Articles

Carbon−Sulfur Bond Cleavage of Methyl-Substituted Thiophenes with Iridium(III)

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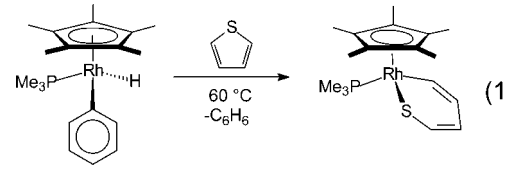
Reaction of $[Cp^*IrHCl]_2$ ($Cp^* = \eta^5$-C_5Me_5) with 2-methylthiophene and 2,5-dimethylthiophene at 120 °C in the presence of H_2 results in the cleavage of the thiophene carbon−sulfur bond(s). In both cases the thiophenes are ring-opened and hydrogenated, resulting in dinuclear Ir complexes with bridging thiolates. The primary product in the reaction involving 2,5-dimethylthiophene is $[Cp^*IrCl]_2(\mu$-H$)(\mu$-S-2-hexyl). This product has been characterized and is present in diastereomeric pairs. In the reaction with 2-methylthiophene a complex mixture consisting of five products is produced. The product distribution consists of mono- and disubstituted bridging thiolate complexes, three of which have been structurally characterized by single-crystal X-ray diffraction. Independent synthesis of each of these products has been performed, and characterization of the reaction mixture has been accomplished by ^{1}H and ^{13}C NMR spectroscopies, as well as by ESI-MS and elemental analysis. Reaction with 2-acetylthiophene showed very similar reactivity; an X-ray structure confirmed the nature of the diastereomeric pairs present.

Introduction

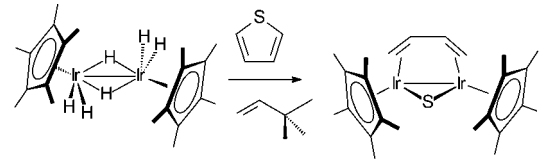
Hydrodesulfurization (HDS) is the process by which environmentally polluting sulfur compounds are removed during the hydroprocessing of crude oil. Unrefined petroleum contains organosulfur compounds that if not removed will undergo combustion to produce SO_2, a major source of air pollution and a poison for precious metal catalysts. Currently catalytic HDS is carried out using a heterogeneous Mo−Co sulfide catalyst (supported on Al_2O_3). This industrial process works well in removing organosulfur compounds such as thiols, sulfides, and disulfides. However alkyl-substituted thiophene derivatives are more difficult to remove with the current catalyst. Presently there is a need for greater reduction in airborne pollutants. These demands require greater effectiveness from the Mo−Co catalyst than is currently available.[1]

Organometallic chemists have sought to improve the HDS process by modeling it with homogeneous organometallic complexes.[2] It is hoped that by modeling HDS homogeneously, mechanistic insight can be provided that will allow the development of more effective catalysts on the industrial scale. To this end, HDS behavior has been modeled by a wide array of transition metals. Our group has been active on this front and has shown through a comprehensive mechanistic study that that the reactive $[Cp^*Rh(PMe_3)]$ fragment is generated by reductive elimination of benzene from $Cp^*Rh(PMe_3)PhH$, and when thiophene is added, C−S bond activation occurs (eq 1).[3]



(1)

These results provided the impetus to study bimetallic systems in an effort to activate both C−S bonds and also provide a better model of a heterogeneous catalyst since more than one metal center is likely involved on the catalyst surface. $[Cp^*IrH_3]_2$ was initially examined since it closely approximates the successful [Cp*Rh] fragment. In a reaction with thiophene with the aid of a hydrogen acceptor, the thiophene was desulfurized (eq 2).[4] Also, in the heterogeneous CoMo system it has been shown that well-dispersed iridium sulfides (such as Ir_2S_3) substantially increase the activity of the catalyst.[5]



(2)

A similar compound was sought that would eliminate the need for a hydride acceptor. The compound $[Cp^*IrHCl]_2$, first developed by Maitlis,[6] has found a wide range of chemical applications and seemed to be an excellent candidate. Heating $[Cp^*IrHCl]_2$ in benzene (90 °C, 3 h) with excess thiophene and

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(1) Topsøe, H.; Clausen, B. S.; Massoth, F. E. *Hydrotreating Catalysis*; Springer-Verlag: Berlin, 1996.

(2) Sanchez-Delgado, R. A. *Organometallic Modeling of the Hydrodesulfurization and Hydronitrogenation Reactions*; Kluwer Academic Publishers: Dordrecht, 2002.

(3) (a) Myers, A. W.; Jones, W. D. *Organometallics* **1996**, *15*, 2905. (b) Jones, W. D.; Vicic, D. A.; Chin, R. M.; Roache, J. H.; Myers, A. W. *Polyhedron* **1997**, *16*, 3115.

(4) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198.

(5) Vit, Z. *Appl. Catal. A: Gen.* **2007**, *322*, 142.

(6) Gill, D. S.; Maitlis, P. M. *J. Organomet. Chem.* **1975**, *87*, 359.

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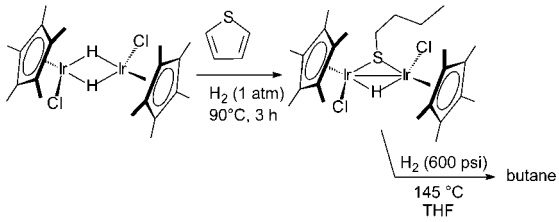
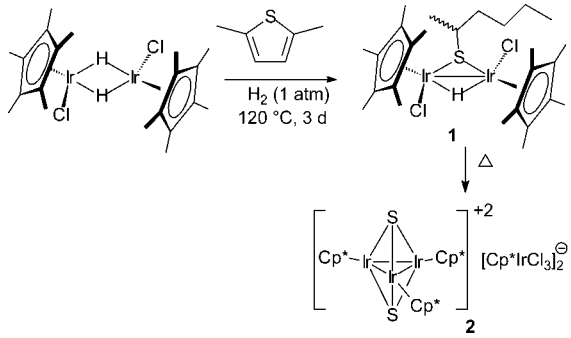
1 atm of H_2 caused the thiophene molecule to be ring-opened and completely hydrogenated, producing a dinuclear iridium complex with a bridging *n*-butane thiolate ligand (eq 3).[7] Desulfurization of the thiolate and generation of butane occurred at higher temperatures and pressures. The reaction also worked for benzothiophene, with ring-opening exclusively at the vinyl−sulfur bond. In this study we report reactions with the more sterically demanding substrates 2-methylthiophene and 2,5-dimethylthiophene.



