Organometallics 1989, 8, 2277-2279

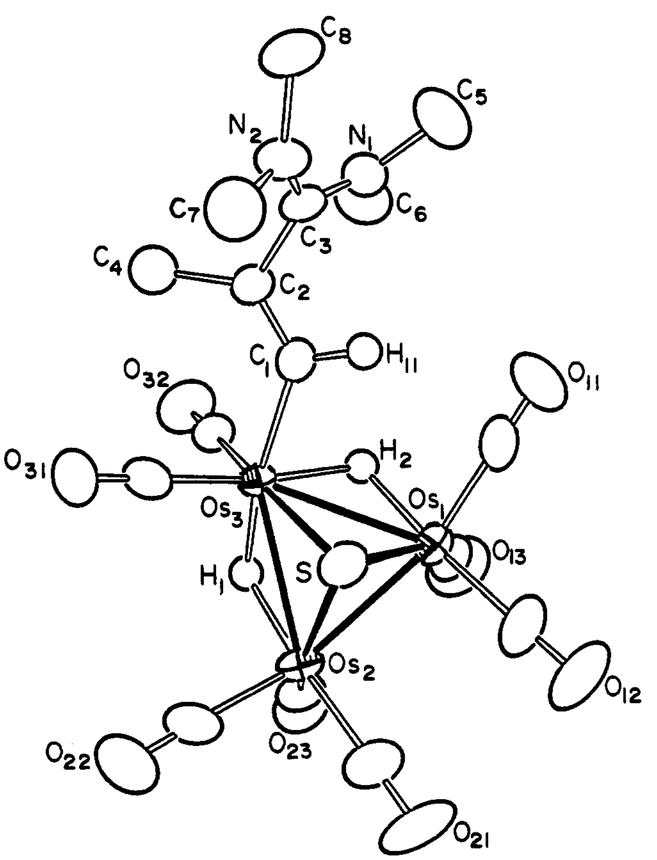
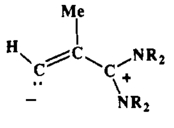


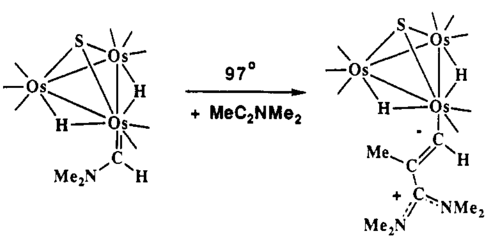
Figure 1. An ORTEP diagram of $Os_3(CO)_8[C(H){=}C(Me)C(NMe_2)_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2**) showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Os(3)–C(1) = 2.067 (9), C(1)–C(2) = 1.34 (1), C(2)–C(3) = 1.48 (1), C(3)–N(1) = 1.32 (1), C(3)–N(2) = 1.32 (1), Os(3)–C(1)–C(2) = 133.6 (6), C(1)–C(2)–C(3) = 119.2 (7), N(1)–C(3)–N(2) = 121.9 (8).

lecular structure of **2** is shown in Figure 1. The $Os_3(CO)_8(\mu_3\text{-}S)(\mu\text{-}H)_2$ cluster contains two bridging hydride ligands which structurally is virtually identical with that grouping in compound **1**.[9] The most interesting ligand is the $HC{\equiv}C(Me)C(NMe_2)_2$ grouping that is terminally coordinated to the metal atom Os(3). This group could be viewed as an amidinium-substituted propenyl ligand B



