# Transfer of Oxygen and Sulfur from Organic Molecules to a Zr–Ir Bond. Evidence for an Unusually Rapid Atom Abstraction Reaction

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**Abstract:** The early–late heterobimetallic complex $Cp_2Zr(\mu\text{-N-}t\text{-Bu})IrCp^*$ (**1**) has been found to undergo oxygen and sulfur abstraction reactions. Imido complex **1** reacts with $Me_3P{=}S$, $S_8$, $H_2S$, and thiiranes to form the bridging sulfido complex **2** ($Cp_2Zr(\mu\text{-N-}t\text{-Bu})(\mu\text{-S})IrCp^*$). The structure of complex **2** was confirmed by an X-ray diffraction study. The addition of *cis*-2-butene sulfide to imido complex **1** gave only **2** and *cis*-2-butene. Similarly, the addition of *trans*-2-butene sulfide resulted only in the formation of *trans*-2-butene. These results argue against mechanisms for sulfur abstraction that involve ring-opened intermediates. Imido complex **1** was found to react with pyridine *N*-oxide, nitrous oxide, and styrene oxide to form the bridging oxo complex **4** ($Cp_2Zr(\mu\text{-N-}t\text{-Bu})(\mu\text{-O})IrCp^*$), but it was unreactive toward *cis*-2-butene oxide or triphenylphosphine oxide. A competition study revealed that *cis*-2-butene sulfide, *trans*-2-butene sulfide, 2-methylpropene sulfide, propene sulfide, and ethylene sulfide reacted with complex **1** at very similar rates. We believe that this weak selectivity is a result of inherently very rapid—perhaps even diffusion-controlled—rates of reaction for the sulfur atom abstraction. It may be that low activation barriers are an inherent property of cooperative two-metal atom transfer reactions.

## Introduction

Early–late heterobimetallic complexes contain two metal centers with very different electronic properties in close proximity to each other. The presence of an electron-rich late transition metal and an electron-poor early transition metal in the same complex creates a bifunctional environment for organic substrates. If both metals participate in reactivity, referred to as "cooperative reactivity", the organic substrate could react differently than it would with either metal center in a mononuclear complex. Cooperative reactivity is particularly likely with polar substrates where the electropositive early transition metal can interact with the more Lewis-basic part of the substrate and the less electropositive late transition metal can interact with the more Lewis-acidic part of the substrate. Despite extensive research on early–late heterobimetallic complexes,[1–19] few examples of direct participation of both metal centers in reactions with organic molecules have been found.[3,7,8,20]

As part of our general interest in this area,[2,21–26] we have synthesized and investigated the reactivity of the imido complex $Cp_2Zr(\mu\text{-N-}t\text{-Bu})IrCp^*$ (**1**). Complex **1** is ideal for cooperative reactivity studies because it contains two unsaturated and thus potentially reactive metal centers, a metal-metal bond that provides a site of reactivity which must necessarily involve both metal centers, and an imido linker to discourage dissociation of the complex. We have reported previously that the Ir–Zr bond in complex **1** reacts readily with the X–H bonds of amines, alcohols, acetone, dihydrogen, and silanes.[27,28] In this paper we extend this work to reactions with substrates capable of transferring sulfur or oxygen to complex **1**: thiiranes, trimethylphosphine sulfide, sulfur, pyridine *N*-oxide, styrene oxide, and nitrous oxide.

We were particularly interested in the mechanism of sulfur abstraction from thiiranes because of the potential general

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[17] Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167.

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0002-7863/95/1517-10041$09.00/0

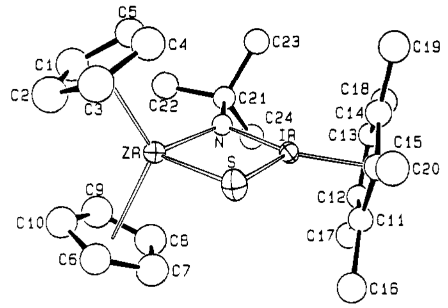
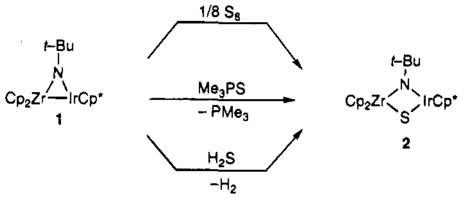


**Figure 1.** ORTEP diagram of $Cp_2Zr(\mu\text{-}N\text{-}t\text{-}Bu)(\mu\text{-}S)IrCp^*$ (**2**).

relevance of these reactions to hydrodesulfurization processes (HDS), the reaction by which sulfur is removed from organosulfur compounds in fuel feedstocks. Despite extensive modeling studies and investigations of heterogeneous catalysts, the mechanism of this reaction is poorly understood.[29-34] Although the sulfur donors described in this paper are not typical HDS substrates,[35] we felt that the heterobimetallic complex **1** might provide a more reasonable approximation than monometallic systems to multimetallic heterogeneous surfaces. Desulfurization reactions with **1** take place across a potentially unsymmetrical metal—metal bond, and the cooperative action of the early and late transition metal centers could provide insight into the role of cocatalysts in HDS processes.

