Reactions of the η^5-2,5-dimethylthiophene complex Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ with nucleophiles (Ph$^-$, Me$^-$, $^-$CH(CO$_2$Me)$_2$ and OH$^-$) [1]

Jiabi Chen [2], Yingzhong Su, Robert A. Jacobson, Robert J. Angelici *

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, IA 50011, USA

Abstract

Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (1), where Cp* = η^5-C$_5$Me$_5$ and 2,5-Me$_2$T = 2,5-dimethylthiophene, reacts with PhLi to give Cp*Ir(2,5-Me$_2$T · 2Ph) and the acylthiolate Cp*Ir(η^4-SC$_3$H$_2$MeC(=O)Me) (3) which incorporates oxygen from the tetrahydrofuran solvent and whose structure was established crystallographically. The analogous reaction of 1 with MeLi gives Cp*Ir(2,5-Me$_2$T · 2Me). Complex 1 reacts with $^-$CH(CO$_2$Me)$_2$ to give Cp*Ir(η^4-2,5-Me$_2$T · C(CO$_2$Me)$_2$) (6), which contains an opened-ring thiolate ligand. With OH$^-$, 1 gives both 3 and Cp*Ir(η^4-2,5-Me$_2$T · O) (7), which incorporates a thiophene S-oxide ligand. These reactions are discussed in the context of related reactions of η^5-thiophene complexes in the literature.

*Keywords:* Iridium; Thiophene; Nucleophiles; Pentamethylcyclopentadienyl

1. Introduction

Monocationic η^5-thiophene complexes often react with nucleophiles to form products resulting from nucleophilic addition at the 2-position. Thus, [(CO)$_3$Mn-(η^5-T)]$^+$, where T = thiophene, reacts

$$(1)$$
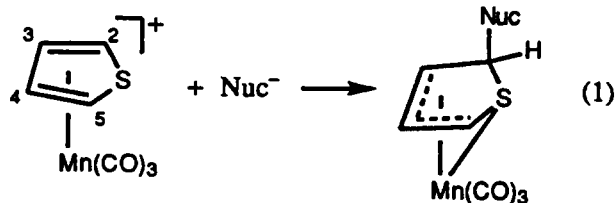
with nucleophiles (e.g. H$^-$, CN$^-$) to give allyl sulfide

complexes [1,2]. Likewise, CpRu(η^5-T)$^+$ undergoes attack

$$(2)$$
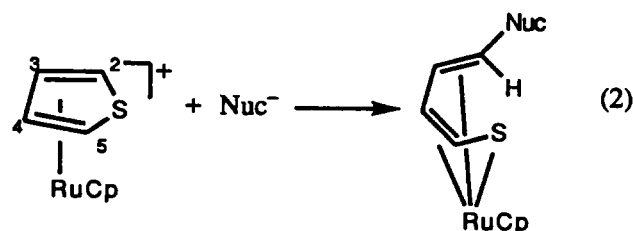
at C(2) by nucleophiles such as H$^-$, OMe$^-$, SR$^-$, and H(CO$_2$Me)$_2$$^-$, but this attack is accompanied by C–S bond cleavage to give butadienethiolate products [3,4].

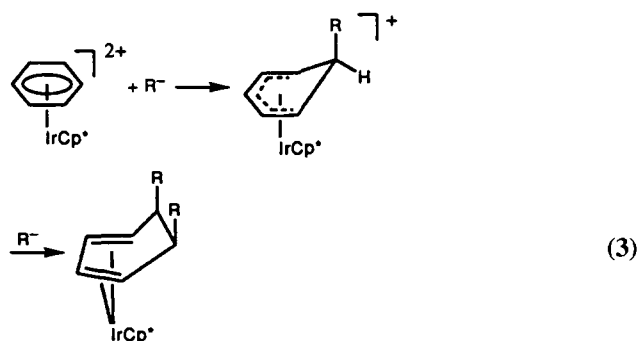In principle, dicationic η^5-thiophene complexes should be capable of adding two nucleophiles. Examples of such dicationic complexes are Cp*Ir(η^5-Th)$^{2+}$ (where Th is thiophene or a methyl-substituted thiophene and Cp* is η^5-C$_5$Me$_5$), Cp*Rh(η^5-Th)$^{2+}$, and (arene)Ru(η^5-Me$_4$T)$^{2+}$ [5,6]. However, none of these complexes are reported to add two nucleophiles, but several examples of such additions to arene complexes

---

* Corresponding author.

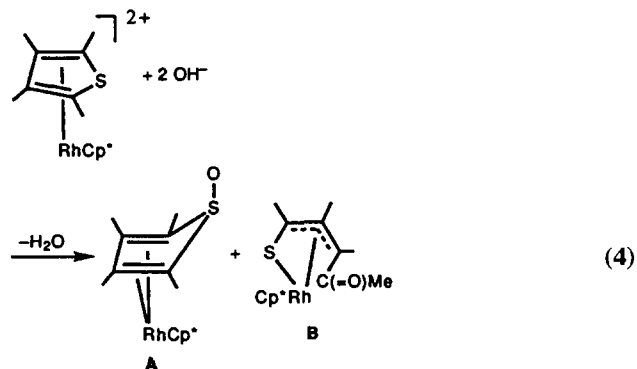[1] With best wishes to Professor Marv Rausch on his 65th birthday.

[2] Permanent address: Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, People's Republic of China.