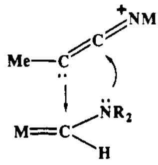
B

that serves as a two-electron donor to Os(3). The C(1)–C(2) distance is short, 1.34 (1) Å, and characteristic of a C–C double bond. The C(2)–C(3) bond of 1.48 (1) Å is only slightly shorter than that of a C–C single bond. The two C–N bond distances to C(3) are identical, 1.32 (1) Å, and both nitrogen atoms exhibit a planar geometry. Both features are consistent with the existence of partial multiple bonding of the amino groups to the carbon C(3) to stabilize the formal positive charge. The plane of the amidinium group is rotated 62° from the plane of the propenyl ligand which indicates a lack of conjugation between these two groupings. The only previous report of an insertion of an alkyne into a heteroatom–carbon bond of a carbene ligand was for the insertion of an ynamine into a C–O bond of the chelating bis(ethoxycarbene)tungsten carbonyl complex $(CO)_4\overline{W[C(OEt)C(H)PhC(H)PhC(OEt)]}$.[12]



1 **2** (3)

The formation of **2** (eq 3) is believed to occur by a direct addition of the β-carbon atom of ynamine to the carbene carbon, C, but unlike the M–C insertion, it is the dialkylamino group of the carbene ligand that is shifted to the α-carbon atom. Studies to investigate the effect of variation of the substituents on the carbene and the ynamine on the course of this reaction are in progress.



C

Acknowledgment. This research was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy.

Supplementary Material Available: Tables of crystal data, positional parameters, intramolecular bond distances and angles, and anisotropic thermal parameters of compound **2** (9 pages); a listing of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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[11] Pale yellow crystals of **2** were grown from solutions in CH_2Cl_2 solvent by cooling to −20 °C. These crystals belonged to the triclinic crystal system: space group $P\bar{1}$; $a = 11.038$ (2) Å, $b = 12.831$ (3) Å, $c = 9.991$ (2) Å, $\alpha = 98.16$ (2)°, $\beta = 108.43$ (1)°, $\gamma = 112.00$ (1)°, $Z = 2$. Diffraction data were collected on a Rigaku AFC6S diffractometer by using Mo Kα radiation. Calculations were performed on a MICROVAX II computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Data were corrected for absorption. The structure was solved by the heavy-atom method and was refined (2954 reflections) to the final values of the residuals, $R = 0.024$ and $R_w = 0.028$. The hydride ligands were located and refined on their positional parameters only. All other hydrogen atom positions were calculated.

[12] Huy, N. H. T; Fischer, E. O.; Reide, J. Thewalt, U.; Dötz, K. H. *J. Organomet. Chem.* **1984**, *273*, C29.

An η^4-Thiophene Ligand. A New Mode of Thiophene Coordination in $Cp^*Ir(\eta^4\text{-}2,5\text{-dimethylthiophene})$

Jiabi Chen and Robert J. Angelici*

Department of Chemistry and Ames Laboratory[1]
Iowa State University, Ames, Iowa 50011

Received May 17, 1989

Summary: A two-electron reduction of the 18-electron complex $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$, where 2,5-$Me_2T$ is 2,5-dimethylthiophene, produces $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$, which contains the novel η^4-thiophene ligand. An X-ray study shows that the η^4-2,5-Me_2T ligand is coordinated to the metal via only the four carbon atoms. The uncoordinated sulfur atom is sufficiently basic to form a strong adduct with BH_3.

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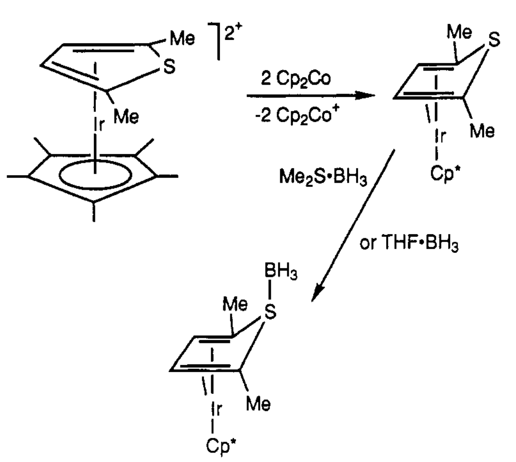
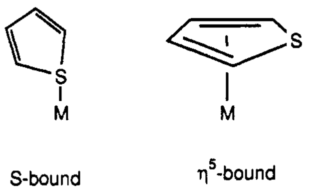
Scheme I