## Results

**Sulfur Transfer Reactions.** The addition of $Me_3P{=}S$ to imido complex **1** resulted in the immediate formation of the dark green sulfido complex **2** ($Cp_2Zr(\mu\text{-}N\text{-}t\text{-}Bu)(\mu\text{-}S)IrCp^*$) at 25 °C (eq 1). Complex **2** was crystallized from diethyl ether at −30 °C in 65% yield. Crystals suitable for an X-ray diffraction study were obtained by slow cooling of a 1:1 mixture of diethyl ether and hexamethyldisiloxane from reflux to 25 °C. An ORTEP drawing of sulfido complex **2** is shown in Figure 1. Crystal parameters are given in Table 1, data collection parameters in Table 2, selected bond lengths in Table 3, and selected bond angles in Table 4. The four-membered ring is planar and asymmetric due to the larger size of the S atom compared to the N atom.[36] The Ir—Zr bond distance is 0.360 Å longer than in imido complex **1**, indicating a lessened or absent bonding interaction.[27] Complex **2** was also found by NMR spectroscopic analysis to be the product of addition of $S_8$ or $H_2S$[37] to imido complex **1** but was not isolated by these routes.



1 2 (1)

**Table 1.** Crystal Parameters for Complex **2**[a,b]

| | |
|---|---|
| empirical formula | $C_{24}H_{34}IrNSZr$ |
| formula wt (amu) | 652.0 |
| crystal size | 0.17 × 0.28 × 0.60 |
| space group | *Pbca* |
| *a* (Å) | 11.1323(17) |
| *b* (Å) | 15.2859(15) |
| *c* (Å) | 27.690(3) |
| α (deg) | 90.0 |
| β (deg) | 90.0 |
| γ (deg) | 90.0 |
| *V* (Å³) | 4711.9(17) |
| Z | 8 |
| $d_{calc}$ (g·cm⁻³) | 1.84 |
| $\mu_{calc}$ (cm⁻¹) | 61.5 |

[a] Unit cell parameters and their esds were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components, 24 reflections with 2θ between 26° and 28°. [b] In this and all subsequent tables the esds of all parameters are given in parentheses, to the right of the least significant digit(s) of the reported value.

**Table 2.** Data Collection Parameters for Complex **2**

| | |
|---|---|
| temp (°C) | −85 |
| rflns measured | $+h,+k,+l$ |
| scan width | $\Delta\omega = 1.00 + 0.35 \tan\theta$ |
| scan speed (θ, deg/m) | 5.49 |
| vert aperture (mm) | 4.0 |
| horiz aperture (mm) | $2.2 + 1.0 \tan\theta$ |
| no. of rflns collected | 3702 |
| no. of unique rflns | 3265 |
| no. of obsd rflns ($F^2 > 3\sigma F^2$) | 2614 |
| $I_{min}/I_{max}$ | 0.67 |
| no. of parameters refined | 128 |
| *R*(*F*) (%) | 3.5 |
| $R_w(F)$ (%) | 4.7 |
| $R_{all}$ (%) | 4.8 |
| goodness of fit | 2.08 |
| *p* factor | 0.03 |

**Table 3.** Selected Intramolecular Distances (Å) for Complex **2**

| atom 1 | atom 2 | distance | atom 1 | atom 2 | distance |
|---|---|---|---|---|---|
| Ir | Zr | 2.968(1) | Ir | Cp3 | 1.830 |
| Ir | N | 1.941(7) | Zr | Cp1 | 2.299 |
| Zr | N | 2.075(7) | Zr | Cp2 | 2.297 |
| Ir | S | 2.360(3) | N | C21 | 1.474(12) |
| Zr | S | 2.389(3) | | | |

**Table 4.** Selected Intramolecular Angles (deg) for Complex 2

| atom 1 | atom 2 | atom 3 | angle |
|---|---|---|---|
| Ir | N | Zr | 95.3(3) |
| Ir | S | Zr | 77.38(8) |
| N | Ir | S | 95.55(22) |
| N | Zr | S | 91.24(22) |
| Ir | N | C21 | 126.5(6) |
| Zr | N | C21 | 138.2(6) |
| Zr | Ir | Cp3 | 168.18 |
| N | Ir | Cp3 | 146.37 |
| S | Ir | Cp3 | 118.05 |
| Cp1 | Zr | S | 106.79 |
| Cp2 | Zr | S | 107.24 |
| Cp1 | Zr | N | 109.90 |
| Cp2 | Zr | N | 109.76 |
| Cp1 | Zr | Cp2 | 126.14 |

Similar sulfur atom transfer was observed in the reaction of imido complex **1** with thiiranes, resulting in immediate formation of sulfido complex **2** and the respective alkenes at −80 °C

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(30) Prins, R.; Beer, V. H. J. D.; Somorjai, C. A. *Catal. Rev.—Sci. Eng.* **1989**, *31*, 1.

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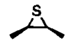
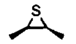
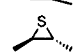
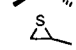
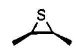
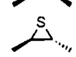
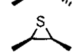
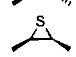
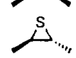
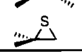
(35) More typical HDS substrates such as thiophene, thianaphthene, and dibenzothiophene do react with complex **1**, but the reaction appears to follow a more complicated pathway than simple sulfur abstraction. Further investigations of these processes will be reported in later publications.

(36) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: San Francisco, 1983; pp 258−259.

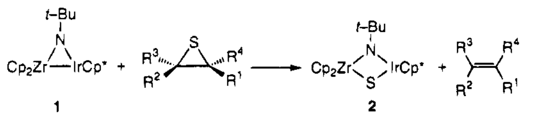
(37) The reaction with $H_2S$ was found to be effectively irreversible. Complex **2** did not react with 300 psi of $H_2$ at room temperature, and more forcing conditions of temperature or pressure led to further unknown compounds or decomposition.

