ygenated under vacuum prior to use.

Infrared spectra were recorded on a Hitachi 260-50 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GX-270 instrument. Field-desorption mass spectra were measured on a Hitachi GC-MS M80 high-resolution mass spectrometer.

Elemental analysis was performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology.

(η^5-C_5Me_5)Ru(μ-H)$_4$Ru(η^5-C_5Me_5) was prepared according to the previously published method.[4]

Crystallographic Data Collection and Structure Refinement. A crystal was mounted on a glass fiber. Unit cell constants were determined from 25 machine-centered reflections. Data were collected with graphite-monochromated Mo Kα radiation at ambient temperature with a Rigaku AFC-5 diffractometer. Data in the range of 2° < 2θ < 60° were collected. Data processing was performed on a FACOM A-70 computer using the R-CRYSTAN structure solving program library obtained from the Rigaku Corp. The crystal of **2** belongs to the triclinic crystal system. The positions of the metal atoms were determined by heavy-atom methods. All non-hydrogen atoms and two bridging hydrogen atoms were located by subsequent difference Fourier synthesis. Ru and C atoms were refined anisotropically by full-matrix least-squares techniques. Hydrogen atoms were refined isotropically.

Reaction of (η^5-C_5Me_5)Ru(μ-H)$_4$Ru(η^5-C_5Me_5) (1) with Diphenylacetylene. Preparation of (η^5-C_5Me_5)Ru(μ-H)$_2$(μ-PhCCPh)Ru(η^5-C_5Me_5) (2) and (η^5-C_5Me_5)Ru(μ-PhCPhCCPhCPh)Ru(η^5-C_5Me_5) (3). To a solution of (η^5-C_5Me_5)Ru(μ-H)$_4$Ru(η^5-C_5Me_5) (1) (0.405 g, 0.85 mmol) in toluene (5 mL) was added diphenylacetylene (0.303 g, 1.70 mmol) at room temperature. After being stirred for 12 h, the resulting reaction mixture was passed through a short column packed with Celite. Solvent was removed from the filtrate under reduced pressure to leave a dark brown solid. The ^{1}H NMR (60 MHz) spectrum of the residual solid in C_6D_6 showed the formation of complexes **2** and **3** in a 1.3:1 ratio, which was determined on the basis of the intensities of two singlet peaks at δ 1.62 and 1.54 ascribed to the C_5Me_5 ligands. Purification of the dark brown residual solid by column chromatography on neutral alumina with toluene afforded **2** and **3** as maroon and dark brown solids, respectively. Crystallization from the mixed solvent of toluene and pentane gave **2** (0.193 g, 35%) as maroon needles. **2**: mp 196 °C; IR (KBr) 3063, 2959, 2887, 1694, 1587, 1488, 1379 cm^{-1}; ^{1}H NMR (C_6D_6, TMS) δ 7.75–7.23 (m, 10 H, *Ph*), 1.62 (s, 30 H, C_5*Me*$_5$), −13.98 (s, 2 H, Ru-*H*-Ru); ^{13}C NMR (C_6D_6, TMS) δ 141.4 (s, *Ph-ipso*), 130.0 (d, J_{CH} = 159.0 Hz, *Ph*), 128.3 (d, J_{CH} = 157.3 Hz, *Ph*), 125.1 (d, J_{CH} = 159.0 Hz, *Ph*), 109.0 (s, *acetylenic*), 89.9 (s, *C_5*Me$_5$), 11.7 (q, J_{CH} = 125.4 Hz, C_5*Me*$_5$). Anal. Calcd for $C_{34}H_{42}Ru_2$: C, 62.55; H, 6.48. Found: C, 62.64; H, 6.75. Complex **3** obtained by means of column chromatography was inevitably contaminated by a small amount of **2**. Crystallization from the mixed solvent of tetrahydrofuran and toluene afforded **3** (0.099 g, 14%) as dark brown powder. **3**: ^{1}H NMR (C_6D_6, TMS) δ 7.64–6.71 (m, 20 H, *Ph*), 1.54 (s, 30 H, C_5*Me*$_5$); ^{13}C NMR (C_6D_6, TMS) δ 155.4 (s, Ru-*C*-(Ph)–C(Ph)–), 147.6 (s, *Ph-ipso*), 138.5 (s, *Ph-ipso*), 131.4 (d, J_{CH} = 157.6 Hz, *Ph*), 131.3 (d, J_{CH} = 157.6 Hz, *Ph*), 127.5 (d, J_{CH} = 161.6 Hz, *Ph*), 127.1 (d, J_{CH} = 163.8 Hz, *Ph*), 126.0 (d, J_{CH} = 160.7 Hz, *Ph*), 124.8 (d, J_{CH} = 159.7 Hz, *Ph*), 101.0 (s, Ru–C(Ph)–*C*-(Ph)–), 88.1 (s, *C_5*Me$_5$), 11.2 (q, J_{CH} = 125.4 Hz, C_5*Me*$_5$). Anal. Calcd for $C_{48}H_{50}Ru_2$: C, 69.56; H, 6.04. Found: C, 69.23; H, 6.34. In the field-desorption mass spectrum of **3**, intensities of the obtained isotopic peaks for $C_{48}H_{50}Ru_2$ agreed with the calculated values within the experimental error.