[7] are known. Most closely related to the results described in the present paper are the reactions

(3)

of $Cp^* Ir(\eta^6\text{-}C_6H_6)^{2+}$. The carbanion nucleophiles (R^-) add to adjacent carbons exo to the metal. In some cases [7], the intermediate cyclohexadienyl complex has been identified. The analogous $Cp^* Ir(\eta^6\text{-}BT)^{2+}$ and $Cp^* Ir(\eta^6\text{-}DBT)^{2+}$ complexes, in which the benzo[b]thiophene (BT) and dibenzothiophene (DBT) ligands are η^6-coordinated through a benzo ring, react [8] with $Na[H_2 Al(OCH_2CH_2OMe)_2]$. These reactions give products, as in Eq. (3), in which two hydrides (H^-) are on adjacent carbons in the coordinated benzo ring.

Another type of reaction occurs when $Cp^* Rh(\eta^5\text{-}Me_4T)^{2+}$ (where Me_4T is tetramethylthiophene) reacts

(4)

with OH^- [9,10]. The relative amounts of products **A** and **B** depend upon the concentration of the KOH reactant. There is good evidence that the reaction proceeds by initial OH^- attack at the sulfur. This intermediate may be deprotonated by another OH^- to give **A**, or the OH^- in the intermediate migrates from S to C(2) to give $Cp^* Rh(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OH)^+$ which is deprotonated by a second OH^- to give product **B** [11].

In this report we describe reactions of the dicationic $Cp^* Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$ complex with the following nucleophiles: PhLi, MeLi, $^-CH(CO_2Me)_2$, and OH^-. Different types of product form depending upon the nucleophile.

2. Experimental

2.1. General methods

All procedures were performed under a dry, oxygen-free N_2 atmosphere by using standard Schlenk techniques. Solvents were reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under an N_2 atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from potassium benzophenone ketyl, while hexane, CH_2Cl_2, and CH_3CN were distilled from CaH_2. The neutral Al_2O_3 (Brockmann Activity I) used for chromatography was deoxygenated under high vacuum at room temperature for 16 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2. The phenyl lithium (1.6 M solution in benzene–Et_2O (70:30)), methyl lithium (1.5 M solution in Et_2O), $(n\text{-}Bu)_4N^+OH^-$ (1.0 M solution in MeOH), HBF_4 (in diethyl ether) and $[(CH_3)_3O]BF_4$ were purchased from Aldrich Chemical Co. $[Cp^* Ir(\eta^5\text{-}2,5\text{-}Me_2T)](BF_4)_2$ (1) was prepared as previously described [12,13]. $NaCH(CO_2Me)_2$ was prepared by a literature method [14]. Elemental analyses were performed by Galbraith Laboratory, Inc. Infrared (IR) spectra were recorded on a Perkin–Elmer 681 spectrophotometer. All ^1H NMR spectra were recorded at ambient temperature on samples in $CDCl_3$ solution with $CHCl_3$ as the internal reference using a Nicolet NT-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

2.2. Reaction of $[Cp^* Ir(\eta^5\text{-}2,5\text{-}Me_2T)](BF_4)_2$ (1) with C_6H_5Li to give $Cp^* Ir(2,5\text{-}Me_2T \cdot 2Ph)$ (2) and $Cp^* Ir(\eta^4\text{-}SC_3H_2MeC(=O)Me)$ (3)

To a stirred suspension of **1** (0.400 g, 0.652 mmol) in THF (30 ml) was added 1.44 mmol (0.9 ml, 1.6 M solution in benzene–Et_2O) of C_6H_5Li at -60 °C. The color of the solution immediately turned blue-green and then to brown. After stirring for 6 h at -60 to -20 °C, the solvent was removed under vacuum. The dark-brown residue was chromatographed on Al_2O_3 (neutral) with hexanes–CH_2Cl_2 (10:1) as the eluant. An orange band was eluted first; then a yellow band was eluted with hexanes–CH_2Cl_2–Et_2O (10:2:1). The solvents were evaporated under vacuum from the above two eluates, and the residues were recrystallized from hexanes or hexanes–CH_2Cl_2 solution at -80 °C. From the first fraction was obtained 0.096 g (25%, based on **1**) of **2** as red crystals (m.p. 97–98 °C, decomp.). ^1H NMR $(CDCl_3)$: δ 7.66–7.20 (m, 10H), 2.66 (m, 1H), 2.03 (m, 1H), 1.99 (s, 3H), 1.94 (s, 15H), 1.81 (s, 3H). MS:

m/e 594 (M$^+$). Anal. Found: C, 56.87; H, 5.43. $C_{28}H_{33}IrS$. Calc.: C, 56.63; H, 5.60%. From the second fraction, 0.084 g (28%, based on **1**) of **3** as yellow crystals were obtained (m.p. 131–132 °C, decomp.). IR (CH_2Cl_2) ν(CO): 1655 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.67 (d, 1H), 2.63 (d, 1H), 2.27 (s, 3H), 2.03 (s, 3H), 1.86 (s, 15H). MS: m/e 456 (M$^+$), 441 (M$^+$–CH$_3$), 360 (Cp*IrS$^+$). Anal. Found: C, 41.81; H, 5.04. $C_{16}H_{23}IrOS$. Calc.: C, 42.18; H, 5.09%.