**Table 5.** Experimental Data for the Relative Rates of Reaction of Thiiranes with Complex **1**

| Expt. # | | Thiiranes (mol x $10^{-4}$) | | [2] (mol x $10^{-5}$) | Alkenes (mol x $10^{-5}$) | Product Ratio (a/b)[a] |
|---|---|---|---|---|---|---|
| 1 | a |  | 1.3 | 0.70 | 0.33 | 1.1 |
| | b |  | 1.6 | | 0.45 | |
| 2[b] | a |  | 1.3 | 0.89 | 0.41[c] | 1.2 |
| | b |  | 1.7 | | 0.62 | |
| 3 | a |  | 2.1 | 1.7 | 0.84 | 1.3 |
| | b |  | 2.7 | | 0.82 | |
| 4 | a |  | 0.93 | 0.64 | 0.29 | 1.1[d] |
| | b |  | 1.4 | | 0.20 | |
| 5 | a |  | 2.4 | 1.5 | 0.59 | 1.2 |
| | b |  | 2.3 | | 0.26 | |
| 6 | a |  | 1.8 | 0.96 | 0.53 | 1.3 |
| | b |  | 1.5 | | 0.34 | |
| 7 | a |  | 1.8 | 1.0 | 0.53 | 1.2 |
| | b |  | 1.8 | | 0.44 | |
| 8 | a |  | 4.5 | 1.5 | 0.83 | 1.0 |
| | b |  | 4.4 | | 0.83 | |
| 9 | a |  | 1.4 | 0.60 | 0.27 | 1.2 |
| | b |  | 2.1 | | 0.35 | |
| 10 | a |  | 0.73 | 0.31 | 0.13 | 1.3 |
| | b |  | 1.2 | | 0.17 | |

[a] Experimental error estimated to be ±15% from comparison of repeated experiments (nos. 1 and 2 and nos. 6−8). [b] Reaction performed with an initial 0.72 × $10^{-5}$ mol of propene (see text). [c] Amount of propylene formed in the reaction. [d] The amount of ethylene formed in the reaction was approximated as twice the amount observed by $^1$H NMR spectroscopy (see text).

(eq 2). The addition of *cis*-2-butene sulfide to imido complex



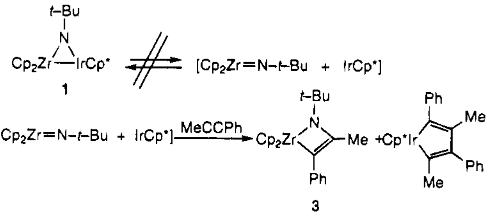
(2)

**1** yielded exclusively *cis*-2-butene with no evidence for the *trans*-alkene (<5%) by $^1$H NMR spectroscopy. Similarly, the addition of *trans*-2-butene sulfide to complex **1** gave only *trans*-2-butene.

Due to the rapid rate of the reaction at −80 °C, a conventional kinetic analysis of the sulfur abstraction reactions could not be performed. A stopped-flow study was attempted, but the reaction was too fast to follow even at −50 °C, with a second-order rate constant of at least 10 000 $s^{-1}$ $M^{-1}$ at this temperature. The relative rates of reaction of excess *trans*-2-butene sulfide, *cis*-2-butene sulfide, 2-methylpropylene sulfide, propylene sulfide, and ethylene sulfide with complex **1** were examined at 25 °C by a competition study. Complex **1** was allowed to react with >10 equiv of pairs of thiiranes in toluene-$d_8$ at 25 °C. The relative rates of reaction were determined by examination of the ratio of alkene products relative to an internal standard by $^1$H NMR spectroscopy. All five thiiranes reacted at similar rates; the experimental data are shown in Table 5. The relative rate of reaction of **1** with ethylene sulfide could not be determined accurately because the ethylene formed did not remain completely dissolved. In order to determine the approximate amount of ethylene dissolved, the yield of the reaction of **1** with ethylene sulfide at concentrations similar to those utilized in the competition experiments was determined. The yield of sulfido complex **2** was found to be 98% by $^1$H NMR spectroscopy, while the yield of $^1$H NMR detectable ethylene was only 40%. Therefore, the amount of ethylene produced in the competition reactions was assumed to be approximately double the value observed. The effect of added alkene on the product ratio in the competition reactions was examined. In experiment no. 2 of Table 5 propene (0.72 × $10^{-5}$ mol) was introduced into the reaction mixture before the addition of imido complex **1**. The product ratio was found to be the same as for the reaction without added propene (experiment no. 1, Table 5) within experimental error.

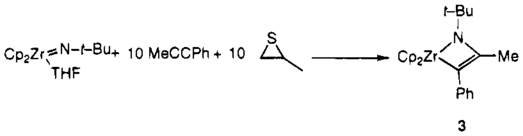
Control experiments were undertaken to investigate the possibility of dissociation of **1** during the desulfurization reaction. One of the most likely directions for dissociation would be formation of the (probably solvated) $Cp_2ZrN$-*t*-Bu and Cp*Ir fragments. One argument against this dissociation is that Cp*Ir(L) is known to undergo rapid C−H activation reactions with hydrocarbons.[38] Presumably, the even more highly unsaturated Cp*Ir would also react readily with the hydrocarbon solvent used in these reactions. However, no Cp* containing side products were observed.