In connection with our efforts to understand the mechanism(s) of thiophene hydrodesulfurization (HDS),[2] we have been interested in possible modes of thiophene coordination at metal centers that are present in HDS catalysts. Two modes of thiophene binding in metal complexes are known:[2] S-bound, where thiophene is a 2-electron donor, and η^5-bound, where thiophene is a 6e donor: In this communication, we describe the first example of an η^4-thiophene ligand, which occurs in Cp*Ir(η^4-2,5-Me$_2$T) (**2**), where 2,5-Me$_2$T is 2,5-dimethylthiophene; the uncoordinated sulfur in this complex is unusually basic and coordinates readily to BH$_3$.



Complex **2** was prepared (Scheme I) by the 2e reduction of the 18e$^-$ complex [Cp*Ir(η^5-2,5-Me$_2$T)](BF$_4$)$_2$[3] (**1**) (0.4 mmol) with Cp$_2$Co (0.8 mmol) in 30 mL of THF at room temperature. After being stirred for 7 h, the solution was evaporated to dryness and the residue was chromatographed on Al$_2$O$_3$ by using hexane as the eluent. The product **2** was isolated as yellow crystals in 37% yield and fully characterized.[5]

The X-ray-determined[6] structure (Figure 1) of **2** shows the 2,5-Me$_2$T ligand coordinated to the Ir through the four C atoms at an average distance of 2.11 ± 0.01 Å. The methyl groups (C(1) and C(6)) lie slightly (0.047 Å average) below the C(2)–C(3)–C(4)–C(5) plane toward Ir, while the S lies 0.905 Å out this plane away from Ir with an Ir–S distance of 2.969 (4) Å. The dihedral angle between the C(2)–C(3)–C(4)–C(5) and C(2)–S–C(5) planes is 42°. The two ligand planes C(2)–C(3)–C(4)–C(5) and C(11)–C(12)–C(13)–C(14)–C(15) are nearly parallel to each other with a dihedral angle of 7.3 ± 2.9° between them.

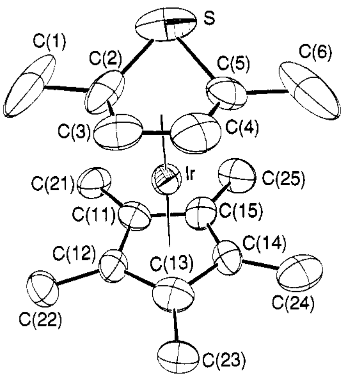


Figure 1. ORTEP plot of Cp*Ir(η^4-2,5-Me$_2$T) (**2**). Selected bond distances (Å) and angles (deg) are C(2)–S = 1.76 (2), C(5)–S = 1.79 (2), C(2)–C(3) = 1.43 (2), C(3)–C(4) = 1.39 (2), C(4)–C(5) = 1.46 (2), C(1)–C(2) = 1.51 (2), C(5)–C(6) = 1.57 (3), C(2)–S–C(5) = 80.8 (6)°, C(1)–C(2)–C(3) = 117 (2)°, and C(4)–C(5)–C(6) = 118 (2)°.

The interior ring angles at the η^4-ligand carbon atoms (C(2) through C(5)) are essentially all the same (107–111 ± 1°), while the interior angle at S is much more acute (80.8 (6)°) than it is in free thiophene (91°)[7] and (Ph$_3$P)$_2$Rh(η^5-thiophene)$^+$ (90°).[8] The three C–C distances (1.43 (2), 1.39 (2), and 1.46 (2) Å) in the η^4-ligand are nearly the same within experimental error with the possibility that C(3)–C(4) is slightly shorter than the other two distances. Thus, the bonding of the η^4-2,5-Me$_2$T ligand to the metal may be represented by the two resonance forms which both contribute about equally. The C–S bond distances (1.76 (2) and 1.79 (2) Å) indicate that they are essentially single bonds by comparison with standard C(sp^2)–S (1.76 Å)[9] and C(sp^3)–S (1.81 Å)[10] single bonds. These bonds are lengthened from the same distances (1.72 Å)[7] in free thiophene. Thus, this type of coordination, if it were to occur on an HDS catalyst, would weaken the C–S bonds and perhaps promote C–S bond cleavage, which is required to give the H$_2$S and hydrocarbon products.