(3)

Results and Discussion

Reaction of [Cp*IrHCl]$_2$ with 2,5-Dimethylthiophene. As anticipated, due to increased steric hindrance of the C−S bond, C−S cleavage in 2,5-dimethylthiophene required more vigorous reaction conditions than the parent thiophene. [Cp*IrHCl]$_2$ was heated in neat 2,5-dimethylthiophene for three days at 120 °C with 1 atm of hydrogen gas to give the bridging thiolate [Cp*IrCl]$_2$(μ-H)(μ-S-2-hexyl) (**1**) (eq 4).



(4)

An intermediate was not observed by ^{1}H NMR spectroscopy in the originally reported thiophene reaction. The slower dimethylthiophene reaction (3 days vs 3 h), however, shows the formation of an unidentified intermediate containing a hydride resonance at δ −13.72 that grows in and then disappears over the course of the reaction.[8] The main product formed was **1**. An orange crystalline solid also precipitated out during the reaction and was identified by single-crystal X-ray diffraction and ^{1}H NMR spectroscopy as [(Cp*Ir)$_3$(μ_3-S)$_2$][Cp*IrCl$_3$]$_2$ (**2**) (eq 4, Figure 1). The [(Cp*Ir)$_3$(μ_3-S)$_2$]$^{2+}$ fragment has been reported previously as the PF_6 and BF_4 salts[9] and consists of an iridium triangle capped by two μ_3-bridging sulfides. The [Cp*IrCl$_3$]$^-$ anion, also known,[10] serves as a counteranion to the cationic fragment. A small quantity of the compound [Cp*IrCl$_2$]$_2$ was also formed as a reaction byproduct, as characterized by X-ray diffraction. Presumably these products are formed by fragmentation and further reaction of **1**. **2** appears to form from the HDS of **1**. A GC/MS of the crude mixture was taken, and *n*-hexane was found to be present, lending support to the occurrence of HDS. Formation of the sulfide compounds seems to increase with increasing reaction temperature, indicating that **2** is the thermodynamic product. In all cases the products and byproducts were found to be in the Ir(III) oxidation state.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Cp*IrCl]$_2$(μ-H)(μ-S-*n*-pentyl) (5)

Bond Lengths			
S(1)−C(21)	1.814(3)	Ir(2)−Cl(2)	2.4086(7)
S(1)−Ir(2)	2.3469(7)	C(21)−C(22)	1.520(4)
S(1)−Ir(1)	2.3514(8)	C(22)−C(23)	1.541(4)
Ir(1)−Cl(1)	2.4093(7)	C(23)−C(24)	1.527(4)
Ir(1)−Ir(2)	2.8923(3)		
Bond Angles			
C(21)−S(1)−Ir(2)	108.81(10)	S(1)−Ir(2)−Ir(1)	52.073(19)
C(21)−S(1)−Ir(1)	110.93(10)	Cl(2)−Ir(2)−Ir(1)	89.023(18)
Ir(2)−S(1)−Ir(1)	75.99(2)	C(22)−C(21)−S(1)	111.5(2)
S(1)−Ir(1)−Cl(1)	94.09(2)	C(23)−C(22)−C(21)	112.6(3)
S(1)−Ir(1)−Ir(2)	51.934(18)	C(22)−C(23)−C(24)	113.9(3)
Cl(1)−Ir(1)−Ir(2)	90.517(18)		

The ^{1}H NMR spectrum of the purified initial product indicates that the ring-opened species **1** was formed. As previously reported, the ^{1}H NMR spectrum of the parent thiophene product (Figure 2) shows two magnetically inequivalent Cp* methyl resonances at δ 1.90 and a hydride resonance at δ −15.4. These data are consistent with the C_1 symmetry seen in its X-ray structure, which showed a pyramidal geometry at sulfur. The observation of inequivalent Cp* rings implies that sulfur inversion does not occur on the NMR time scale.[7] With the dimethylthiophene ring-opened product **1**, an additional set of Cp* methyl resonances and two hydride resonances near δ −15.5 are observed, indicating the presence of isomers. The ring-opened dimethylthiophene product has a chiral carbon atom in addition to the chiral sulfur atom, which leads to the appearance of two diastereomers that are distinguishable by NMR spectroscopy. The ^{13}C NMR spectrum supports this proposal, with 12 alkyl carbon resonances present instead of the expected six for a single isomer, and four resonances for the Cp* ring carbons instead of two found for the ring-opened thiophene product.

1 is a dark red solid that is highly soluble in solvents ranging from *n*-pentane to methanol. It is both air and water stable. Due

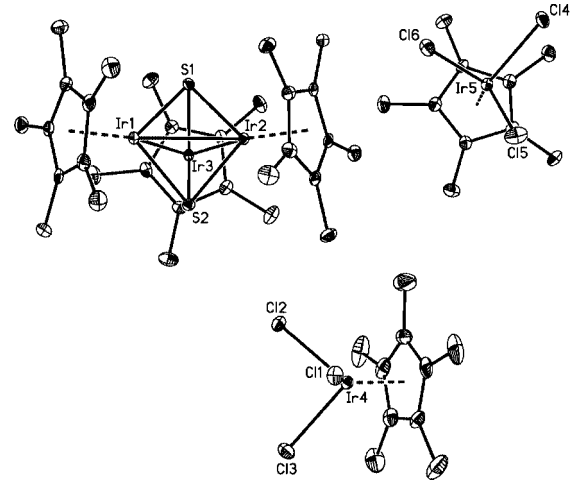


Figure 1. Crystal structure of [(Cp*Ir)$_3$(μ_3-S)$_2$][Cp*IrCl$_3$]$_2$, **2**. Hydrogen atoms from the Cp* ligand have been omitted for clarity. Ellipsoids are shown at the 50% probability level.

(7) Vicic, D. A.; Jones, W. D. *Organometallics* **1997**, *16*, 1912.

(8) This species is also observed if [Cp*IrHCl]$_2$ is heated with H_2 in the absence of a thiophene.