In order to examine further the probability of this dissociation, we investigated the reaction of complex **1** with propylene sulfide in the presence of a large excess of 1-phenylpropyne. Previous work in our laboratory has shown that the reaction of $Cp_2ZrN$-*t*-Bu with this alkyne leads to the formation of metallacycle **3**.[39] Cp*Ir might also be expected to react with the alkyne to give a metallacyclopentadiene.[40,41] If dissociation takes place, we therefore would expect to see the products illustrated in eq 3. As a control experiment, we determined that the reaction of



(3)

$Cp_2Zr$(N-*t*-Bu)(THF) with 1-phenylpropyne in the presence of propylene sulfide gave azametallacycle **3** (eq 4). In the absence



(4)

of the alkyne, propylene sulfide reacted with $Cp_2(THF)Zr=N$-*t*-Bu to form a product with a Cp resonance in the $^1$H NMR spectrum at 5.78 ppm. This product was not isolated or characterized. It was not observed in the desulfurization reactions and was a minor product (17%) in the control experiment with 1-phenylpropyne.

We then carried out the reaction of **1** with propylene sulfide and a large excess of 1-phenylpropyne. No metallacycle **3**, the product expected from the reaction of 1-phenylpropyne with

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(38) Bergman, R. G. *Science* **1984**, *223*, 902.

(39) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

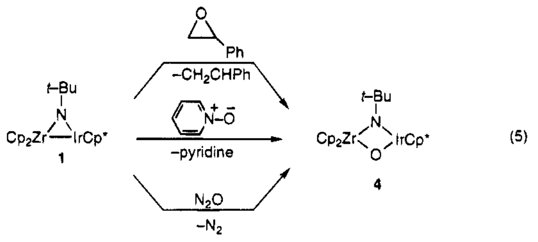
(40) Coorigan, P. A.; Dickson, R. S.; Fallon, G. D.; Michel, L. J.; Mok, C. *Aust. J. Chem.* **1978**, *31*, 1937.

(41) Baimbridge, C. W.; Dickson, R. S.; Fallon, G. D.; Grayson, I.; Nesbit, R. J.; Weigold, J. *Aust. J. Chem.* **1986**, *39*, 1187.

$Cp_2ZrN$-*t*-Bu, was observed. We feel that this argues strongly against dissociation of **1** to Cp*Ir and $Cp_2ZrN$-*t*-Bu.

It is also possible that complex **1** dissociates to form $Cp_2Zr$ and Cp*IrN-*t*-Bu. $Cp_2Zr$ would be expected to react rapidly with 1-phenylpropyne to form a metallacyclopentadiene, but this was not observed.[42,43] Reagents that could be used to trap Cp*-IrN-*t*-Bu also react rapidly with imido complex **1**, so this intermediate is difficult to dismiss.

**Oxygen Transfer Reactions.** In analogy to the sulfur abstraction reactions, the addition of pyridine *N*-oxide to imido complex **1** at 25 °C rapidly gave the bridging oxo complex **4** ($Cp_2Zr(\mu$-N-*t*-Bu)($\mu$-O)IrCp*, eq 5). Complex **4** was crystallized from toluene layered with pentane in 92% yield, and characterized by spectroscopic and microanalytical methods. The addition of $N_2O$ and styrene oxide to imido complex **1** also yielded oxo complex **4** along with Cp*IrN-*t*-Bu and unidentified zirconocene products. Imido complex **1** did not react with either $O{=}PPh_3$ or *cis*-2-butene oxide. Attempts to remove oxygen from complex **4** with $PMe_3$ failed.



(5)

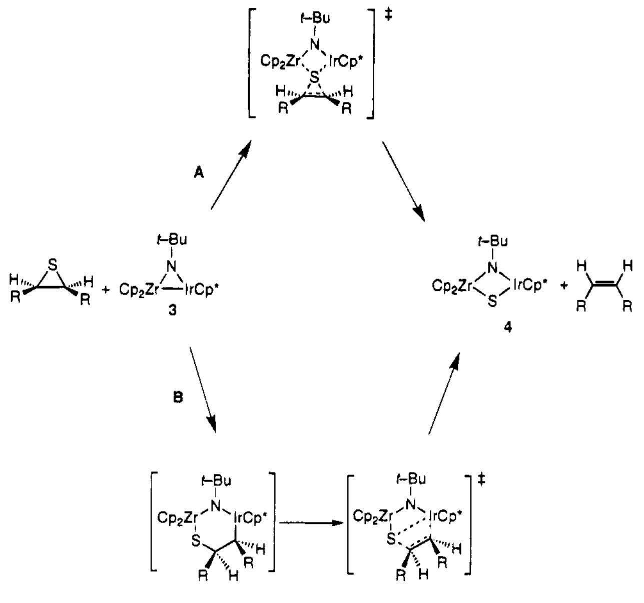
## Discussion

**Investigation of the Dissociation of 1 during Desulfurization of Thiiranes.** An important aspect of elucidating the mechanisms of heterobimetallic reactions is determining whether the complex reacts in its intact binuclear form or whether it dissociates, reacts as monometallic fragments, and then reassociates. Thus, it is important to consider whether the sulfur atom abstraction reactions occur by dissociation of imido complex **1**, reaction of one of the two fragments with the thiirane, and then reassociation of the fragments to form product. The lack of side reactions (with solvent, for example) expected of the proposed fragments, and the lack of trapping by excess 1-phenylpropyne argue strongly against the presence of monometallic intermediates.