2.3. Reaction of 1 with CH$_3$Li to give Cp*Ir(2,5-Me$_2$T · 2Me) (4) and Cp*Ir(2,5-Me$_2$T(O)) (5)

To a stirred suspension of **1** (0.500 g, 0.815 mmol) in THF (30 ml) was added 1.65 mmol (1.1 ml, 1.5 M solution in Et$_2$O) of CH$_3$Li at −60 °C. The color of the solution immediately turned blue-green and then to brown. After stirring for 6 h at −60 to −20 °C, the solvent was removed under vacuum. The dark-brown residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes–CH$_2$Cl$_2$ (10:1) as the eluant. An orange band which eluted first was collected; then a yellow band was eluted with hexanes–CH$_2$Cl$_2$–Et$_2$O (10:1:1). After evaporation of the solvents from the above two eluates, the crude products were recrystallized from hexanes at −80 °C. From the first fraction was obtained 0.030 g (7.8%, based on **1**) of **4** as orange crystals (m.p. 171–173 °C, decomp.). ^{1}H NMR (CDCl$_3$): δ 3.95 (d, 1H), 3.13 (s, 3H), 3.10 (d, 1H), 2.79 (s, 3H), 2.17 (s, 3H), 1.98 (s, 3H), 1.94 (s, 15H). MS: m/e 456 (455), 454, 360. Anal. Found: C, 46.10; H, 6.37. $C_{18}H_{29}IrS$. Calc.: C, 46.03; H, 6.22%. From the second fraction, 0.023 g (6%, based on **1**) of **5** as yellow crystals were obtained (m.p. 92–93 °C, decomp.). ^{1}H NMR (CDCl$_3$): δ 7.66 (dd, 1H), 7.32 (dd, 1H), 2.03 (s, 3H), 1.87 (s, 3H), 1.62 (s, 15H). MS: m/e 456 (M$^+$). Anal. Found: C, 42.30; H, 5.34. $C_{16}H_{23}IrOS$. Calc.: C, 42.18; H, 5.09%.

2.4. Reaction of 1 with NaCH(CO$_2$Me)$_2$ to give Cp*Ir(η^4-2,5-Me$_2$T · C(CO$_2$Me)$_2$) (6)

To a stirred suspension of NaH (0.030 g, 1.25 mmol) in THF (15 ml) was added dropwise 0.130 g (0.984 mmol) of CH$_2$(CO$_2$Me)$_2$ over a 5 min period. The solution was stirred at room temperature for 10 min during which time H$_2$ gas was evolved. The resulting mixture was filtered, and the filtrate was added to a stirred suspension of **1** (0.300 g, 0.489 mmol) in THF (30 ml). As the reaction mixture was stirred for 6 h at room temperature, the solution gradually turned orange-red in color. After evaporating the solution to dryness in vacuo, the residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes–CH$_2$Cl$_2$ (10:1) as the eluant. An orange band was collected; removal of the solvent in

vacuo gave a crude orange-red product which was recrystallized from hexanes–CH$_2$Cl$_2$ at −80 °C to give 0.120 g (43%, based on **1**) of **6** as orange-red crystals (m.p. 153–154 °C, decomp.). ^{1}H NMR (CDCl$_3$): δ 5.43 (d, 1H), 3.76 (s, 3H, CH$_3$O), 3.71 (s, 3H, CH$_3$O), 3.00 (d, 1H), 2.30 (s, 3H), 1.99 (s, 3H), 1.83 (s, 15H). MS: m/e 570 (M$^+$), 540 (M$^+$–2CH$_3$), 508 (M$^+$–2CH$_3$O), 360 (Cp*IrS$^+$). Anal. Found: C, 44.23; H, 5.21. Calc.: $C_{21}H_{29}IrO_4S$. C, 44.19; H, 5.30%.

2.5. Reaction of 1 with (n-Bu)$_4$N$^+$OH$^-$ to give Cp*Ir-(η^4-2,5-Me$_2$T · O) (7) and 3

To a stirred suspension of **1** (0.500 g, 0.815 mmol) in CH$_3$CN (50 ml) was added 1.70 mmol (1.70 ml, 1.0 M solution in CH$_3$OH) at 0 °C. The color of the solution immediately turned purple-red. After being stirred for 7 h at room temperature, the solution was evaporated to dryness under vacuum. The residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes–CH$_2$Cl$_2$ (5:1) as the eluant. A light yellow band eluted first followed by a yellow band that was eluted with hexanes–CH$_2$Cl$_2$–Et$_2$O (5:1:1). The solvents were removed under vacuum from the above two eluates, and the residues were recrystallized from hexanes–CH$_2$Cl$_2$ at −80 °C. From the first fraction, 0.084 g (23%, based on **1**) of **7** were obtained as light yellow crystals (m.p. 133–135 °C, decomp.). IR (CH$_2$Cl$_2$) ν(SO): 1078 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.45 (s, 2H), 1.93 (s, 15H), 1.63 (s, 6H). MS: m/e 456 (M$^+$), 440 (M$^+$–O), 410 (M$^+$–O–2CH$_3$), 360 (Cp*IrS$^+$). Anal. Found: C, 42.33; H, 5.21. $C_{16}H_{23}IrOS$. Calc.: C, 42.18; H, 5.09%. From the second fraction was obtained 0.137 g (37%, based on **1**) of **3** as yellow crystals (m.p. 131–132 °C, decomp.). IR (CH$_2$Cl$_2$) ν(CO): 1655 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.67 (d, 1H), 2.63 (d, 1H), 2.27 (s, 3H), 2.03 (s, 3H), 1.86 (s, 15H).