(9) (a) Venturelli, A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1994**, *116*, 4824. (b) Nishioka, T.; Isobe, K. *Chem. Lett.* **1994**, *23*, 1661.

(10) (a) Kennedy, D. F.; Messerle, B. A.; Smith, M. K. *Eur. J. Inorg. Chem.* **2007**, 80. (b) Pettinari, C.; Pettinari, R.; Marchetti, F.; Macchioni, A.; Zuccaccia, D.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **2007**, *46*, 896.

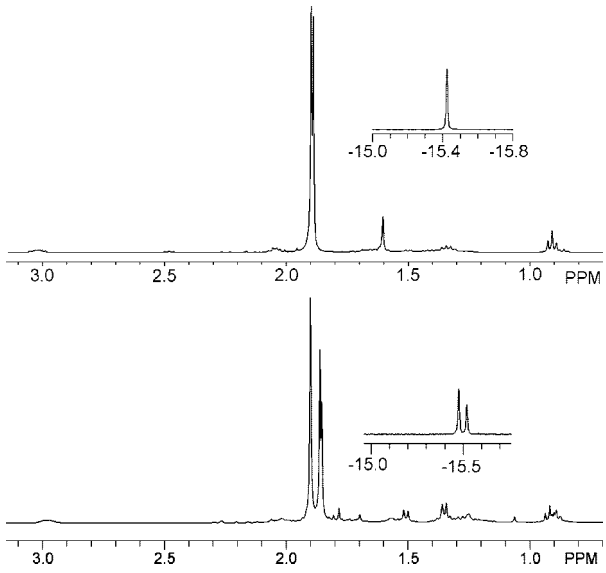
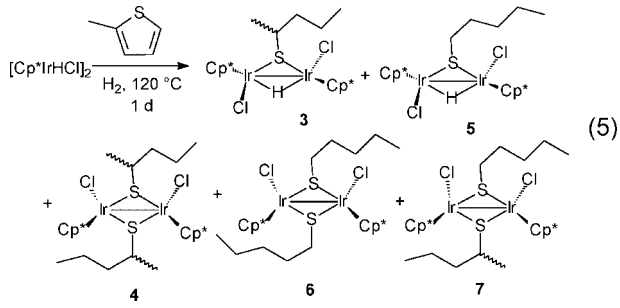


Figure 2. Comparison of the ^{1}H NMR spectra of the ring-opened thiophene product (top) with the ring-opened 2,5-dimethylthiophene product **1** (bottom).

to the high solubility of the compound and the mixture of isomers present, X-ray quality crystals could not be grown. The compound was characterized by ESI-MS. Reaction of **1** with hydrogen sulfide and HCl in toluene afforded the free thiol, 2-hexanethiol, which was detected in the reaction solution by EI GC/MS.

Reaction of [Cp*IrHCl]$_2$ with 2-Methylthiophene. Ring-opening and hydrogenation of 2-methylthiophene was also accomplished by reaction with [Cp*IrHCl]$_2$. The conditions employed (1 atm H_2, 120 °C) were the same as those used for 2,5-dimethylthiophene. The reaction with 2-methylthiophene occurred much faster and was complete after one day, but it was slower than the reaction with thiophene (3 h at 90 °C).[7] The different reaction rates were attributed to the increasing steric hindrance of each added methyl group. During the course of the reaction two red-orange crystalline products were deposited and were determined to be [(Cp*Ir)$_3$(μ_3-S)$_2$]Cl$_2$ and [Cp*IrCl$_2$]$_2$ by X-ray diffraction and ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the soluble reaction products revealed a complex mixture, as ring-opening of 2-methylthiophene can occur from either the substituted 2-position or the unsubstituted 5-position. A total of five ring-opened products were found in the reaction mixture and were identified by independent synthesis (eq 5).



(5)

The ^{1}H NMR spectrum of the reaction mixture of 2-methylthiophene showed very similar resonances to the ring-opened thiophene products seen with dimethylthiophene except there were many more resonances present (Figure 3). Several sets of Cp* methyl peaks were present, and maybe most telling was

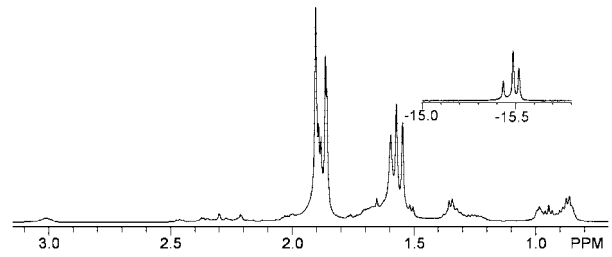


Figure 3. ^{1}H NMR spectrum of the isolated product mixture with 2-methylthiophene.

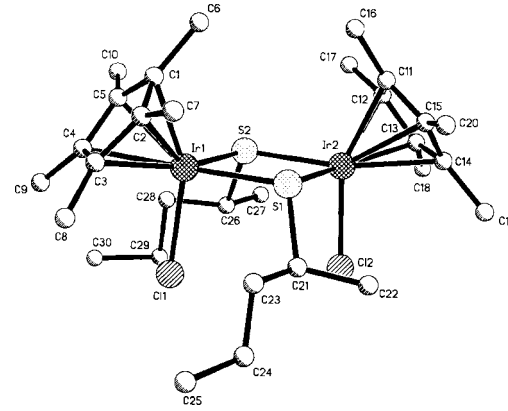
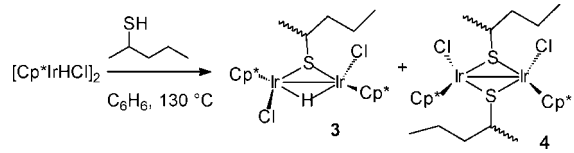


Figure 4. X-ray structure establishing the atom connectivity of [Cp*IrCl(μ-S-2-pentyl)]$_2$, **4**.