**Mechanism of Sulfur Abstraction Reactions.** There are several pathways for the desulfurization of thiiranes by imido complex **1** which would lead to inversion at one carbon of the product alkene, or a mixture of regioisomeric products. One would be an $S_N2$-type attack by one of the metal centers (most likely the more electron-rich Ir atom) at the backside of the C−S bond, resulting in inversion of configuration at one carbon center. Alternatively, attack by the metal center at sulfur, rather than carbon, leading to cleavage of only one C−S bond, could give radical or charged intermediates capable of rotation about the central C−C bond. This should give both *cis*- and *trans*-alkene stereoisomers from each diastereomerically pure thiirane. The fact that cis-substituted thiiranes lead only to *cis*-alkenes and trans-substituted thiiranes give *trans*-alkenes (overall retention of configuration) argues strongly against these possibilities.

Two possible pathways that are consistent with our observations are shown in Scheme 1. Mechanisms A and B are routes that result in overall retention of configuration at the alkene carbon centers. Mechanism A is a completely concerted sulfur transfer reaction, while mechanism B is initiated by insertion of the Zr−Ir moiety into the S−C bond. Mechanism B is presented with sulfur bonded to zirconium but could also occur to give a metallacycle having sulfur bonded to iridium.

**Scheme 1**



One way to distinguish these stereochemically retentive alternatives is to recognize that the transition state for pathway A has higher symmetry than that for pathway B. In pathway A, modifying substituents at one carbon and then both carbons of the thiirane should produce a multiplicative effect on the rate of the desulfurization. In contrast, pathway B would not predict a multiplicative increase in rate when comparing the rates of reaction of propylene sulfide and 2-butene sulfide.[44] In competition studies designed to investigate this question, we found that **1** reacts with propylene sulfide, *cis*-2-butene sulfide, *trans*-2-butene sulfide, 2-methylpropylene sulfide, and ethylene sulfide at very similar rates. Because the reactions appear to be very fast even at low temperatures, it appears that the reactions of **1** with all these thiiranes have very low activation barriers. To explain both the rapid overall rate of sulfur transfer and the inability of the dinuclear complex to discriminate in its reactivity toward thiiranes, we suggest that the sulfur transfers occur at very rapid—perhaps even diffusion-controlled—rates. If this is the case, small differences in the almost negligible barriers for desulfurization would not allow the system to differentiate substantially between different thiiranes. Thus, our data argue against the pathways that lead to inversion or a mixture of products but do not allow us to distinguish between mechanisms A and B.

## Conclusion

We have found that the early−late heterobimetallic complex **1** reacts with sulfur and oxygen atom donors to form the bridging sulfido complex **2** and the bridging oxo complex **4**, respectively. Imido complex **1** reacts with a wider range of sulfur atom donors than oxygen atom donors. The desulfurization of thiiranes was demonstrated to involve either a concerted reaction or a two-step insertion of the Ir−Zr bond into the S−C bond, both of which would result in the observed retention of stereochemistry when *cis*- and *trans*-2-butene sulfides were used as substrates. We feel that the direct abstraction pathway is more likely as the insertion transition state should be more sterically crowded.

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(42) Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1.

(43) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.

(44) For a recent example of the use of this principle, see: Yueh, W.; Bauld, N. L. *J. Am. Chem. Soc.* **1995**, *117*, 5671.

Rather unexpectedly, competition studies with differently substituted thiiranes revealed very similar rates of reaction. It is possible that each of these reactions is associated with a relatively large barrier, and the sulfur abstraction transition state energy is not very sensitive to changes in the structure of the thiirane. However, this does not seem very reasonable, and it therefore is more likely that the weak selectivity is a result of inherently very rapid—perhaps even diffusion-controlled—rates of reaction for the sulfur atom abstraction. If this is the case, there must be a very low or negligible barrier to the atom transfer process. To our knowledge there is little precedent for such a rapid reaction in analogous systems, especially in view of the fact that the transformation involves reorganization of at least three bonding pairs. Further experiments will be required to determine whether these rapid rates are an inherent property of systems in which two metals can cooperate in the atom abstraction process.

## Experimental Section

**General Procedures.** Unless otherwise noted, all manipulations were carried out under an inert atmosphere in a Vacuum Atmospheres 553-2 drybox with attached MO-40-2 Dritrain, or by using standard Schlenk or vacuum line techniques. Solutions were degassed by sequentially freezing to −196 °C, evacuating under high vacuum, and thawing. This sequence was repeated three times in each case. Glass reaction vessels fitted with ground glass joints and Teflon stopcocks are referred to as bombs.

$^1$H NMR spectra were obtained on a 250, 300, 400, or 500 MHz Fourier transform spectrometer at the University of California, Berkeley (UCB), NMR facility. The 250 and 300 MHz instruments were constructed by Mr. Rudi Nunlist and interfaced with either a Nicolet 1180 or a Nicolet 1280 computer. The 400 and 500 MHz instruments were commercial Bruker AM series spectrometers. Two additional (300 and 400 MHz) instruments were commercial Bruker AMX series spectrometers.