Acknowledgment. Support from the Ministry of Education, Science, and Culture of the Japanese Government (Grant No. 02650600) is gratefully acknowledged.

Registry No. 1, 116887-45-7; 2, 138062-27-8; 3, 138062-28-9; PhC≡CPh, 501-65-5; *trans*-stilbene, 103-30-0; bibenzyl, 103-29-7.

Supplementary Material Available: Tables of thermal parameters and selected distances and angles (8 pages); a table of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

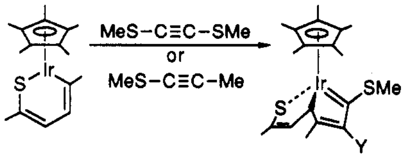
Acetylene Insertion Reactions of the C,S and η^4 Isomers of Cp*Ir(2,5-dimethylthiophene) with MeSC≡CSMe and MeSC≡CMe. Formation of Novel Chelated Bicyclocarbene Complexes

Jiabi Chen and Robert J. Angelici*

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

Received August 26, 1991

Summary: The reactions of Cp*Ir(*C*,*S*-2,5-Me_2T) (**2**) with the acetylenes MeSC≡CSMe and MeSC≡CMe give the bicyclocarbene insertion products **3** and **4**. The same



2 **3** (Y = SMe), **4** (Y = Me)

products are obtained from the reactions of these acetylenes with Cp*Ir(η^4-2,5-Me_2T) (**1**). The carbene–diene structure of **3** was established by an X-ray crystallographic study.

As part of our interest in the mechanism of thiophene hydrodesulfurization on heterogeneous catalysts,[2,3] we have examined various modes of thiophene coordination and reactivity in model transition-metal complexes. In one of these studies, we observed[4,5] that Cp*Ir(η^5-2,5-Me_2T)$^{2+}$, where Cp* = η^5-C_5Me_5 and 2,5-Me_2T = 2,5-dimethylthiophene, undergoes a 2-electron reduction to the neutral complex Cp*Ir(2,5-Me_2T) which has been isolated in two isomeric forms (eq 1); isomer **1**, Cp*Ir(η^4-2,5-Me_2T), rearranges in the presence of bases to the more thermodynamically stable **2**, Cp*Ir(*C*,*S*-2,5-Me_2T). The sulfur in

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

[3] Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2544.

[4] Chen, J.; Angelici, R. J. *Organometallics* **1989**, *8*, 2277.

[5] (a) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199. (b) Chen, J.; Angelici, R. J. *Organometallics* **1990**, *9*, 849.