the observation of three hydride peaks in the δ −15.5 ppm region. Another key difference between this reaction and the others was that there were two clusters of Cp* methyl peaks; one cluster appeared between 1.80−1.90 ppm and the other between 1.50−1.60 ppm. The cluster of peaks in the latter region had not been observed in the previous reactions. The identity of this second set of peaks was discovered to be those of disubstituted complexes containing two bridging thiolates. This discovery was made during the course of independent synthesis of the monosubstituted complexes. [Cp*IrHCl]$_2$ was reacted with 1 equiv of 2-pentane thiol in benzene (eq 6). The reaction gave a 50:50 mixture of [Cp*IrCl]$_2$(μ-H)(μ-S-2-pentyl) (**3**) and [Cp*IrCl(μ-S-2-pentyl)]$_2$ (**4**), but no [Cp*IrHCl]$_2$ remained (a 10:90 ratio was obtained at 100 °C). Two hydride peaks were present in the mixture, indicating that **3** contains diastereomers as established in the dimethylthiophene reaction. Complex **4** was synthesized exclusively (93%) by reacting [Cp*IrHCl]$_2$ with 2.5 equiv of 2-pentane thiol. A crystal structure was obtained at low resolution (14.6% *R*-value); however, the connectivity is clearly defined (Figure 4). The Cp* methyl groups and chlorides are cis to one another with a planar Ir$_2$S$_2$ core and both alkyl groups cis to one another. The ^{1}H NMR spectrum is consistent with the crystal structure obtained, allowing for another diastereomer, and the ^{13}C NMR spectrum shows two sets of alkyl resonances.



(6)

Independent synthesis was also accomplished with the straight chain thiolate. Reaction of [Cp*IrHCl]$_2$ with an equivalent of 1-pentane thiol (benzene, 130 °C) gave a 90:10 mixture of

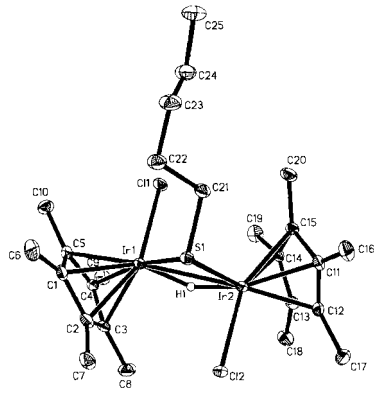


Figure 5. X-ray structure of $[Cp^*IrCl]_2(\mu\text{-H})(\mu\text{-S-}n\text{-pentyl})$, **5**. Hydrogen atoms from the Cp* ligand have been omitted for clarity. Ellipsoids are shown at the 50% probability level.

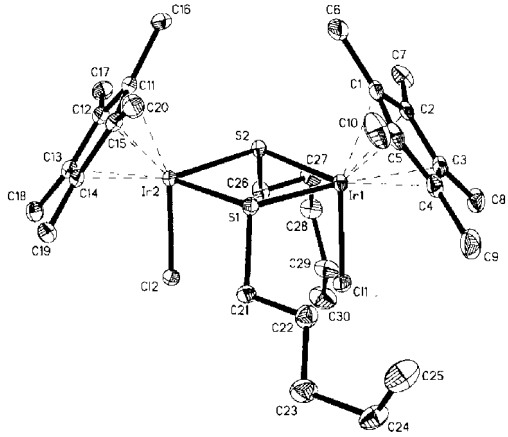
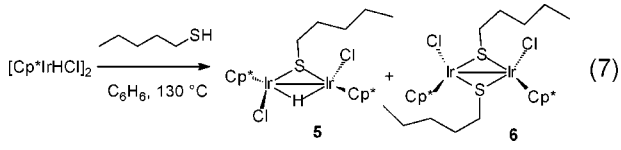


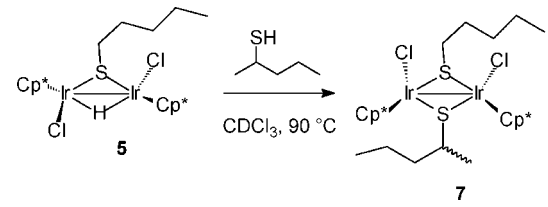
Figure 6. Crystal structure of $[Cp^*IrCl(\mu\text{-S-n-pentyl})]_2$, **6**. Hydrogen atoms from the Cp* ligand have been omitted for clarity. Ellipsoids are shown at the 50% probability level.

$[Cp^*IrCl]_2(\mu\text{-H})(\mu\text{-S-}n\text{-pentyl})$ (**5**) to $[Cp^*IrCl(\mu\text{-S-}n\text{-pentyl})]_2$ (**6**), a reversal in the product distribution seen for the branched products (eq 7). Only one hydride resonance is present, indicating that diastereomers are not present in **5**. A crystal structure was obtained of **5** (Figure 5). The structure is very similar to that obtained previously from the reaction with thiophene. The structure shows trans Cp* and chloride ligands and a pyramidal sulfur atom. The C21−C22, C22−C23, and C23−C24 have respective bond lengths of 1.52(4), 1.54(4), and 1.53(4) Å, which shows that hydrogenation of the double bonds has occurred.



(7)

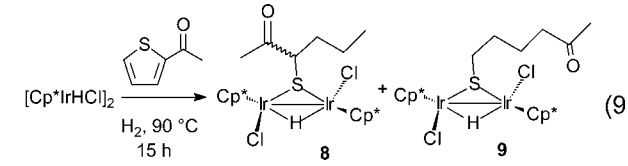
6 was synthesized pure in 90% yield by reaction with excess 1-pentanethiol. A single-crystal X-ray structure of **6** revealed a planar Ir_2S_2 core with cis Cp* ligands and cis alkyl groups (Figure 6), the same geometry that was established with **4**. Hidai and co-workers synthesized similar disubstituted compounds such as $[Cp^*IrCl(\mu\text{-SR})_2Cp^*IrCl]$ ($R = Pr^i$, cyclohexyl, CH_2Ph).[11] Their complexes show the same geometry, Ir_2S_2 core with cis Cp* ligands and cis alkyl groups, with very similar physical and spectral properties. The ^{13}C NMR spectrum of **6** showed only one set of alkyl resonances, which indicates that (stereo)isomers are not present for the molecule. A third disubstituted complex, $[Cp^*IrCl]_2(\mu\text{-S-2-pentyl})(\mu\text{-S-}n\text{-pentyl})$ (**7**), containing a branched thiolate and a straight chain thiolate, was synthesized as shown in eq 8. As further confirmation that **3**−**7** are formed in the reaction, the independently synthesized compounds were used to spike the product mixture from the 2-methylthiophene reaction.