IR spectra were obtained on a Nicolet 510 FT-IR or Mattson Galaxy Series FTIR 3000 spectrometer. Mass spectroscopic (MS) analyses were obtained at the UCB mass spectrometry facility on AEI MS-12 and Kratos MS-50 mass spectrometers. Elemental analyses were obtained from the UCB Microanalytical Laboratory or Oneida Research Services. Sealed NMR tubes were prepared using Wilmad 505-PP and 504-PP tubes attached by Cajon adapters directly to Kontes vacuum stopcocks and degassed using freeze–pump–thaw cycles before flame sealing. Known volume bulb vacuum transfers were accomplished with an MKS baratron gauge attached to a high vacuum line.

Stopped-flow experiments were performed at constant injection pressure (60 psi) on a modified Hi-Tech Scientific SF-41 Canterbury stopped-flow spectrometer and OLIS RSM 1000 rapid scanning spectrometer. The SF-41 was modified for anaerobic use as described previously.[45]

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Propylene sulfide and ethylene sulfide were dried over 4 Å molecular sieves, vacuum transferred into glass bombs, and stored at −30 °C. Pentane and hexanes (UV grade, alkene free) were distilled from sodium benzophenone ketyl/tetraglyme under nitrogen. Benzene, toluene, diethyl ether, and THF were distilled from sodium benzophenone ketyl under nitrogen. Deuterated solvents for use in NMR experiments were dried in the same way as their protiated analogs but were vacuum transferred from the drying agent. $Cp_2Zr(\mu\text{-N-}t\text{-Bu})IrCp^*$ (1) was reported elsewhere.[27,28] *cis*-2-Butene sulfide, *trans*-2-butene sulfide, and 2-methylpropylene sulfide were prepared by literature methods from the respective epoxides.[46,47]

**$Cp_2Zr(\mu\text{-N-}t\text{-Bu})(\mu\text{-S})IrCp^*$ (2).** To a solution of $Cp^2Zr(\mu\text{-N-}t\text{-Bu})$-$IrCp^*$ (1) (105 mg, $1.70 \times 10^{-4}$ mol) in 5 mL of diethyl ether was added a slurry of $SPMe_3$ (19.9 mg, $1.84 \times 10^{-4}$ mol, 1.1 equiv) in 1 mL of diethyl ether. The solution turned dark green within 5 min. The volatile materials were removed under reduced pressure, and the resulting green solid was crystallized from 5 mL of diethyl ether at −30 °C to give dark green crystals of **2** (71.8 mg, $1.10 \times 10^{-4}$ mol, 65%): $^1$H NMR ($C_6D_6$) $\delta$ 5.74 (s, 10H), 1.69 (s, 9 H), 1.47 (s, 15H); $^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ 109.2 , 88.9, 71.6, 35.4, 11.0; IR (Nujol) 3082 (m), 3025 (m), 2990 (m), 1761 (w), 1660 (w), 1553 (w), 1479 (m), 1436 (m), 1379 (m), 1370 (m), 1344 (s), 1209 (m), 1185 (s), 1071 (w), 1014 (s), 987 (m), 882 (w), 787 (s), 680 (s) cm$^{-1}$. Anal. Calcd for $C_{24}H_{34}IrNSZr$: C, 44.21; H, 5.26; N, 2.15. Found: C, 44.60; H, 5.16; N, 2.18.

**Crystal Structure Determination of 2.** Dark green blocklike crystals of **2** were obtained by slow cooling of a solution of the complex in a 1:1 mixture of diethyl ether and hexamethyldisiloxane from reflux to 25 °C. One of these crystals was mounted on a glass fiber using Paratone N hydrocarbon oil. The crystal was then transferred to an Enraf-Nonius CAD-4 diffractometer and centered in the beam. It was cooled to −85 °C by a nitrogen flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the sample position. The final cell parameters and specific data collection parameters for this data set are given in Tables 1 and 2. The 3702 raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background, and Lorentz and polarization effects. No correction for crystal decay was necessary. Space group *Pbca* was confirmed by refinement. The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. For the sake of economy, only the Ir, Zr, and S atoms were refined anisotropically. An empirical absorption correction based on the differences of $F_o$ and $F_c$ was applied to the data after refinement of all atoms with isotropic thermal parameters ($T_{max} = 0.997$, $T_{min} = 0.673$). The final residuals for 128 parameters refined against the 2614 data set for which $F^2 > 3\sigma(F^2)$ were $R = 3.5\%$, $wR = 4.7\%$, and GOF = 2.08. The $R$ value for all 3265 data was 4.8%. The largest peak in the final difference Fourier map had an electron density of $+1.14$ e$^-$/Å$^3$, and the lowest excursion $-0.47$ e$^-$/Å$^3$. The quantity minimized by the least-squares program was $\sum[w(|F_o| - |F_c|)^2]$, where $w$ is the weight of a given observation. The $p$ factor, used to reduce the weight of intense reflections, was set to 0.03 in the last cycles of refinement. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion. The positional parameters with isotropic thermal parameters are given in Table S-1 and the anisotropic thermal parameters are given in Table S-2 in the supporting information.