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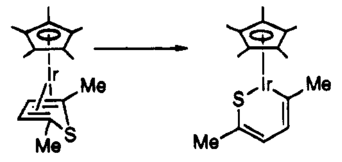

1 2 (1)

1 is an unusually strong Lewis basic donor, as demonstrated by its formation of adducts with the following Lewis acids: BH_3,[4,5] CH_3^+,[5b] $Fe(CO)_4$,[3] $Fe_2(CO)_7$,[3] and $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$.[6] Surprisingly these same adducts are also formed in reactions of 2 with most of these Lewis acids. An analogous Rh complex $Cp^*Rh(\eta^4\text{-}C_4Me_4S{\cdot}Fe(CO)_4)$ has also been reported.[7]

Structural and NMR data for isomer 2 suggest that the π system of the six-membered ring is delocalized. However, in the resonance form shown in eq 1, the Ir is a 16-electron center, and 2 often reacts as if it sought to achieve an 18-electron configuration. Thus, it undergoes an oxidative-addition reaction[8] with H_2 to form the dihydride complex $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)(H)_2$. It also reacts with the 2-electron donor ligands (L) CO, PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, and $P(OPh)_3$ to give the 18-electron complexes $Cp^*Ir(C,S,\text{-}2,5\text{-}Me_2T)(L)$.[8] Analogous Rh adducts $Cp^*Rh(C,S\text{-thiophene})(L)$ have been prepared by another route.[9] The ability of 2 to form the $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)(L)$ complexes suggests that it may also react with acetylenes and olefins to form adducts which may then react with the ring-opened $C,S\text{-}2,5\text{-}Me_2T$ ligand to give new types of organosulfur complexes. In this paper are reported the results of studies of acetylenes and olefins with both 2 and 1.

Experimental Section

All operations were carried out under an N_2 atmosphere using Schlenk techniques. Reagent grade solvents were dried by refluxing over appropriate drying agents and were stored over 4-Å molecular sieves under an N_2 atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over sodium benzophenone ketyl, while hexane and CH_2Cl_2 were distilled from CaH_2. The neutral Al_2O_3 (Brockman, activity I) used for chromatography was deoxygenated under high vacuum at room temperature for 16 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2. $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (1) and $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (2) were prepared as previously reported.[5a] 2,5-Dithiahex-3-yne, $CH_3SC{\equiv}CSCH_3$,[10] and 2-thiapent-3-yne, $CH_3SC{\equiv}CCH_3$,[11] were prepared by literature methods. Elemental analyses were performed by Galbraith Laboratory, Inc. The ^1H NMR spectra were recorded on a Nicolet NT-300 spectrometer using deuteriated solvents as internal locks. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrophotometer. The melting points were determined in sealed, nitrogen-filled capillaries and are not corrected.

Reaction of $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (1) with $MeSC{\equiv}CSMe$ To Give $Cp^*Ir[{=}C(SMe)C(SMe){=}C(Me)CHCH{=}C(Me)S]$ (3). To a solution of 0.040 g (0.091 mmol) of 1 dissolved in 30 mL of hexanes at room temperature was added 0.025 g (0.21 mmol) of $MeSC{\equiv}CSMe$. The reaction solution was stirred at room temperature, the light yellow solution gradually turning green. After being stirred for 30 h, the solvent was removed under vacuum, and the residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. The red band which eluted first was collected; then the green band was eluted with hexanes/Et_2O (15:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes and hexanes/CH_2Cl_2, respectively, at −80 °C. From the first fraction, 0.010 g (25%, based on 1) of dark-red crystals of 2 were obtained (mp 146–147 °C dec). ^1H NMR ($CDCl_3$): δ 7.47 (d, 1 H), 7.34 (d, 1 H), 3.10 (s, 3 H), 2.78 (s, 3 H), 1.93 (s, 15 H). From the second fraction was separated 0.007 g (14%, based on 1) of green crystals of 3 (mp 142–144 °C dec). ^1H NMR ($CDCl_3$): δ 5.02 (d, 1 H), 3.85 (d, 1 H), 2.72 (s, 3 H), 2.10 (s, 3 H), 1.90 (s, 3 H), 1.89 (s, 3 H), 1.70 (s, 15 H). MS: m/e 558 (M^+). Anal. Calcd for $C_{20}H_{29}S_3Ir$: C, 43.06; H, 5.24. Found: C, 43.03; H, 5.37.