The long C–S bond distances in **2** suggest that the two-electron pairs on the sulfur do not interact with the diene system. This would leave these electron pairs, as in sulfides (R$_2$S), available for donation to Lewis acids. In fact, it appears that the sulfur in **2** is even more basic than it is in Me$_2$S. Thus, **2** (0.06 mmol) reacts with Me$_2$S·BH$_3$ (0.20 mmol) in 20 mL of THF at 0–15 °C over a period of 3 h during which time the yellow solution gradually turns colorless. After the solution is evaporated, the residue is

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[1] Ames Laboratory is operated by the U.S. Department of Energy by Iowa State University under Contract W-7405-ENG-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.

[2] Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.

[3] This complex was prepared in an entirely analogous manner to that reported[4] for [Cp*Ir(η^5-thiophene)](BF$_4$)$_2$, where Cp* = η^5-C$_5$Me$_5$.

[4] Huckett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686.

[5] Anal. Calcd for C$_{16}$H$_{23}$SIr: C, 43.71; H, 5.27. Found: C, 43.68; H, 5.40. ^{1}H NMR (CDCl$_3$): δ 4.53 (s, 2 H), 1.11 (s, 6 H), 1.92 (s, 15 H). EIMS: m/e 440 (M$^+$). Melting point: 117–118 °C dec.

[6] Crystallographic data for **2**: mol wt 439.63; orthorhombic, space group $P2_12_12_1$; a = 10.954 (3) Å, b = 11.623 (1) Å, c = 12.513 (1) Å; V = 1593.1 (5) Å^3; ρ_{calcd} = 1.833 g/cm^3 for Z = 4 at 22 ± 1 °C; μ = 84.58 cm^{-1} (Mo Kα). Diffraction data were collected at 22 ± 1 °C by using an Enraf-Nonius CAD4 automated diffractometer. A total of 3062 reflections were collected. Of the 1601 unique data, 1398 were considered observed, having $F_o^2 > 3\sigma(F_o^2)$. The position of the Ir atom was taken from a Patterson map. The remainder of the non-hydrogen atoms were located in difference Fourier maps. Refinement of the enantiomorph produced no significant difference in the structure or the R values: R = 0.0300 and R_w = 0.0391.

[7] Bak, B.; Christensen, D.; Rastrup-Andersen, J.; Tannenbaum, E. *J. Chem. Phys.* **1956**, *25*, 892.

[8] Sanchez-Delgado, R. A.; Marquez-Silva, R. L.; Puga, J.; Tiripicchio, A.; Camellini, M. T. *J. Organomet. Chem.* **1986**, *316*, C35.

[9] (a) Rozsondai, B.; Schultz, G.; Hargittai, I. *J. Mol. Struct.* **1981**, *70*, 309. (b) Samdal, S.; Seip, H. M.; Torgrimsen, T. *J. Mol. Struct.* **1979**, *57*, 105.

[10] Yokozeki, A.; Bauer, S. H. *J. Phys. Chem.* **1976**, *80*, 618.

recrystallized from hexane/CH_2Cl_2 (20:1) at −78 °C to give white crystalline $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T\cdot BH_3)$ (**3**) in 89% yield. Complex **3** has also been prepared by the reaction of **2** with $THF\cdot BH_3$ and was fully characterized.[11] The X-ray structure[12] of **3** is very similar to that of **2**, except BH_3 is coordinated to the sulfur. The ability of **2** to displace Me_2S from $Me_2S\cdot BH_3$ demonstrates the strong donor ability of the sulfur in **2**. From other studies in progress, it appears that the sulfur in **2** is also a strong donor toward other electron-pair acceptors.