**$Cp_2Zr(\mu\text{-N-}t\text{-Bu})(\mu\text{-O})IrCp^*$ (4).** To a solution of $Cp^2Zr(\mu\text{-N-}t\text{-Bu})$-$IrCp^*$ (1) (124 mg, $2.00 \times 10^{-4}$ mol) in 10 mL of toluene was added pyridine *N*-oxide (20.2 mg, $2.13 \times 10^{-4}$ mol, 1.1 equiv) in 1 mL of toluene. The solution turned from dark brown to dark red immediately. The volatile materials were removed under reduced pressure, and the resulting solid was crystallized form 5 mL of toluene layered with 1 mL of pentane to give dark red needles of **1** (117 mg, $1.84 \times 10^{-4}$ mol, 92%): $^1$H NMR ($C_6D_6$) $\delta$ 5.91 (s, 10H), 1.60 (s, 9H), 1.43 (s, 15H); $^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ 109.7, 85.0, 67.1, 35.1, 10.4; IR (Nujol) 2727 (w), 1461 (s), 1378 (s), 1348 (m), 1190 (m), 1025 (m), 1010 (m), 813 (m), 783 (s), 774 (s), 715 (s), 670 (m) cm$^{-1}$. Anal. Calcd for $C_{24}H_{34}IrNOZr$: C, 45.33; H, 5.39; N, 2.20. Found: C, 45.15; H, 4.99; N, 2.05.

**Yield of the Reaction of Styrene Oxide with 1.** An NMR tube was loaded with $Cp_2Zr(\mu\text{-N-}t\text{-Bu})IrCp^*$ (**1**) (8.1 mg, $1.3 \times 10^{-5}$ mol), *p*-dimethoxybenzene (1.4 mg, $1.0 \times 10^{-5}$ mol), and 0.6 mL of $C_6D_6$. Two one-scan $^1$H NMR spectra were taken. Styrene oxide (1.6 $\mu$L, $1.4 \times 10^{-5}$ mol) was added to the reaction mixture. Two more one-scan $^1$H NMR spectra were taken. The yield of **4** was determined to be 44%, the yield of styrene was 77%, and the yield of $Cp^*IrN\text{-}t\text{-Bu}$ was 31% by integration versus *p*-dimethoxybenzene.

**Yield of the Reaction of $N_2O$ with 1.** An NMR tube was loaded with $Cp_2Zr(\mu\text{-N-}t\text{-Bu})IrCp^*$ (**1**) (13.2 mg, $2.13 \times 10^{-5}$ mol), *p*-dimethoxybenzene (1.8 mg, $1.3 \times 10^{-5}$ mol), and 0.6 mL of $C_6D_6$. Two one-scan $^1$H NMR spectra were taken. The solution was degassed, and a known volume of $N_2O$ (18.5 Torr in 23.5 mL, $2.34 \times 10^{-5}$ mol) was condensed into the tube. The NMR tube was sealed, and the solution turned red upon thawing. Two more one-scan $^1$H NMR spectra

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(46) Trost, B. M.; Ziman, S. D. *J. Org. Chem.* **1973**, *38*, 932.

(47) Bordwell, F. G.; Andersen, H. M. *J. Am. Chem. Soc.* **1953**, *75*, 4959.

were taken. By integration versus *p*-dimethoxybenzene, the yield of **4** was determined to be 54% and the yield of Cp*IrN-*t*-Bu was 27%.

**Yield of the Reaction of $S_8$ with 1.** An NMR tube was loaded with $Cp_2Zr$($\mu$-N-*t*-Bu)IrCp* (**1**) (10.6 mg, $1.71 \times 10^{-5}$ mol), *p*-dimethoxybenzene (1.5 mg, $1.1 \times 10^{-5}$ mol), and 0.6 mL of $C_6D_6$. Two one-scan $^1$H NMR spectra were taken. Sulfur (0.6 mg, $1.9 \times 10^{-5}$ mol) was added to the reaction mixture. Two more one-scan $^1$H NMR spectra were taken. The yield of **2** was determined to be 76% by integration versus *p*-dimethoxybenzene.

**General Procedure for Competition Experiments Involving the Reaction of Thiiranes with Imido Complex 1.** The general procedure for a typical experiment is given below. An NMR tube equipped with a screw cap and septum was charged with *cis*-2-butene sulfide (14.8 mg, $1.68 \times 10^{-4}$ mol, 17.3 equiv), propylene sulfide (11.0 $\mu$L, $1.40 \times 10^{-4}$ mol, 14.4 equiv), *p*-dimethoxybenzene (1.7 mg, $1.2 \times 10^{-5}$ mol, 1.3 equiv), and 0.8 mL of toluene-$d_8$. Two one-scan $^1$H NMR spectra were taken. $Cp_2Zr$($\mu$-N-*t*-Bu)IrCp* (**1**) (6.0 mg, $9.7 \times 10^{-6}$ mol, 1 equiv) was dissolved in 100 $\mu$L of toluene-$d_8$ and injected through the septum into the bulb at the top of the NMR tube at 25 °C. The solution was shaken vigorously and immediately turned dark green. A four-scan $^1$H NMR spectrum with a 3 min delay between scans was taken. The product alkenes were integrated against the internal standard, and the yield was found to be 81%, but we believe it to be higher due to difficulties in injecting the entire sample of $Cp_2Zr$($\mu$-N-*t*-Bu)IrCp* (**1**) into the reaction mixture. The determination of the yield with *cis*-2-butene sulfide is reported below. The results of the competition experiments are listed in Table 5. Concentrations are reported relative to the internal standard.