(8)

In the C−S activation of 2-methylthiophene, integration of the three hydride peaks was used to calculate the ratio of **3** to **5**, which was consistently found to be 4:1. This ratio can be explained by the greater difficulty in activating the C−S bond adjacent to the methyl substituent. It was difficult to calculate the yields of the individual disubstituted products **4**, **6**, and **7** since the Cp* methyl peaks for each overlap and make accurate integration difficult. It appears, however, that **7** is the predominant product. Integration of the Cp* peaks was used to find the ratio between the mono- and disubstituted products, and this was found to be 57:43, (**3** + **5**):(**4** + **6** +**7**). This ratio of products in the mixture was confirmed by elemental analysis of the mixture. The reaction mixture was also characterized by ESI-MS, which showed two clusters of peaks, one centered at 795 and the other at 897, corresponding to the mono- and disubstituted products minus a chloride ion.

The stereoisomerism that has been discussed so far was confirmed when $(Cp^*IrHCl)_2$ was reacted with 2-acetylthiophene (eq 9). The ^1H NMR spectrum of the isolated product shows three hydride peaks, similar to Figure 3; however there is a greater disparity between the ratio of stereoisomers formed (76% vs 18%). The diastereomeric nature of the branched product was confirmed by X-ray diffraction (Figure 7). The asymmetric unit shows two independent molecules of **8** that are diastereomers of one another. A ^1H NMR of the crystals used showed a nearly 50:50 mixture of the two isomers. The increased steric bulk of the acyl group presumably causes a preference of one diastereomer over the other during the course of the reaction, but upon crystallization they cocrystallize in a 1:1 ratio. The observation of two *different* ratios of the diastereomers of **8** demonstrates that inversion at sulfur is slow not only on the NMR time scale (0.1 s at RT) but also on the laboratory time scale (hours at RT).



(9)

It is worth comparing the ring-opening selectivity of 2-methylthiophene seen here with that seen in other thiophene ring-opening reactions. Here, both the hindered and unhindered C−S bonds were cleaved in a ∼2:3 ratio. By comparison, reaction of 2-methylthiophene with the $[Cp^*Rh(PMe_3)]$ fragment showed

(11) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Hidai, M. *Inorg. Chim. Acta* **1997**, *263*, 119.

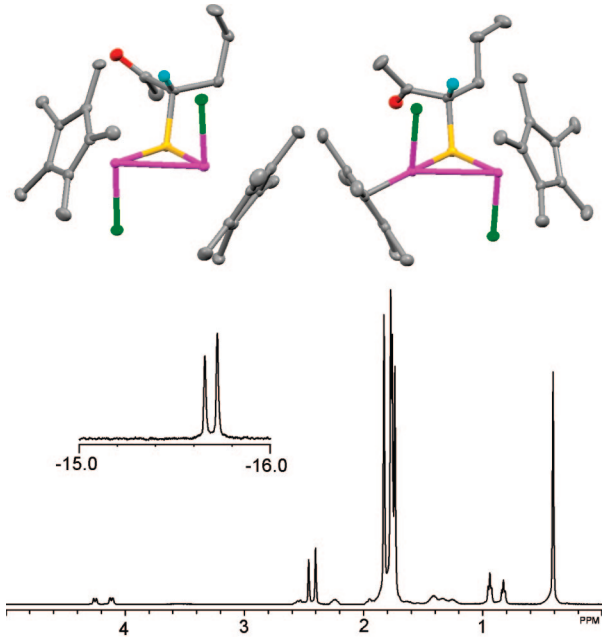


Figure 7. (Top) X-ray structure of **8** showing the two diastereomers that formed in the unit cell. Ellipsoids are shown at the 50% probability level; Cp* methyl hydrogens and the bridging hydride have been omitted. (Bottom) ^{1}H NMR of the crystals of **8** obtained for X-ray diffraction.

exclusive insertion into the unhindered C−S bond,[12] but DFT calculations on this system suggest that this observation is a reflection of the thermodynamic selectivity, not the kinetic selectivity of the C−S cleavage step.[13] The fragment [Pt(dippe)], however, reacts with 2-cyanothiophene[14] and 3-cyanothiophene[15] to first give kinetic products that can be observed to convert slowly to thermodynamic products. In its reaction with 2-methylthiophene, only one product is ever observed, the product resulting from cleavage of the less hindered C−S bond.[15] Consequently, the $[Cp^*IrHCl]_2$ system displays a lack of sensitivity to the presence of a methyl group in selecting the C−S bond to be cleaved, yet the overall rate of reaction of methylated thiophenes decreases significantly compared to thiophene. These seemingly opposite effects can be reconciled by recognizing that there are two steps involved in thiophene activation: (1) binding of the thiophene, either η^2-C,C or η^1-S, followed by (2) oxidative cleavage of the C−S bond. Apparently, with $[Cp^*IrHCl]_2$, the binding of the thiophene (step 1) is affected significantly by methyl substitution, whereas once bound, the C−S cleavage (step 2) can occur almost as fast at a methyl-substituted C−S bond as at an unsubstituted C−S bond. One is led to conclude that a likely monomeric intermediate species such as Cp*IrHCl(thiophene) is not so crowded that cleavage of one C−S bond versus another is that different.

Conclusions

Arrested HDS of 2,5-dimethylthiophene and 2-methylthiophene has been accomplished with the compound $[Cp^*IrHCl]_2$. Bond breakage of the C−S bond and hydrogenation of the unsaturated bonds results in bridged thiolate products present in diastereomeric pairs. Cleavage of the second C−S bond then occurs, resulting in the formation of the compounds $[(Cp^*Ir)_3(\mu_3\text{-}S)_2][Cp^*IrCl_3]_2$ (**2**), $[(Cp^*Ir)_3(\mu_3\text{-}S)_2]Cl_2$, and $[Cp^*IrCl_2]_2$. *n*-Hexane was detected in the reaction mixture for the 2,5-dimethylthiophene reaction, lending support to the occurrence of HDS.

Reaction of 2-methylthiophene with $[Cp^*IrHCl]_2$ results in an even more complex mixture due to the asymmetric nature of the thiophene; nevertheless the same HDS reaction process occurs. A strong steric preference for the cleavage of the unhindered C−S bond is readily apparent as well as disubstitution of the bridging iridium atoms. Independent synthesis was accomplished for each of the components, which allowed for their identification in the reaction mixture. Consequently, what initially appeared to be an intractable, complex mixture was found to be completely characterized by independent synthesis of the component compounds. A similar pattern of reactivity was found for the reaction with 2-acetylthiophene. Crystallization of both diastereomers served as confirmation of the stereoisomers that were found for the methyl-substituted thiophene reactions.

