	Mn1–C4	2.304(10)
Mn1–S	2.319(3)	Mn1–C5	2.151(10)
Mn1–C6	2.136(11)	Mn1–C7	2.230(10)
Cr–C4	2.068(10)	S–C4	1.768(10)
S–C7	1.763(10)	C4–C5	1.421(13)
C5–C6	1.425(12)	C6–C7	1.385(13)
Mn2–C7	2.065(10)		
	Bond Angles		
C4–C5–C6	117.6(10)	C5–C6–C7	116.6(10)
C6–C7–S	103.9(8)	C4–S–C7	99.9(5)
S–C4–C5	101.9(7)	S–Cr–Cr	126.7(6)
C5–C4–Cr	130.3(7)	S–C7–Mn2	125.7(6)
C6–C7–Mn2	128.3(8)		

Results and Discussion

Complex 1, which is unstable at room temperature, converts almost quantitatively into 2 in polar solvents (Scheme I). The irreversible metal exchange process (η^1-tnlMn, η^5-tnlCr) → (η^1-tnlCr, η^5-tnlMn) afforded the thermodynamically favored trimetallic compound 2. Complexes 2 and 3 are stable crystalline compounds. Higher yields of 3 (15%) were obtained by repeating the reaction under a CO atmosphere. Interestingly, no metal exchange was found for 3, which indicated that the acyl group in the 2-position (C7) of thienylene ligand stabilizes the Mn1–C4 σ-bond of the 5-position and inhibits η^1-tnl $\rightleftarrows$ η^5-tnl conversion. Furthermore, carbonyl insertion to give 3 represents an alternative, competitative pathway of modifying 1 and yielding a less reactive trimetallic complex. The fact that carbonyl insertion occurs only in one of the two Mn–C σ-bonds also supports the idea that the electron-withdrawing abilities of the acyl substituent stabilizes the remaining Mn–C(tnl) σ-bond. The stabilization of complexes with metal–alkyl σ-bonds by carbonyl insertion to afford σ-bonded acyl analogs is well-known in Mn and Co chemistry[19] and was previously also found for bimetallic complexes that were obtained from the reaction of lithiated arenes of chromium tricarbonyl and $Mn(CO)_5Br$.[20]

Patterns, typical for carbonyl frequencies of the independent $Cr(CO)_3$ and $Mn(CO)_5$ moieties, were found for the bands in the IR spectrum of 1. In contrast, the IR spectrum of 2 is complicated by the overlapping of the recorded spectral bands for the $Mn(CO)_3$ and $Cr(CO)_5$ fragments, making unique assignments difficult. The bands assigned to the $Cr(CO)_3$ unit of 1 are observed at lower wavenumbers compared to those of the same unit of 3, which indicates that the thienylene ligand places

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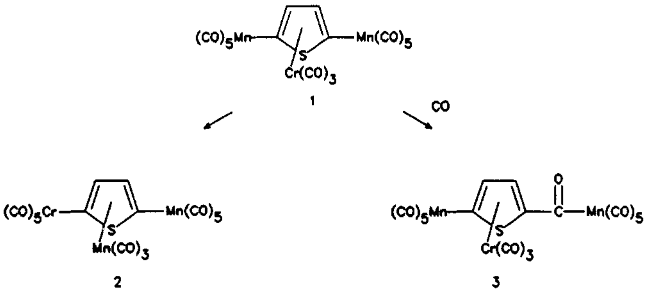
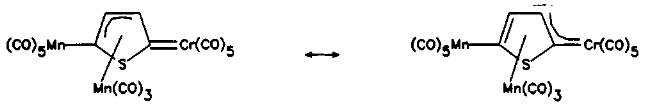
Table V. Selected Bond Distances (Å) and Bond Angles (deg) for 3