2.6. Reaction of 7 with HBF$_4$ to give 1

A 0.012 g (0.026 mmol) sample of **7** was dissolved in 0.5 ml of CH$_2$Cl$_2$ at 0 °C. Upon adding 0.005 g (ca. 6 μl, 0.057 mmol) of HBF$_4$, the solution turned light yellow. After 15 min of stirring at 0–20 °C, white product **1** precipitated. It was separated by decanting the solution and then dried in vacuo to give 0.014 g (88%, based on **7**). ^{1}H NMR (CD$_3$NO$_2$): δ 7.23 (s, 2H), 2.73 (s, 6H), 2.42 (s, 15H).

2.7. Crystal structure determination of Cp*Ir(η^4-S-C$_3$H$_2$MeC(=O)Me) (3)

A crystal of approximate dimensions 0.3 × 0.4 × 0.5 mm was mounted on a glass fiber which was then

Table 1

Crystal and data collection parameters for Cp*Ir(η^4-SC$_3$H$_2$MeC-(=O)Me) (3)

Empirical formula	C$_{16}$H$_{23}$IrOS
Formula weight	455.63
Crystal system	Orthorhombic
Lattice parameters:	
a (Å)	11.371 (36)
b (Å)	18.434 (10)
c (Å)	7.562 (3)
v (Å^3)	1585 (5)
Space group	$P2_12_12_1$ (No. 19)
Z	4
d_{calc} (g cm^{-3})	1.91
μ (Mo Kα) (cm^{-1})	42.546 (correction applied)
Diffractometer	Rigaku AFC6
Radiation	Mo Kα (λ = 0.71069) graphite-monochromated
Temperature (°C)	−70
$2\theta_{max}$ (deg)	60.0
No. observations	7963
($I > 3.00\sigma$ (I))	
No. variables	172
Residuals: [a] R; R_w	0.0392; 0.0465

[a] $R = \Sigma \| R_0 | - | F_c \| / \Sigma | F_0 |$; $R_w = [\Sigma w(| F_0 | - | F_c |)^2 / \Sigma w | F_0 |^2]^{1/2}$; $w = 1/\sigma^2(| F_0 |)$.

attached to a goniometer head; the latter was placed onto a Rigaku AFC6 diffractometer with graphite-monochromated Mo Kα radiation from a 12 kW rotating anode generator. All measurements were made at −70 °C. Using a search procedure, 15 reflections were selected within the range of $14° < 2\theta < 35°$. Indices for these reflections were obtained from an automatic indexing program INDEX and cell parameters were determined using this set of reflections. Within the range of

Table 2

Positional ($\times 10^4$) and equivalent isotropic thermal (Å$^2 \times 10^3$) parameters and their e.s.d.s for Cp*Ir(η^4-SC$_3$H$_2$MeC(=O)Me) (3)

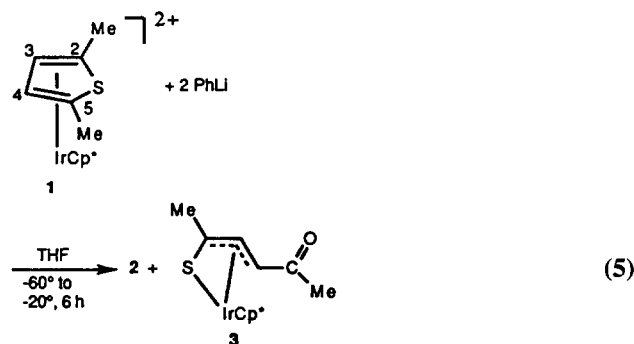| Atom	x	y	z	U (ave)
Ir	9184.6(4)	1378.2(2)	9168.6(5)	18
S	7846(3)	1919(2)	1218(4)	32
O	1953(9)	804(6)	875(16)	47
C1	9199(12)	2328(6)	786(16)	26
C2	244(12)	1922(7)	1150(15)	25
C3	63(15)	1190(7)	1719(16)	30
C4	1049(12)	680(8)	1632(19)	31
C5	909(19)	−42(9)	2559(27)	58
C6	9287(19)	3107(8)	10102(19)	48
C13	8468(13)	593(7)	7336(18)	26
C14	7557(17)	13(9)	7641(20)	43
C15	8187(14)	1338(9)	6732(14)	26
C16	7001(14)	1630(10)	6427(19)	40
C17	9241(15)	1691(8)	6392(15)	30
C18	9376(18)	2465(7)	5734(18)	47
C19	10155(16)	1215(12)	6747(18)	41
C20	11481(15)	1356(12)	6540(23)	45
C21	9708(12)	536(8)	7262(16)	24
C22	10408(15)	−135(8)	7668(25)	43

$0° < 2\theta < 60°$, 9944 reflections were measured using the ω–2θ scan technique; of these, 7963 reflections were considered to be 'observed' with $I \geq 3\sigma(I)$. The space group was uniquely determined to be $P2_12_12_1$, from conditions limiting possible reflections: $h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$. Further experimental details are given in Table 1.

The structure was solved by the program HYPAD [15], developed in this group, which combines Patterson superposition methods with direct methods to establish a structure model. The model was refined by full matrix least squares refinement to a conventional residual index of 3.92%. Final positional and equivalent isotropic thermal parameters, bond distances and bond angles are given in Tables 2 and 3. The ORTEP [16] drawing of 3 is shown in Fig. 1.