Reaction of $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (2) with $MeSC{\equiv}CSMe$ To Give 3. To a solution of 2 (0.040 g, 0.091 mmol) in 30 mL of hexanes was added $MeSC{\equiv}CSMe$ (0.025 g, 0.211 mmol) at 0 °C. The reaction solution was stirred at 0–15 °C during which time the red solution gradually turned green. After stirring for 6 h, the resulting mixture was evaporated to dryness under vacuum, and the residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. After small amounts of unreacted 2 eluted from the column, the green band was eluted with hexanes/Et_2O (15:1) and collected. The solvent was removed from this eluate under vacuum, and the crude product was recrystallized from hexanes/CH_2Cl_2 solution at −80 °C to give 0.010 g (19%, based on 2) of 3 as green crystals (mp 142–143 °C dec). ^1H NMR ($CDCl_3$): δ 5.03 (d, 1 H), 3.85 (d, 1 H), 2.72 (s, 3 H), 2.10 (s, 3 H), 1.90 (s, 3 H), 1.89 (s, 3 H), 1.70 (s, 15 H).

Reaction of 1 with $MeSC{\equiv}CMe$ To Give $Cp^*Ir[{=}C(SMe)C(Me){=}C(Me)CHCH{=}C(Me)S]$ (4). To a solution of 0.055 g (0.12 mmol) of 1 dissolved in 20 mL of THF at room temperature was added $MeSC{\equiv}CMe$ (0.060 g, 0.70 mmol). The reaction solution was stirred at room temperature for 60 h during which time the light yellow solution gradually turned green. After the solution was evaporated in vacuo, subsequent treatment of the resulting residue in the same manner as described above for the reaction of 1 with $MeSC{\equiv}CSMe$ gave 0.012 g (18%, based on 1) of dark red crystalline 2 (mp 147–148 °C dec) and 0.005 g (8%, based on 1) of green crystals of 4 (mp 136–138 °C dec). ^1H NMR ($CDCl_3$): 2 δ 7.47 (d, 1 H), 7.34 (d, 1 H), 3.10 (s, 3 H), 2.78 (s, 3 H), 1.93 (s, 15 H); 4 δ 5.28 (d, 1 H), 3.54 (d, 1 H), 2.28 (s, 3 H), 2.02 (s, 3 H), 1.93 (s, 3 H), 1.91 (s, 3 H), 1.86 (s, 15 H). MS: m/e 526 (M^+). Anal. Calcd for $C_{20}H_{29}S_2Ir$: C, 45.69; H, 5.56. Found: C, 45.58; H, 5.39.

Reaction of 2 with $MeSC{\equiv}CMe$ To Give 4. In 30 mL of hexanes at room temperature was dissolved 0.050 g (0.11 mmol) of 2. To this solution was added 0.050 g (0.58 mmol) of $MeSC{\equiv}CMe$. The reaction solution was stirred at room temperature for 24 h; during that time the red solution gradually turned green. Further treatment of the resulting mixture as described above for the reaction of 2 with $MeSC{\equiv}CSMe$ gave 0.007 g (11%, based on 2) of 4 as green crystals (mp 137–138 °C dec). ^1H NMR ($CDCl_3$): δ 5.28 (d, 1 H), 3.54 (d, 1 H), 2.28 (s, 3 H), 2.02 (s, 3 H), 1.93 (s, 3 H), 1.91 (s, 3 H), 1.86 (s, 15 H). MS: m/e 526 (M^+).

X-ray Crystal Structure Determination of 3. Crystals of complex 3 suitable for X-ray diffraction were obtained by recrystallization from hexane/CH_2Cl_2 solution at −80 °C. A single crystal of approximate dimensions 0.025 × 0.06 × 0.04 mm was mounted on the end of a glass fiber and moved to the Enraf-Nonius CAD4 diffractometer. The intensity data of 2818 independent reflections, of which 1444 having $F_o^2 > 3\sigma(F_o^2)$ were observable, were collected at −70 °C using Mo Kα radiation with the θ–2θ scan method within the range $4° < 2\theta < 45°$. Complex 3 crystallized in the monoclinic crystal system; its cell constants were determined from a list of reflections found by an automated search routine. An empirical absorption correction was made, on the basis of a series of ψ scans.