Experimental Section

General Procedures. All operations were performed under a nitrogen atmosphere unless otherwise stated. The complex $[Cp^*IrHCl]_2$ was prepared as previously reported.[4] 2,5-Dimethylthiophene (98.5%), 2-acetylthiophene (98%), and 2-methylthiophene (98%) were purchased from Aldrich Chemical Company, distilled, degassed, and then stored under nitrogen. Silica gel was heated overnight at 200 °C and then stored under nitrogen. 1-Pentanethiol was purchased from TCI America and used without further purification. 2-Pentanethiol was prepared as previously reported.[16] GC/MS spectra were recorded on a Shimadzu GC/MS, and ESI-MS spectra were recorded on an Agilent LC/MS. A Bruker-AXS SMART platform diffractometer equipped with an APEX II CCD detector was used for X-ray crystal structure determination. Elemental analyses were obtained from Desert Analytics. All ^{1}H and ^{13}C spectra were recorded on Bruker Avance 400 and 500 MHz spectrometers, and all ^{1}H chemical shifts are reported relative to the residual proton resonance in the deuterated solvent.

Preparation of $[Cp^*IrCl]_2(\mu\text{-}H)(\mu\text{-}S\text{-}2\text{-hexyl})$ (1). In a nitrogen-filled drybox 3 mL of 2,5-dimethylthiophene was added to $[Cp^*IrHCl]_2$ (93 mg, 0.128 mmol) in a 10 mL ampule fitted with a Teflon valve. The solution was then freeze−pump−thaw degassed to remove nitrogen from the system, and 1 atm of hydrogen gas was added. The solution was heated in an oil bath at 120 °C for three days. The solution changed from dark blue to dark red. Some $[(Cp^*Ir)_3(\mu_3\text{-}S)_2][Cp^*IrCl_3]_2$, $[(Cp^*Ir)_3(\mu_3\text{-}S)_2]Cl_2$, and $[Cp^*IrCl_2]_2$ precipitated as orange crystalline solids during the course of the reaction. The reaction solution was then concentrated to dryness. The residue was dissolved in THF and eluted through a Pasteur pipet packed with silica (2 in.) using 20:80 THF:hexanes as the eluent. The isolated product was obtained by concentrating the solution to dryness to obtain a dark red solid (55.1 mg, 51%). The isolated solid is a mixture of diastereomers of **1** that are present in an approximately 50:50 mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 3.05 (m, 2H, α-CH), 2.3−2.0 (m, 4H, β-CH_2), 1.90 (s, 30 H, $C_5\underline{Me_5}$), 1.86 (d, 28 H, $C_5\underline{Me_5}$), 1.51 (d, 4H), 1.35 (d, 6H, J = 6 Hz, α-CH_3), 0.92 (overlapping t, 6H, terminal CH_3), −15.47 (s, 1H, Ir−H), −15.52 (s, 1H, Ir−H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 90.74 (s, $\underline{C_5}Me_5$), 90.68 (s, $\underline{C_5}Me_5$), 90.02 (s, $\underline{C_5}Me_5$), 89.94 (s, $\underline{C_5}Me_5$), 38.85 (s, α-CH), 38.81 (s, α-CH),

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37.92 (s, CH_2), 36.48 (s, CH_2), 30.30 (s, CH_2), 29.79 (s, CH_2), 23.16 (s, CH_2), 22.82 (s, CH_2), 21.61 (s, α-CH_3), 19.22 (s, α-CH_3), 14.15 (s, terminal CH_3), 14.10 (s, terminal CH_3), 9.98 (s, $C_5\underline{Me}_5$), 9.95 (s, $C_5\underline{Me}_5$), 9.75 (s, $C_5\underline{Me}_5$). Anal. Calcd (found) for $C_{26}H_{44}SCl_2Ir_2$: C, 37.00 (36.76); H, 5.25 (5.10). ESI-MS: see Supporting Information.

[(Cp*Ir)$_3$(μ_3-S)$_2$](Cp*IrCl$_3$)$_2$ (2). Isolated as red-orange crystals from solution. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 2.38 (s, 30H, $C_5\underline{Me}_5$), 1.59 (s, 45H, $C_5\underline{Me}_5$).