3. Results and Discussion

3.1. Reactions of Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (1) with PhLi and MeLi

The reaction

$$ (5) $$

of 1 with PhLi in THF gives the products Cp*Ir(2,5-Me$_2$T · 2Ph) (2) (25%) and Cp*Ir(η^4-SC$_3$H$_2$MeC-(=O)Me) (3) (28%). The composition of complex 3 was established by elemental analyses, mass spectrometry, and ^{1}H NMR and IR spectroscopy, all of which are consistent with the structure shown in Eq. (5). The ν(C=O) value (1655 cm^{-1}) for 3 is similar to that (1667 cm^{-1}) of Cp*Rh(η^4-SC$_3$Me$_3$C(=O)Me) (B in Eq. (4)) [11]. The structure (Fig. 1) determined by X-ray diffraction studies shows the same general structure as B, except that the acyl (C(=O)Me) group in 3 is syn not anti as in B. The allyl portion of the acylthiolate ligand is delocalized, as indicated by the equivalent C(1)–C(2) and C(2)–C(3) distances (1.43(2) Å). The carbonyl carbon is planar, as indicated by the sum of the angles (360°) around C(4). The C(1)–S bond length (1.74(1) Å) is slightly shorter than that of a typical

Table 3
Bond distances (Å) and selected angles (deg) in Cp*Ir(η^4-SC$_3$H$_2$-MeC(=O)Me) (3)

Bond distances [a]			
Ir–C1	2.14(1)	C2–C3	1.43(2)
Ir–C19	2.16(2)	C3–C4	1.47(2)
Ir–C13	2.16(1)	C4–C5	1.51(2)
Ir–C15	2.17(1)	C13–C21	1.42(2)
Ir–C2	2.17(1)	C13–C15	1.48(2)
Ir–C17	2.18(1)	C13–C14	1.51(2)
Ir–C3	2.20(1)	C15–C17	1.39(2)
Ir–C21	2.20(1)	C15–C16	1.47(2)
Ir–S	2.390(5)	C17–C18	1.52(2)
S–C1	1.74(1)	C17–C19	1.39(3)
O–C4	1.20(2)	C19–C21	1.41(3)
C1–C2	1.43(2)	C19–C20	1.54(3)
C1–C6	1.53(2)	C21–C22	1.50(2)

Bond angles [a]			
S–C1–C6	121.8(11)	C3–C4–C5	117.6(13)
S–C1–C2	118.1(9)	C3–C4–O	123.7(14)
C6–C1–C2	120.1(13)	O–C4–C5	118.7(14)
C1–C2–C3	115.5(13)	S–Ir–C3	77.7(4)
C2–C3–C4	118.8(14)	C1–Ir–C3	67.9(5)

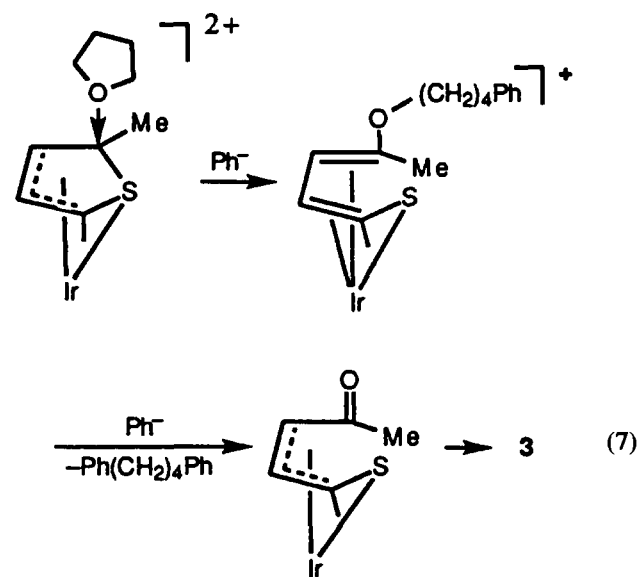[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

(C(sp^2)–S single bond (1.77 Å) [17] suggesting that there is some π-delocalization into the C–S bond.

Formation of **3** is unexpected, since the source of the oxygen is not obvious. Previously, we showed [18] that **3** was formed in 77% yield by the reaction of Cp*Ir(η^4-2,5-Me$_2$T) or Cp*Ir(C,S-2,5-Me$_2$T) with O$_2$; however, these reactions required several hours at room temperature. In contrast, reaction (5) occurs rapidly in an inert N$_2$ atmosphere at −60 to −20 °C. Thus, it seems unlikely that **3** forms in Eq. (5) from adventitious O$_2$. The only other source of oxygen in this reaction is the THF solvent. In the reaction [19] of Mo$_3$S$_7$Br$_4$ with (n-Bu)$_3$P, the THF solvent provides the oxygen for the

Fig. 1. ORTEP drawing of Cp*Ir(η^4-SC$_3$H$_2$MeC(=O)Me) (3).

formation of Mo$_2$O$_2$S$_2$Br$_4$$^{2-}$, whose counter cation is (n-Bu)$_3$P(CH$_2$)$_4$P(n-Bu)$_3$$^{2+}$. The mechanism proposed

$$\frac{P(n\text{-Bu})_3}{} \rightarrow Mo-O^{2-} + (n\text{-Bu})_3P(CH_2)_4P(n\text{-Bu})_3^{2+} \quad (6)$$

for the transfer of oxygen to Mo involves nucleophilic attack of P(n-Bu)$_3$ on the α-carbons of the coordinated THF. In reaction (5), the transfer of oxygen to the 2,5-Me$_2$T ligand could occur by an analogous pathway as shown in,

$$(7)$$

where the Ph$^-$ anion acts as the nucleophile.