The position of the Ir atom was determined from a Patterson map. The remaining non-hydrogen atoms were located in subsequent series of difference maps and least-squares refinement cycles. Following isotropic refinement of all of the non-hydrogen atoms, a numerical absorption correction was applied to the

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(6) Chen, J.; Angelici, R. J. *Organometallics* **1990**, *9*, 879.

(7) Luo, S.; Ogilvy, A. E.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1991**, *10*, 1002.

(8) Chen, J.; Daniels, L. M.; Angelici, R. *J. Polyhedron* **1990**, *9*, 1883.

(9) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559.

(10) Brandsma, L. *Preparative Acetylene Chemistry*; Elsevier Scientific Publishing Co.: New York, 1971; p 92.

(11) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier Scientific Publishing Co.: New York, 1981; p 106.

Table I. Crystal Data and Experimental Details for the Structure of Cp*Ir[=C(SMe)C(SMe)=C(Me)CHCH=C(Me)S] (3)

formula	$IrS_3C_{20}H_{29}$
fw	557.85
space group	$P2_1/c$ (No. 14)
a, Å	8.853 (2)
b, Å	24.642 (3)
c, Å	10.396 (2)
β, deg	114.29 (1)
V, Å^3	2067.2 (6)
Z	4
d_{calc}, g/cm^3	1.792
cryst size, mm	0.25 × 0.06 × 0.04
μ(Mo Kα), cm^{-1}	67.26
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
no. of orientation reflns, range (2θ), deg	24, $15 < 2\theta < 33$
temp, °C	−70
scan method	θ–2θ
data col range (2θ), deg	4–45
total no. of unique data	2818
no. with $F_o^2 > 3\sigma(F_o^2)$	1444
no. of params refined	152
trans. factors, max, min (ψ scans)	1.0, 0.825
corrn factors, max, min (numerical)	1.41, 0.788
R^a	0.0481
$R_w{}^b$	0.0557
quality-of-fit indicator^c	1.26
largest shift/esd, final cycle	0.02
largest peak, e/Å^3	1.25

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

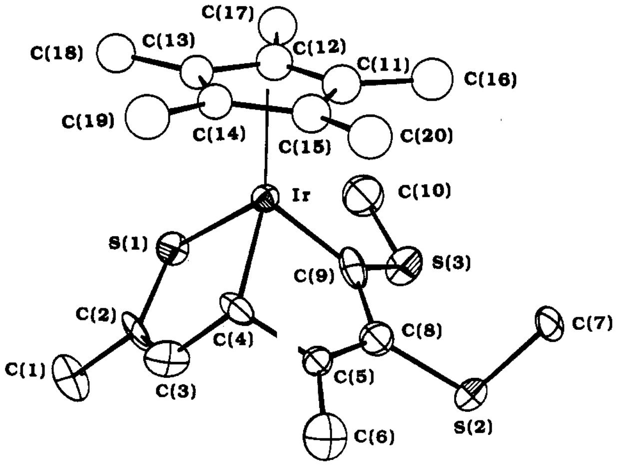

Figure 1. ORTEP drawing of **3**, with ellipsoids drawn at the 50% probability level.

unaveraged data set and the data were reaveraged.[12] The agreement factor for the averaging of the corrected data set was 9.0%, based on F_o. In the final cycles of refinement, the Ir and S atoms were allowed to refine anisotropically, as were 7 of the 10 carbon atoms in the chelating ligand. Three of the carbon atoms were not well behaved during anisotropic refinement and so were left with isotropic thermal parameters. The 10 carbon atoms of the Cp* group were refined with isotropic temperature factors only. The refinement included 152 variable parameters and converged with unweighted and weighted agreement factors[13] of $R = 0.0481$ and $R_w = 0.0557$.