**Reaction of *cis*-2-Butene Sulfide with Complex 1 at −80 °C and Determination of the Yield.** An NMR tube equipped with a screw cap and septum was charged with $Cp_2Zr$($\mu$-N-*t*-Bu)IrCp* (**1**) (9.0 mg, $1.4 \times 10^{-5}$ mol), *p*-dimethoxybenzene (2.8 mg, $2.0 \times 10^{-5}$ mol), and 0.6 mL toluene-$d_8$. A one-scan $^1$H NMR spectrum was taken. The NMR tube was submerged in a dry ice−acetone bath, and *cis*-2-butene sulfide (3.0 mg, $3.4 \times 10^{-5}$ mol, 2.4 equiv) was injected via syringe through the septum down the sides of the tube. The solution was mixed with as little warming as possible and immediately turned green. A $^1$H NMR spectrum taken at −80 °C showed complete formation of $Cp^2Zr$($\mu$-N-*t*-Bu)($\mu$-S)IrCp* (**2**) and *cis*-1-butene. The sample was warmed to 25 °C in the probe, a one-scan $^1$H NMR spectrum was taken, and the yield of the reaction was determined to be 97% in $Cp^2Zr$($\mu$-N-*t*-Bu)($\mu$-S)IrCp* and 98% in *cis*-2-butene by integration against the internal standard.

**Stopped-Flow Experiments.** A typical experiment involved purging the thermostated oil bath with purified argon for at least 24 h. The oil bath was then cooled to −60 °C. Due to the water-sensitive nature of the compounds used, it was necessary that a drying agent ($Cp_2ZrMe_2$, which reacts rapidly with water to give $[Cp_2(Me)Zr]_2O$) be present in solution to scavenge water which diffused from the oil bath into the Teflon tubing of the flow circuit. All toluene solutions used were dried over sodium/benzophenone and vacuum transferred prior to use.

Solid samples were loaded into vacuum ampules in a nitrogen drybox, and toluene was vacuum transferred into the ampules using a high-vacuum line. Solutions were then transferred via gas tight syringes from the vacuum ampules under argon to the argon-purged stopped-flow reservoirs. A toluene solution of $Cp_2ZrMe_2$ was first rinsed through the stopped-flow circuit to remove any traces of water. Solutions of $Cp_2Zr$($\mu$-N-*t*-Bu)IrCp* (**1**) ($1.39 \times 10^{-3}$ M) and propylene sulfide ($1.14 \times 10^{-2}$ M) both contained excess $Cp_2ZrMe_2$ (*ca.* 0.04 M) to trap residual water. The reaction was monitored independently by UV/vis and $^1$H NMR spectroscopy to ensure the $Cp_2ZrMe_2$ did not interfere in the reaction. Rapid-scan UV/Vis spectra taken upon injection into the mixing chamber at −60 °C revealed conversion of starting material to product more rapidly than could be measured on the stopped-flow time scale, with the loss of 40% of the starting material apparently due to reaction with water or oxygen.

**Yield of Ethylene and Complex 2 from the Reaction of Complex 1 with Ethylene Sulfide.** The procedure was the same as that for the determination of the yield with *cis*-2-butene sulfide above except that the addition of ethylene sulfide (3.0 $\mu$L, $5.0 \times 10^{-5}$ mol, 5 equiv) to $Cp^2Zr$($\mu$-N-*t*-Bu)IrCp* (**1**) (6.2 mg, $1.00 \times 10^{-5}$ mol) was performed at 25 °C. The yield of $Cp_2Zr$($\mu$-N-*t*-Bu)($\mu$-S)IrCp* (**2**) was found to be 98%, and the yield of ethylene was determined to be 40%.

**Addition of Complex 1 to an Excess of MeCCPh and Propylene Sulfide.** $Cp_2Zr$($\mu$-N-*t*-Bu)IrCp* (**1**) (5.2 mg, $8.4 \times 10^{-6}$ mol) was dissolved in 100 $\mu$L of benzene-$d_6$ and added to a stirred solution of propylene sulfide (3.3 $\mu$L, $4.22 \times 10^{-5}$ mol, 5 equiv) and 1-phenyl-1-propyne (50 $\mu$L, $4.00 \times 10^{-4}$ mol, 48 equiv) in 0.6 mL of benzene-$d_6$. The solution immediately turned dark green and was loaded into an NMR tube. No peaks were observed in the $^1$H NMR spectrum for the metallacycle **3** that would result from the reaction of 1-phenyl-1-propyne with $Cp_2ZrN$-*t*-Bu.

**Relative Rates of Reaction of Propylene Sulfide and 1-Phenyl-1-propyne with $Cp_2Zr$(N-*t*-Bu)(THF).** $Cp_2Zr$(N-*t*-Bu)(THF) (5.0 mg, $1.4 \times 10^{-5}$ mol) was dissolved in 0.1 mL of benzene-$d_6$ and then added to a solution of propylene sulfide (10 $\mu$L, $1.28 \times 10^{-4}$ mol, 9 equiv) and 1-phenyl-1-propyne (17.5 $\mu$L, $1.40 \times 10^{-4}$ mol, 10 equiv) in 0.6 mL of benzene-$d_6$. The solution immediately turned bright green. The $^1$H NMR spectrum showed formation of metallacycle **3**: $^1$H NMR ($C_6D_6$) $\delta$ 7.37 (m, 2H), 7.07 (m, 3H), 5.86 (s, 10H), 2.02 (s, 3H), 1.14 (s, 9H) (lit.[39] $^1$H NMR ($C_6D_6$) $\delta$ 7.38 (m, 2H), 7.07 (m, 3H), 5.85 (s, 10H), 2.02 (s, 3H), 1.14 (s, 9H)).

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**Supporting Information Available:** Tables giving additional structural data for complex **2** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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