Reaction of 2-Methylthiophene with [Cp*IrHCl]$_2$. In a nitrogen-filled glovebox 1 mL of 2-methylthiophene was added to [Cp*IrHCl]$_2$ (0.0737 g, 0.101 mmol) in a 10 mL ampule fitted with a Teflon valve. The solution was then freeze−pump−thaw degassed to remove nitrogen from the system, and 1 atm of hydrogen gas was added. The solution was then heated in an oil bath at 120 °C. After an hour the solution changed from blue to red with the precipitation of orange crystals ([(Cp*Ir)$_3$(μ_3-S)$_2$]Cl$_2$, and [Cp*IrCl$_2$]$_2$). After 1 day of heating, the solution was concentrated to dryness by vacuum. The residue was dissolved in THF and eluted through a Pasteur pipet filled with silica. The solvent was removed by vacuum to give a red-orange residue. The isolated solid consisted of a mixture of compounds **3**−**7**. Yield: 0.0536 g. The chemical shifts of each compound were determined by independent synthesis of each compound and then adding it to the mixture. This method allowed the identification of each of the Cp* methyl peaks as well as the hydride peaks. Many of the alkyl peaks (i.e., terminal CH_3) have common areas of overlap.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 3.57 (m, α-CH, **4**), 3.02 (m), 2.48 (t, J = 7 Hz, CH_3, **6**), 2.4−2.1 (m), 1.90 (s, $C_5\underline{Me}_5$, **3**), 1.88 (d, $C_5\underline{Me}_5$, **5**), 1.86 (d, $C_5\underline{Me}_5$, **3**), 1.60 (s, $C_5\underline{Me}_5$, **6**), 1.57 (s, $C_5\underline{Me}_5$, **7**), 1.55 (s, $C_5\underline{Me}_5$, **4**), 1.51 (d, 14H, $C_5\underline{Me}_5$), 1.35 (d, 6H, J = 7 Hz), 1.30−1.20 (m, CH_2), 0.99−0.85 (m, CH_3), −15.43 (s, $C_5\underline{Me}_5$, **5**), −15.49 (s, $C_5\underline{Me}_5$, **3**), −15.52 (s, $C_5\underline{Me}_5$, **3**). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 90.96 (s, $\underline{C}_5Me_5$), 90.90 (s, $\underline{C}_5Me_5$), 90.23 (s, $\underline{C}_5Me_5$), 90.17 (s, $\underline{C}_5Me_5$), 89.89 (s, $\underline{C}_5Me_5$), 86.44 (s, $\underline{C}_5Me_5$), 41.32 (s), 39.34 (s), 39.08 (s), 38.94 (s), 38.01 (s), 37.90 (s), 33.14 (s), 33.08 (s), 31.46 (s), 31.36 (s), 31.23 (s), 29.84 (s), 28.72 (s), 27.30 (s), 22.96 (s), 22.78 (s), 21.78 (s), 21.56 (s), 21.21 (s), 21.13 (s), 21.04 (s), 20.80 (s), 19.38 (s), 18.63 (s), 18.54 (s), 14.98 (s, CH_3), 14.94 (s, CH_3), 14.89 (s, CH_3), 14.58 (s, CH_3), 14.36 (s, CH_3), 10.19 (s, $C_5\underline{Me}_5$), 10.10 (s, $C_5\underline{Me}_5$), 10.05 (s, $C_5\underline{Me}_5$), 9.99 (s, $C_5\underline{Me}_5$), 9.59 (s, $C_5\underline{Me}_5$), 9.49 (s, $C_5\underline{Me}_5$), 8.52 (s, $C_5\underline{Me}_5$). Anal. Calcd (found) for $C_{25}H_{42}SCl_2Ir_2$ (57% by integration of the Cp* methyl peaks in the ^{1}H NMR) and $C_{30}H_{52}S_2Cl_2Ir_2$ (43% by integration of the Cp* methyl peaks in the ^{1}H NMR): C, 37.23 (37.35); H, 5.32 (5.25). ESI-MS: see Supporting Information.

Independent Synthesis of [Cp*IrCl]$_2$(μ-H)(μ-S-*n*-pentyl) (5). In a nitrogen-filled glovebox 1-pentanethiol (6 μL, 0.0484 mmol) was added to [Cp*IrHCl]$_2$ (35 mg, 0.0481 mmol) in 3 mL of benzene in a 10 mL ampule fitted with a Teflon valve. The solution was then freeze−pump−thaw degassed to remove nitrogen from the system, and 1 atm of hydrogen gas was added. The solution was then heated in an oil bath at 130 °C for 19 h. The solution changed from dark blue to deep red. The benzene was evaporated by vacuum to give a red solid (10% of the product contains [Cp*IrCl(μ-S-*n*-pentyl)]$_2$, which cannot be separated).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.01 (m, 1H, α-CH), 2.47 (m, 1H, α-CH), 2.1−2.0 (m, 2H, β-CH_2), 1.91−1.89 (d, 15H, $C_5\underline{Me}_5$), 1.59 (s, 15H, $C_5\underline{Me}_5$), 1.36−1.32 (m, 4H, γ-CH_2), 0.90 (t, 3H, J = 7 Hz, CH_3), −15.43 (s, 1H, IrH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 90.97 (s, $\underline{C}_5Me_5$), 90.26 (s, $\underline{C}_5Me_5$), 31.38 (s, CH_2), 31.23 (s, CH_2), 22.77 (s, CH_2), 14.27 (s, CH_3), 10.09 (s, $C_5\underline{Me}_5$), 10.04 (s, $C_5\underline{Me}_5$).

Independent Synthesis of [Cp*IrCl]$_2$(μ-H)(μ-S-2-pentyl) (3) and [Cp*IrCl(μ-S-2-pentyl)]$_2$ (4). The complexes were prepared as for **5** adding 2-pentanethiol (6 μL, 0.0484 mmol) to [Cp*IrHCl]$_2$ (34.1 mg, 0.0468 mmol) in 3 mL of benzene. The solution was heated at 130 °C for 28 h. The benzene was evaporated by vacuum to give a red and yellow solid. ^{1}H NMR showed a 50:50 mixture of **3** and **4**. **3** showed peak shifts very similar to **1**, with Cp* methyl peaks at δ 1.91 and 1.86. Due to peak overlap, the percentage of each diastereomer was difficult to determine but appeared to be roughly equal. The Cp* methyl peak corresponded to the hydrides at δ −15.48 and −15.51 in a 30:1 ratio. The mixture was primarily **4** if the reaction was heated at 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.56 (m, 2H, α-CH), δ3.01 (m, 1H, α-CH), 2.4−2.1 (m), 1.91 (s, $C_5\underline{Me}_5$), 1.86 (s, $C_5\underline{Me}_5$), 1.35 (m, CH_2), 0.99 (d, 3H, branched CH_3), 0.98 (t, 3H, J = 3 Hz, terminal CH_3), −15.48 (s, 1H, IrH), −15.51 (s, 1H, IrH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 90.97 (s, $\underline{C}_5Me_5$), 90.91 (s, $\underline{C}_5Me_5$), 90.24 (s, $\underline{C}_5Me_5$), 90.18 (s, $\underline{C}_5Me_5$), 89.89 (s, $\underline{C}_5Me_5$), 41.33 (s), 39.09 (s), 38.95 (s), 38.06 (s), 37.91 (s), 33.16 (s), 30.58 (s), 29.14 (s), 23.96 (s), 23.20 (s), 21.78 (s), 21.55 (s), 21.20 (s), 21.12 (s), 20.81 (s), 19.38 (s), 18.60 (s), 14.93 (s), 14.88 (s), 14.57 (s), 14.26 (s), 10.19 (s, $C_5\underline{Me}_5$), 9.98 (s, $C_5\underline{Me}_5$), 8.54 (s, $C_5\underline{Me}_5$). ESI-MS: see Supporting Information.