We were unable to obtain X-ray quality crystals of product **2** (Eq. (5)). However, from the elemental analyses, mass and ^{1}H NMR spectra, its composition, Cp*Ir(2,5-Me$_2$T · 2Ph), corresponds to that in which two Ph$^-$ anions have added to the starting Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ cation. Unfortunately, the ^{1}H NMR spectrum is not sufficient to establish the structure of **2**. If the reaction proceeds as reported (Eq. (3)) for Cp*Ir(η^6-C$_6$H$_6$)$^{2+}$ with MeLi, one would expect a product in which the two Ph groups are on adjacent carbon atoms, probably in the 2,3-positions. However, it is possible that Ph$^-$ attack may occur on the sulfur as suggested [11] for the reaction in Eq. (4). Complicating the prediction of the structure of **2** even further is the possibility that a C–S bond could be cleaved (Eq. (2)) as R$^-$ adds to C(2). Thus, it is not possible to assign a structure to **2** at this time.
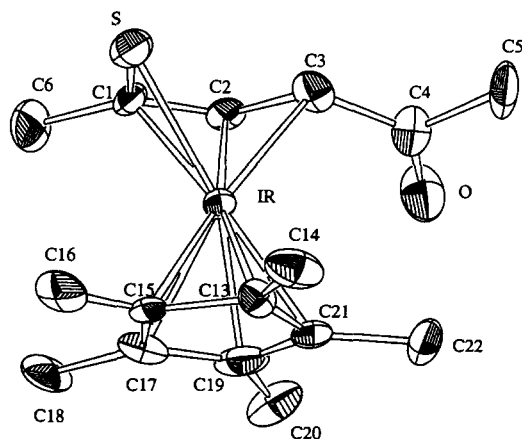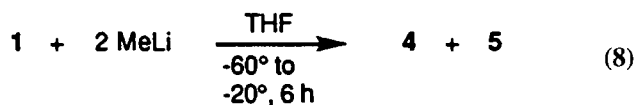
The reaction of **1** with MeLi gives two products, **4** (7.8%) and **5** (6%), isolated in low yields.

$$1 \quad + \quad 2\,\text{MeLi} \quad \xrightarrow[\substack{-60° \text{ to} \\ -20°,\,6\,\text{h}}]{\text{THF}} \quad 4 \quad + \quad 5 \tag{8}$$
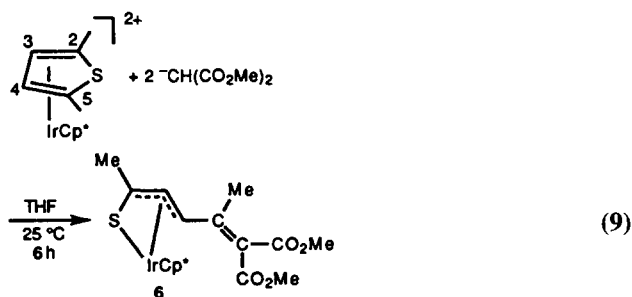
Neither of them could be obtained as crystals suitable for X-ray studies. Elemental analyses, mass and ^{1}H NMR spectra of **4** show that it has the composition Cp*Ir(2,5-Me$_2$T·2Me) expected for the addition of two Me$^-$ groups to Cp*Ir(η^5-Me$_2$T)$^{2+}$ (**1**). However, as for **2**, it is not possible to assign its structure with certainty.

Elemental analyses, mass and ^{1}H NMR spectra of **5** show that it has the composition Cp*Ir(2,5-Me$_2$T(O)), which is the same as those of the acylthiolate **3** and Cp*Ir(η^4-2,5-Me$_2$T·O) (**7**, discussed below). However, from its ^{1}H NMR spectrum, it is obvious that its structure is different from those of **3** or **7**. Without additional information, its structure cannot be assigned.

When only one molar equivalent, instead of two, of PhLi and MeLi was used in reactions (5) and (8), the same products were obtained. Complexes **2**, **3**, **4** and **5** are readily soluble in both polar and non-polar organic solvents. They are sensitive to air in solution but are stable for short periods in the solid state.

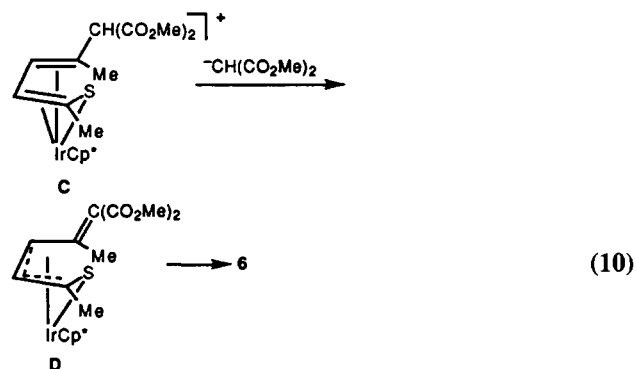### 3.2. Reaction of Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (1) with $^-$CH-(CO$_2$Me)$_2$