Acknowledgment. We are grateful to Dr. Lee M. Daniels of the Iowa State University Molecular Structure Lab for determining the structure of **2**. The diffractometer was funded in part by the National Science Foundation (Grant No. CHE-8520787). We thank Johnson Matthey, Inc., for a loan of $IrCl_3$.

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes and torsion angles (12 pages); a listing of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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[11] Anal. Calcd for $C_{16}H_{26}BSIr$: C, 42.38; H, 5.78. Found: C, 42.50; H, 5.91. ^1H NMR ($CDCl_3$): δ 4.46 (s, 2 H), 1.28 (s, 6 H), 1.96 (s, 15 H), 0.91 (m, 3 H, BH_3). EIMS: m/e 454 (M^+), 440 ($M^+ - BH_3$). Melting point: 106–108 °C dec.

[12] Chen, J.; Angelici, R. J. *J. Am. Chem. Soc.*, submitted for publication.

Copper(II)-Mediated Stereoselective Reduction of Acetylenic Sulfones by Hydrosilanes

Ilhyong Ryu,* Nobuo Kusumoto, Akiya Ogawa, Nobuaki Kambe, and Noboru Sonoda*

Department of Applied Chemistry, Faculty of Engineering Osaka University, Suita, Osaka 565, Japan

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Summary: The stereoselective reduction of acetylenic sulfones to cis vinylic sulfones was effected by using a novel reduction system consisting of copper(II) salts ($Cu(BF_4)_2$, $Cu(OTf)_2$, CuF_2, etc.) and a hydrosilane. The best result was obtained by the use of $Cu(BF_4)_2$. A divalent copper hydride is proposed to be responsible for this reduction.

The usefulness of copper(I) hydride (**1**) as an efficient reagent for conjugate hydride addition to α,β-unsaturated carbonyl compounds has been amply established so far.[1,2] However, little is known concerning the generation and synthetic behavior of copper(II) hydride, such as **2**. We envisaged that an appropriate combination of a metal hydride with a copper(II) salt would give copper(II) hydride **2**,[3] which might exhibit unique reducing behavior different from that of **1**. In this communication, we report that the system consisting of a copper(II) salt and a hydrosilane effects the stereoselective 1,2-reduction of acetylenic sulfones **4** to cis vinylic sulfones **5**, a reaction for which a stereoselective syn addition pathway to the triple bond by the copper(II) hydride, generated in situ from CuX_2 and $HSiR_3$, appears likely.

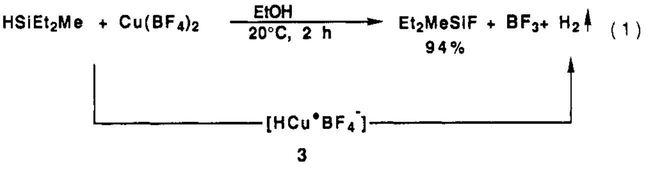
HCu(I)

1

HCu(II)X

2

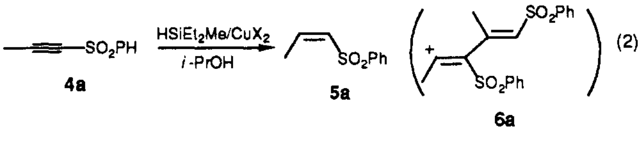
The reaction of $Cu(BF_4)_2$[4] with diethylmethylsilane ($HSiEt_2Me$) in ethanol at 20 °C took place with the evolution of hydrogen gas (identified by GC) and the deposition of copper(0), giving a 94% yield (NMR) of diethylmethylfluorosilane (Et_2MeSiF) after 2 h. This result has suggested that $Cu(BF_4)_2$ reacted with the hydrosilane to give the silyl fluoride and a copper(II) hydride, such as **3**, which then decomposed to yield molecular hydrogen. Similar hydrogen evolution was observed with other copper(II) salts such as $Cu(OTf)_2$, $Cu(NO_3)_2$, and CuF_2.