	Bond Distances		
Cr–center	1.823	Cr–C4	2.299(2)
Cr–S	2.365(1)	Cr–C5	2.227(3)
Cr–C6	2.178(3)	Cr–C7	2.168(2)
Mn1–C4	2.078(2)	S–C4	1.767(2)
S–C7	1.768(2)	Cr–C5	1.388(3)
C5–C6	1.427(3)	C6–C7	1.391(3)
C7–C18	1.490(3)	Mn2–C18	2.075(3)
	Bond Angles		
C4–C5–C6	115.7(2)	C5–C6–C7	113.3(2)
C6–C7–S	109.1(2)	C4–S–C7	93.8(1)
S–C4–C5	107.9(2)	S–C4–Mn1	120.3(1)
C6–C7–C18	133.6(2)	S–C7–C18	117.2(2)

Scheme I. Products of the Rearrangement and Carbonyl Insertion Reaction of 1



Scheme II. Resonance Structures of 2



more electron density on the chromium in 1. This we again attribute mainly to the electron-withdrawing ability of the acyl unit. The band at 1564 cm^{-1} was assigned to the carbonyl group of the bridging thienylene ligand and is lower than the values recorded for [Mn(CO)$_5$COMe] (1663)[21] and [Mn(CO)$_5$(COC$_6$H$_4$F-*p*)] (1606).[22]

Whereas the ^{1}H NMR spectrum of 1 displays only one resonance for the C5 and C6 protons, these protons are different in the spectrum of 2 and resonate at 6.75 and 6.46 ppm. The resonances of 1 and 3 are shifted upfield compared to those for 2, reflecting a less shielded thienylene ring. This we ascribe to the greater electron-withdrawing ability of the Mn(CO)$_3$ moiety compared to Cr(CO)$_3$ for 1 and the effect of the acyl substituent for 3 compared to a Mn(CO)$_5$ fragment. Conclusive spectral evidence for the structural formulations of 1–3 are found in the carbonyl region of the ^{13}C NMR spectra. Chemical shifts for the resonances observed for Mn(CO)$_5$ (broad, 208 ppm), Cr(CO)$_5$ (218, 222 ppm), Cr(CO)$_3$ (235 ppm), and Mn(CO)$_3$ (219 ppm) correspond to typical values reported for these fragments in the literature.[8,23]

X-ray diffraction studies were performed on suitable crystals of 2 and 3. Although the thienylene rings in both complexes are planar, they are tilted with C5 and C6 closer and C4 and C7 further away from the η^5-coordinated transition metal. The distance between the smaller Mn atom and the center of the thiophene ring in 2 is 1.797 Å, significantly shorter than the distance of 1.823 Å observed for the Cr–center distance in 3. The bond lengths of the bridging thienylene ligand in 3 are typical for η^5-coordinated thiophene ligands:[1b] the C4–C5 (1.388(3) Å) and C6–C7 (1.391(3) Å) distances are clearly shorter than the C5–C6 (1.427(3) Å) distance. In contrast, the corresponding C4–C5 (1.421(13) Å) distance in 2 is the same as the C5–C6 (1.425(12) Å) bond length, which indicates allylic character, and they are longer than the C6–C7 (1.385(13) Å) distance (Scheme II). The acyl unit of 3 is in the plane of the disubstituted thiophene ligand, facilitating the removal of electron density from the thienylene ring, supporting conclusions drawn from the spectral data. The Cr and Mn atoms are on the same side of the thiophene ring (0.30 and 0.40 Å, respectively, from the thiophene plane). The η^1-tnl bonded to the Cr and Mn metals in 2 have comparable M–C(tnl) distances, indicating some carbene character in the Cr–C(tnl) bond.[24] Both these metal fragments are on the same side of the thienylene plane (0.30(1) and 0.40(1) Å, respectively, from the plane toward the open side of the ring).

In conclusion, we have shown that the metal exchange process reported previously[8] also applies to analogous trimetallic complexes. This method can successfully be utilized to prepare trimetallic compounds with different metal fragments in the 2- and 5-positions of a π-coordinated thienylene ligand. We are presently extending our investigation to include other metal fragments that may also promote the η^1-tyl $\rightleftarrows$ η^5-tyl (tyl = thienyl) conversion. At this point the mechanism of the exchange process is not fully understood and still under investigation.

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Supplementary Material Available: Tables of bond distances and angles and anisotropic thermal parameters and perspective drawings of the unit cell contents for 2 and 3 (12 pages). Ordering information is given on any current masthead page.

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