Table II. Positional Parameters and Their Estimated Standard Deviations for 3

atom	x	y	z	B, Å^{2a}
Ir	0.20403 (8)	0.11247 (2)	0.29356 (6)	1.60 (1)
S(1)	0.4521 (5)	0.1353 (2)	0.4820 (4)	2.28 (9)
S(2)	−0.1637 (6)	0.2476 (2)	0.2647 (4)	2.6 (1)
S(3)	0.1454 (6)	0.2414 (2)	0.1942 (5)	2.9 (1)
C(1)	0.524 (2)	0.1390 (7)	0.771 (2)	3.4 (5)
C(2)	0.388 (3)	0.1296 (6)	0.619 (1)	2.7 (4)
C(3)	0.227 (2)	0.1194 (7)	0.596 (2)	2.7 (4)
C(4)	0.098 (2)	0.1103 (7)	0.448 (1)	2.9 (4)
C(5)	−0.031 (2)	0.1525 (6)	0.410 (1)	1.6 (3)*
C(6)	−0.148 (3)	0.1502 (7)	0.475 (2)	3.8 (5)
C(7)	−0.301 (2)	0.2257 (7)	0.091 (1)	2.2 (4)
C(8)	−0.026 (2)	0.1912 (6)	0.317 (2)	2.3 (3)*
C(9)	0.106 (2)	0.1847 (6)	0.265 (2)	2.7 (4)
C(10)	0.320 (3)	0.2271 (8)	0.157 (2)	4.5 (4)*
C(11)	0.104 (2)	0.0877 (7)	0.066 (2)	3.1 (3)*
C(12)	0.276 (2)	0.0762 (7)	0.119 (2)	2.9 (3)*
C(13)	0.312 (2)	0.0352 (6)	0.232 (1)	2.3 (3)*
C(14)	0.162 (2)	0.0229 (6)	0.244 (2)	2.2 (3)*
C(15)	0.027 (2)	0.0569 (7)	0.144 (2)	2.7 (3)*
C(16)	0.008 (3)	0.1260 (7)	−0.056 (2)	3.7 (4)*
C(17)	0.397 (3)	0.0932 (8)	0.063 (2)	3.5 (4)*
C(18)	0.480 (3)	0.0114 (7)	0.312 (2)	3.2 (3)*
C(19)	0.137 (3)	−0.0196 (7)	0.337 (2)	3.3 (4)*
C(20)	−0.155 (2)	0.0527 (7)	0.109 (2)	3.2 (3)*

^{a}Starred values refer to atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

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

Bond Distances^a			
Ir–S(1)	2.332 (4)	Ir–C(11)	2.24 (1)
Ir–C(4)	2.17 (2)	Ir–C(12)	2.33 (3)
Ir–C(9)	1.95 (2)	Ir–C(13)	2.34 (5)
S(1)–C(2)	1.74 (2)	Ir–C(14)	2.261 (6)
S(2)–C(7)	1.80 (1)	Ir–C(15)	2.18 (2)
S(2)–C(8)	1.78 (2)	C(11)–C(12)	1.42 (2)
S(3)–C(9)	1.68 (2)	C(11)–C(15)	1.46 (4)
S(3)–C(10)	1.78 (2)	C(11)–C(16)	1.53 (5)
C(1)–C(2)	1.56 (2)	C(12)–C(13)	1.48 (6)
C(2)–C(3)	1.36 (3)	C(12)–C(17)	1.48 (4)
C(3)–C(4)	1.51 (2)	C(13)–C(14)	1.41 (4)
C(4)–C(5)	1.47 (2)	C(13)–C(18)	1.49 (3)
C(5)–C(6)	1.45 (3)	C(14)–C(15)	1.48 (3)
C(5)–C(8)	1.37 (2)	C(14)–C(19)	1.51 (5)
C(8)–C(9)	1.49 (3)	C(15)–C(20)	1.51 (4)