Unlike most copper(I) hydride species, which effect conjugate reduction of α,β-unsaturated ketones,[1,2] the present system consisting of a hydrosilane and a copper(II) salt reduced them only reluctantly under similar reaction conditions.[5] However, it was found that when acetylenic sulfone **4a** was treated with $HSiEt_2Me$ in the presence of copper(II) salts in i-PrOH, syn reduction of **4a** took place to give the cis vinylic sulfone **5a** in good yields (Table I). Among the copper(II) salts examined, $Cu(BF_4)_2$ gave the best result. The use of CuF_2 resulted in the formation of significant amounts of dimeric product **6a** together with vinylic sulfone **5a**.

Table II presents the results of the reductions of several acetylenic sulfones **4**[6] by $HSiEt_2Me/Cu(BF_4)_2$. Reduction proceeded smoothly to give the corresponding cis vinylic sulfones **5** in good yield after purification by flash chro-

Table I. Effect of Copper Salt in the Reduction of Acetylenic Sulfone 4a[a]



run[a]	copper salt	condn (°C, h)	yield,[b] % 5a	yield,[b] % 6a	recovered 4a
1	$Cu(BF_4)_2$	15, 3	94		
2[c]	CuF_2	25, 6	48[d]	31[d]	
3	$Cu(OTf)_2$	15, 6	55		45
4	$Cu(NO_3)_2$	15, 6	55		25
5	$CuCl_2$	15, 3			97
6	e	15, 3			99

[a] Unless otherwise specified, reduction was carried out by adding $HSiEt_2Me$ (2 equiv) to a mixture of **4a** (1 equiv) and copper salt (2 mol equiv) in i-PrOH. [b] Determined by GLC analysis. [c] Reaction was conducted in MeOH. [d] Isolated yield after purification by PTLC. [e] $BF_3\cdot OEt_2$ (2 equiv) was used in place of copper salts.

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[1] For ate complexes of **1**, see: (a) Tsuda, T.; Yoshida, T.; Kawamoto, T.; Saegusa, T. *J. Org. Chem.* **1987**, *52*, 1624. (b) Tsuda, T.; Fujii, T.; Kawasaki, K.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1980**, 1013. (c) Semmelhack, M. F.; Stauffer, R. D.; Yamashita, A. *J. Org. Chem.* **1977**, *42*, 3180. (d) Ashby, E. C.; Lin, J.-J.; Goel, A. B. *Ibid.* **1978**, *43*, 183. (e) House, H. O.; DuBose, J. C. *Ibid.* **1975**, *40*, 788. (f) Semmelhack, M. F.; Stauffer, R. D. *Ibid.* **1975**, *40*, 3619. (g) Boeckman, R. K., Jr.; Michalak, R. *J. Am. Chem. Soc.* **1974**, *96*, 1623. (h) Masamune, S.; Bates, G. S.; Georghiou, P. E. *Ibid.* **1974**, *96*, 3686.

[2] For phosphine complexes of **1**, see: (a) Mahoney, W. S.; Brestensky, D. M.; Stryker, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 291. (b) Brestensky, D. M.; Huseland, D. E.; McGettigan, C.; Stryker, J. M. *Tetrahedron Lett.* **1988**, *29*, 3749. (c) Sorrell, T. N.; Pearlman, P. S. *J. Org. Chem.* **1980**, *45*, 3449. (d) Whitesides, G. M.; Filippo, J. S., Jr.; Stedronsky, E. R.; Casey, C. P. *J. Am. Chem. Soc.* **1969**, *91*, 6542. (e) Dilts, J. A.; Shriver, D. F. *Ibid.* **1969**, *91*, 4088.

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