The reaction

$$\tag{9}$$

of **1** with two molar equivalents of the malonate anion $^-$CH(CO$_2$Me)$_2$ gives compound **6** in 43% isolated yield. When only one equivalent of malonate was used, the same product was obtained. The structure of **6** shown in Eq. (9) is supported by an X-ray diffraction study [20] that gave an R value of only 12%. However, elemental analyses and mass and ^{1}H NMR spectra are

all consistent with this geometry. In the ^{1}H NMR spectrum, there are signals for the two inequivalent CO$_2$Me groups (δ 3.73, 3.71), two for the Me groups (δ 2.30, 1.99), and two for the CH groups (δ 5.43d, 3.00d).
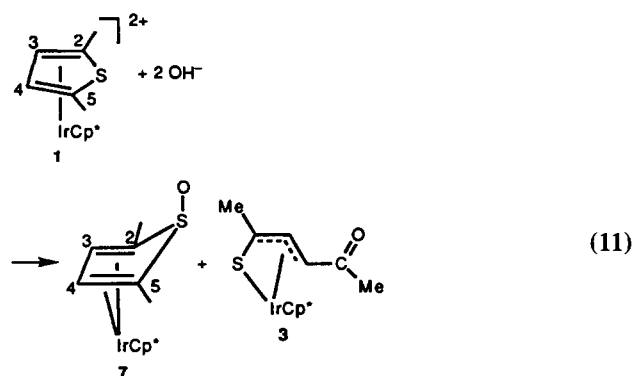
Complex **6** presumably forms as a result of $^-$CH(CO$_2$Me)$_2$ addition

$$\tag{10}$$

at C(2) of **1**, which is accompanied by C–S bond cleavage. Another mole of the malonate anion removes the relatively acidic proton alpha to the ester groups. The resulting intermediate isomerizes to **6** in which the [C(Me)=C(CO$_2$Me)$_2$] group is in the syn position. This mechanism is very similar to that proposed [9,10] for the formation of **B** in Eq. (4). The first intermediate **C** in Eq. (10) is shown with a cleaved C–S bond. The structure of a related complex Cp*Rh(η^4-C$_4$Me$_4$S-2-OH)$^+$ in which OH$^-$, instead of $^-$CH(CO$_2$Me)$_2$, has added to C(2) shows a long C–S bond (1.906(5) Å). Thus, it is not certain whether the C–S bond is completely broken in the formation of **C** or **D**.
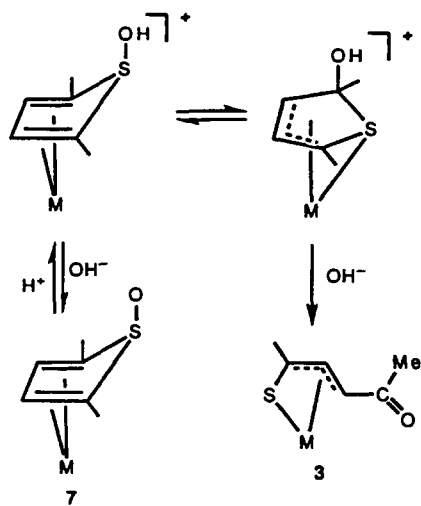
3.3. Reaction of Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (1) with OH$^-$

Complex **1** reacts with two equivalents of (n-Bu)$_4$N$^+$OH$^-$ in MeCN–MeOH solvent to give **7** (23%) and **3** (37%).

$$\tag{11}$$

Product **3** was identified by its IR and ^{1}H NMR spectra (Eq. (5)). Complex **7**, Cp*Ir(η^4-2,5-Me$_2$T · O), was characterized by its IR and ^{1}H NMR spectra, which are very similar to those of the previously reported Rh analog (η^5-C$_5$Me$_4$Et)Rh(η^4-Me$_4$T · O), which was characterized crystallographically [10]. The IR spectrum of **7** contains an ν(SO) band at 1078 cm^{-1} which is similar to that (1010 cm^{-1}) in the Rh complex. Elemental analyses and the molecular ion in the mass spectrum confirm its composition. Chemical shifts (δ 4.45) of the protons on C(3) and C(4) are similar to those of other complexes with η^4-2,5-Me$_2$T ligands: Cp*Ir(η^4-2,5-Me$_2$T) (δ 4.53) [12,13], Cp*Ir(η^4-2,5-Me$_2$T · BH$_3$) (δ 4.46) [12,13], Cp*Ir(η^4-2,5-Me$_2$T · CH$_3$)$^+$ (δ 4.92) [21], and Cp*Ir(η^4-2,5-Me$_2$T · Fe(CO)$_4$) (δ 4.54) [22]. Complex **7** is readily soluble in polar organic solvents but only sparingly in non-polar solvents; it is stable in air for several hours.
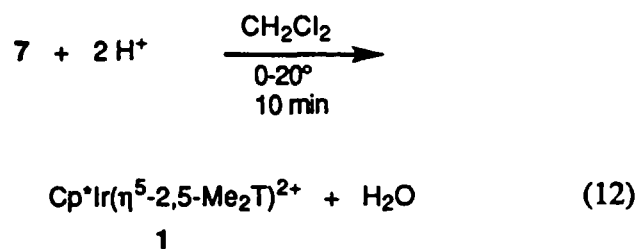
The formation of **3** and **7** in reaction (11) is not surprising since the analogous Cp′Rh(η^5-Me$_4$T)$^{2+}$ reacts (Eq. (4)) with OH$^-$ to give the same mixture of products [9,10]. Rauchfuss and co-workers found that the sulfoxide product (analogous to **7**) was the major one at high OH$^-$ concentration, whereas the acylthiolate (analogous to **3**) predominates at low OH$^-$ concentration. This and other evidence support the mechanism shown in Scheme 1.