Selected Bond Angles^a			
S(1)–Ir–C(4)	85.9 (5)	C(4)–C(5)–C(8)	116 (2)
S(1)–Ir–C(9)	96.5 (5)	C(6)–C(5)–C(8)	126 (1)
C(4)–Ir–C(9)	80.5 (7)	S(2)–C(8)–C(5)	123 (1)
Ir–S(1)–C(2)	99.1 (7)	S(2)–C(8)–C(9)	121 (1)
C(7)–S(2)–C(8)	99.7 (8)	C(5)–C(8)–C(9)	116 (1)
C(9)–S(3)–C(10)	107 (1)	Ir–C(9)–S(3)	132 (1)
S(1)–C(2)–C(1)	116 (1)	Ir–C(9)–C(8)	114 (1)
S(1)–C(2)–C(3)	122 (2)	S(3)–C(9)–C(8)	114 (1)
C(1)–C(2)–C(3)	121 (2)	C(12)–C(11)–C(15)	110 (2)
C(2)–C(3)–C(4)	121 (2)	C(11)–C(12)–C(13)	107 (2)
Ir–C(4)–C(3)	112 (1)	C(12)–C(13)–C(14)	108 (2)
Ir–C(4)–C(5)	108 (1)	C(13)–C(14)–C(15)	110 (3)
C(3)–C(4)–C(5)	111 (1)	C(11)–C(15)–C(14)	105 (3)
C(4)–C(5)–C(6)	118 (1)		

^{a}Numbers in parentheses are estimated standard deviations in the least significant digits.

All relevant crystallographic information for **3** appears in Table I. Final positional and thermal parameters are given in Table II; bond distances and selected angles are listed in Table III. The ORTEP drawing of **3** is given in Figure 1.

Results and Discussion

Reactions of Cp*Ir(C,S-2,5-Me$_2$T) (2) and Cp*Ir(η^4-2,5-Me$_2$T) (1) with MeSC≡CSMe and MeSC≡CMe. Preparations of Complexes 3 and 4. Complex

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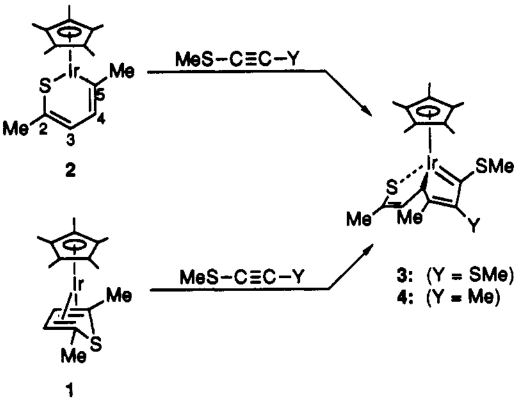
(12) Walker, D. N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

(13) Neutral-atom scattering factors and anomalous scattering corrections were taken from: *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

2 reacts with 2,5-dithiahex-3-yne, MeSC≡CSMe, in THF at 0–15 °C for 6–7 h to give the novel chelated bicyclocarbene complex (**3**) (eq 2) in 19% isolated yield. The



(2)

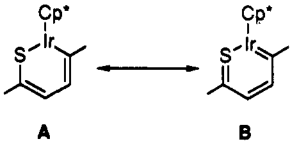
η^4-complex Cp*Ir(η^4-2,5-Me_2T) (**1**) also reacts with MeSC≡CSMe to give the same bicyclocarbene complex **3** (eq 2). However, **1** is much less reactive than **2**, requiring a higher reaction temperature (25 °C) and longer reaction time (30 h), and the yield (14%) is somewhat lower.