Preparation of [Cp*IrCl(μ-S-2-pentyl)]$_2$ (4). In a nitrogen-filled glovebox 14 μL of 2-pentanethiol (0.113 mmol) was added to a J-Young NMR tube containing [Cp*IrHCl]$_2$ (23.6 mg, 0.0324 mmol) in 1 mL of C_6D_6. Evolution of H_2 began immediately. The NMR tube was placed in a 100 °C oil bath. After 5 min the dark blue solution turned orange. The reaction was monitored by ^{1}H NMR and was complete when the hydride peak at δ −13.4 disappeared. After 6 h the reaction was stopped and the solvent removed by vacuum. The yellow solid was dried under vacuum at 90 °C to remove residual thiol (27.3 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 3.56 (m, 2H, α-CH), 1.55 (s, 30H, $C_5\underline{Me}_5$), 1.33 (m, 8H, β-CH_2, γ-CH_2), 0.98 (d, 6H, J = 3 Hz, branched CH_3), 0.86 (t, 6H, J = 7 Hz, terminal CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 89.88 (s, $\underline{C}_5Me_5$), 38.02 (s, α-CH), 37.99 (s, α-CH), 33.12 (s, CH_2), 21.19 (s, CH_2), 21.11 (s, CH_2), 18.57 (s, branched CH_3), 18.52 (s, branched CH_3), 14.93 (s, terminal CH_3), 14.88 (s, terminal CH_3), 8.52 (s, $C_5\underline{Me}_5$). Anal. Calcd (found) for $C_{30}H_{52}S_2Cl_2Ir_2$: C, 38.65 (38.48); H, 5.62 (5.34).

Preparation of [Cp*IrCl(μ-S-*n*-pentyl)]$_2$ (6). The complex was prepared as for **4** using 12 μL of 1-pentanethiol (0.0967 mmol, 10 mg) and [Cp*IrHCl]$_2$ (30.6 mg, 0.0420 mmol) in 1 mL of C_6D_6. The NMR tube was heated in a 100 °C oil bath for 12 h. Yellow solid (36.3 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.48 (t, 4H, α-CH_2, J = 7 Hz), 1.60 (br s, 30H, $C_5\underline{Me}_5$), 1.28 (m, 12H, CH_2), 0.86 (t, 6H, terminal CH_3, J = 7 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 89.77 (s, $\underline{C}_5Me_5$), 31.39 (s, α-CH_2), 29.95 (s, CH_2), 27.13 (s, CH_2), 22.93 (s, CH_2), 14.33 (s, CH_3), 8.46 (s, $C_5\underline{Me}_5$). Anal. Calcd (found) for $C_{30}H_{52}S_2Cl_2Ir_2$: C, 38.65 (38.82); H, 5.62 (5.52).

Preparation of [Cp*IrCl]$_2$(μ-S-2-pentyl)(μ-S-*n*-pentyl) (7). 5 (38.7 mg, 0.0466 mmol) was dissolved in 1 mL of $CDCl_3$ and placed in a J-Young NMR tube. 2-Pentanethiol (5.8 μL, 0.0466 mmol) was added to the solution. The solution was heated at 90 °C for one day, during which time the solution changed from red to orange. The final product contained a small amount (approximately 10% by NMR) of **4** that was carried over from the first reaction in the formation of **5**. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.59 (m, 1H, α-CH branched chain), 2.48 (t, 2H, J = 7 Hz, α-CH_2 straight chain), 1.58 (s, 30H, $C_5\underline{Me}_5$), 1.4−1.2 (m, 10H, CH_2), 0.99 (d, 3H,, J = 7 Hz, CH_3 branched chain), 0.89−0.84 (m, 6H, terminal CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): 89.85 (s, $\underline{C}_5Me_5$), 38.09 (s, α-CH), 33.10 (s, CH_2), 31.47 (s, CH_2), 29.86 (s, CH_2), 27.33 (s, CH_2), 22.96 (s, CH_2), 21.05 (s, CH_2), 18.63 (s, branched CH_3), 14.97 (s, terminal CH_3), 14.36 (s, terminal CH_3), 8.52 (s, $\underline{C}_5Me_5$).

Preparation of [Cp*IrCl]$_2$(μ-H)[μ-SCH(COCH$_3$)C$_3$H$_7$] (8). The complex was prepared as for **1** adding 2-acetylthiophene (89 μL, 0.824 mmol) to a benzene solution (2 mL) containing [Cp*IrHCl]$_2$ (29.6 mg, 0.0407 mmol). The solution was then heated

in an oil bath at 90 °C for 28 h. The solution changed from dark blue to a clear cherry red within a few hours. The reaction solution was then filtered through a pipet with a Celite plug. The benzene was then evaporated by vacuum, and the excess 2-acetylthiophene was evaporated by heating at 90 °C under vacuum. The residue was purified by dissolving in benzene and eluting with THF through a Pasteur pipet packed with silica (2 in.). After concentrating to dryness the red residue was extracted with pentanes and concentrated to dryness (18.1 mg, 52%). The isolated mixture consisted of 76% of one diastereomer of **8**, 18% of the other diastereomer of **8**, and 5% of **9**. The NMR data are given for the predominant isomer. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 4.12 (dd, 1H, $J = 4$, 11.8 Hz α-CH), 2.40 (s, 3H, CO$\underline{C}H_3$), 2.22 (s, 2H, α-CH_2), 1.83 (s, 15 H, $C_5\underline{Me}_5$), 1.77 (s, 15 H, $C_5\underline{Me}_5$), 1.37 (m, 3H, β-CH_2), 0.93 (t, 3H, $J = 7.3$ Hz, terminal CH_3), −15.72 (s, 1H, Ir−H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 173.23 (s, −$\underline{C}OCH_3$), 91.28 (s, $\underline{C}_5Me_5$), 91.11 (s, $\underline{C}_5Me_5$), 53.99 (s, CO$\underline{C}H_3$), 39.06 (s, α-CH), 25.81 (s, α-CH_2), 21.99 (s, β-CH_2), 14.44 (s, terminal CH_3), 10.26 (s, $C_5\underline{Me}_5$), 10.22 (s, $C_5\underline{Me}_5$). Anal. Calcd (found) for $C_{26}H_{42}OSCl_2Ir_2$: C, 36.40 (37.20); H, 4.93 (4.96). ESI-MS: see Supporting Information.

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Supporting Information Available: Tables of ESI-MS data and X-ray structure determination details for **2**, **4**, **5**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org. The structures are available in the Cambridge Crystallographic Database as CCDC #720099−720103.

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