$$7 \ + \ 2\,H^+ \ \xrightarrow[\substack{0\text{-}20° \\ 10\,\text{min}}]{CH_2Cl_2}$$

$$Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+} \ + \ H_2O \qquad (12)$$
1

by reaction with acid (HBF$_4$) to give the starting dication Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ in high yield (88%). Although not identified, H$_2$O is presumed to be the other product. This conversion likely occurs by stepwise protonation of the oxygen atom in **7** followed by dissociation of H$_2$O. The same type of reaction of Cp*Rh(η^4-Me$_4$T · O) with acid to give Cp*Rh(η^5-Me$_4$T)$^{2+}$ was reported previously [9,10].

The formation of acylthiolate (as in **3**) and sulfoxide (as in **7**) complexes appears to occur in essentially the same way in reactions of Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (**1**) and Cp′Rh(η^5-Me$_4$T)$^{2+}$ with OH$^-$. In contrast, reactions of their η^4-thiophene complexes with O$_2$ give quite different products. Thus, Cp*Rh(η^4-Me$_4$T) with O$_2$ gives the sulfoxide Cp*Rh(η^4-Me$_4$T · O) quantitatively [9,10], but Cp*Ir(η^4-2,5-Me$_2$T) gives the acylthiolate product Cp*Ir(η^4-SC$_3$H$_2$MeC(=O)Me) (**3**) in 77% yield.

4. Supplementary material available

For **3**, tables of hydrogen atom positional parameters, anisotropic thermal parameters, and complete bond angles are available from author R.J.A.

Acknowledgments

Scheme 1.

This mechanism, which presumably also applies to reaction (11), involves initial OH$^-$ addition at the sulfur. The resulting intermediate can either be deprotonated to give product **7** or it can rearrange by OH$^-$ migration to C(2) followed by deprotonation to give **3**.

Complexes **3** and **7** are not in equilibrium in reaction (11), since **7** is not converted to **3** in the presence of (n-Bu)$_4$N$^+$OH$^-$ under the conditions of reaction (11). However, **7** is deoxygenated

References

[1] D.A. Lesch, J.W. Richardson, Jr., R.A. Jacobson and R.J. Angelici, *J. Am. Chem. Soc.*, 106 (1984) 2901.

[2] S.C. Huckett, N.N. Sauer and R.J. Angelici, *Organometallics*, 6 (1987) 591.

[3] G.H. Spies and R.J. Angelici, *Organometallics*, 6 (1987) 1897.

[4] J.W. Hachgenei and R.J. Angelici, *J. Organomet. Chem.*, 355 (1988) 359.

[5] T.B. Rauchfuss, *Prog. Inorg. Chem.*, 39 (1991) 259.

[6] S. Luo, T.B. Rauchfuss and S.R. Wilson, *J. Am. Chem. Soc.*, 114 (1992) 8515.

[7] S.L. Grundy, A.J. Smith, H. Adams and P.M. Maitlis, *J. Chem. Soc. Dalton Trans.* (1984) 1747.

[8] J. Chen, Y. Su, R.A. Jacobson and R.J. Angelici, *J. Organomet. Chem.*, *428* (1992) 415.

[9] A.E. Skaugset, T.B. Rauchfuss and S.R. Wilson, *J. Am. Chem. Soc.*, *114* (1992) 8521.

[10] A.E. Skaugset, T.B. Rauchfuss and C.L. Stern, *J. Am. Chem. Soc.*, *112* (1990) 2432.

[11] A.E. Skaugset, T.B. Rauchfuss and S.R. Wilson, *Organometallics*, *9* (1990) 2875.

[12] J. Chen, L.M. Daniels and R.J. Angelici, *J. Am. Chem. Soc.*, *112* (1990) 199.

[13] J. Chen and R.J. Angelici, *Organometallics*, *8* (1989) 2277.

[14] L.S. Hegedus and Y. Inoue, *J. Am. Chem. Soc.*, *104* (1982) 4917.

[15] T.L. Hendrixson, *Ph.D. Thesis*, Department of Chemistry, Iowa State University, Ames, IA, 1989.

[16] C.A. Johnson, ORTEP-II: A FORTRAN thermal-ellipsoid plot program for crystal structure illustration, *Rep. ORNL-3794*, 1970 (2nd revision with supplemental instruction) (US Atomic Energy Commission Oak Ridge National Laboratory, Oak Ridge, TN).

[17] B. Rozsondai, G. Schultz and I. Hargittai, *J. Mol. Struct.*, *70* (1981) 309.

[18] J. Chen and R.J. Angelici, *Inorg. Chim. Acta*, *235* (1995) 61.

[19] (a) F.A. Cotton, R.L. Luck and C.S. Miertschin, *Inorg. Chem.*, *30* (1991) 1155. (b) T.L. Breen and D.W. Stephan, *Inorg. Chem.*, *31* (1992) 4019.

[20] R.A. Jacobson and Y. Su, unpublished results, 1993.

[21] J. Chen and R.J. Angelici, *Organometallics*, *9* (1990) 849.

[22] J. Chen, L.M. Daniels and R.J. Angelici, *J. Am. Chem. Soc.*, *113* (1991) 2544.