While elemental analyses and ^{1}H NMR and mass spectra of **3** are consistent with the structure shown in eq 2, it is the X-ray diffraction study that establishes the unexpected geometry (Figure 1). Although the mechanism is considered in greater detail below, **3** appears to result from the MeSC≡CSMe acetylene insertion into the Ir—C(5) bond of **2**. Complex **3** has an approximately octahedral structure with the Cp* on one face while the other three donor atom positions are distorted (80.5 (7), 85.9 (5), and 96.5 (5)°) from being at mutually 90° angles by the two five-membered rings. The assignment of C(9) as having carbene character is supported by its planarity, as indicated by the 360° sum of the angles around C(9). Also the Ir—C(9) distance (1.95 Å) is shorter than the Ir—C(sp^2) single-bond distance (2.054 (4) Å) in Cp*(PMe_3)(H)Ir(–CH=CH_2)[14] but is still not as short as the Ir=C carbene distance (1.869 (9) Å) in Ir(=CH_2)[N($SiMe_2CH_2PPh_2$)$_2$].[15] The lengthening of Ir—C(9) from a simple Ir=C carbene bond is undoubtedly due to stabilization of the carbene carbon by donation of π electron density from S(3). A similar Fe=C lengthening has been reported for several thiocarbene complexes, such as Cp$(CO)_2$Fe=C$(SMe)_2^+$.[16] Evidence for C(9)—S(3) π-bonding is seen in this bond distance (1.68 (2) Å), which is significantly shorter than C(sp^2)—S single bonds (1.76 Å)[17] and C(8)—S(2) (1.78 (2) Å). The two localized C=C double bonds (1.36 (3) and 1.37 (2) Å) at C(2)=C(3) and C(5)=C(8) have typical C=C distances. The S(1), C(1)—C(4) atoms of one ring lie in a plane (±0.01 Å), but the Ir is out of this plane (0.15 Å) toward the Cp*. The Ir lies 0.53 Å out of the plane defined by C(4), C(5), C(6), C(8), C(9), and S(2) (±0.03 Å).

Like 2,5-dithiahex-3-yne, 2-thiapent-3-yne, MeSC≡CMe, reacts with **2** to afford the corresponding bicyclocarbene complex **4** (eq 2). However, this reaction requires 24 h at room temperature as compared with 6 h at 0–15 °C for MeSC≡CSMe. Complex **1** also reacts with MeSC≡CMe to give the same product **4**. However, a longer reaction time (60 h) is required, and the yield is lower (8%). There are two possible structures for **4**: (1) one (eq 2) in which the SMe of the MeSC≡CMe reactant is attached to the carbene carbon and (2) that in which the Me group is attached to the carbene carbon. The ^{1}H NMR spectrum of **4** shows that only one isomer is formed, but it does not allow an unequivocal assignment to either isomer. On the basis of the carbene-stabilizing ability of the SMe group, it seems likely that **4** exists in the form shown in eq 2.

The diamagnetic complexes **3** and **4** are soluble in polar organic solvents such as THF, CH_2Cl_2, and acetone and slightly soluble in nonpolar solvents such as hexane. In the solid state they decompose upon exposure to air at room temperature within several hours, and in solution they are rapidly air-oxidized.

In considering the mechanism for the reaction of **2** with MeSC≡CSMe and MeSC≡CMe, it is important to realize that **2** has a delocalized π-system,[5a] which has been represented by the two resonance forms A and B (eq 3).



(3)

Form A contains a 16-electron Ir center which could π-coordinate the acetylene. Insertion of the acetylene into the Ir—C bond to form an eight-membered ring, followed by rearrangement could lead to **3** and **4**. Alternatively, the Ir=C carbene bond of form B could combine with the acetylene to give an iridacyclobutene which would rearrange to the product. Since other acetylenes do not react similarly (vide infra), the SMe groups are important; they probably promote this reaction by forming the MeS-stabilized carbene. It is also possible that coordination of the sulfur is involved.

For the reaction (eq 2) of **1** with MeSC≡CSMe or MeSC≡CMe, the mechanism is likely to involve initial isomerization of **1** to **2** in the presence of the thiaalkyne. The bases Et_3N[5a] and phosphines[8] are known to catalyze this isomerization. Indeed, a byproduct of the reaction of **1** with MeSC≡CSMe and MeSC≡CMe is **2**, which was isolated in 25% and 18% yields, respectively.

In contrast to MeSC≡CSMe and MeSC≡CMe, the alkynes phenylacetylene, diphenylacetylene, and 3-hexyne do not react with **2** and **1** under the conditions for eq 2. The alkenes 1-hexene, 1,3-cyclohexadiene, and 1,3-cyclooctadiene also do not react with complexes **2** and **1**. However, dimethyl acetylenedicarboxylate, MeO_2CC≡CCO_2Me, reacts with **2** (1:1 to 4:1 mol ratio) in THF at room temperature within 7–8 h to give a purple-red adduct (mp 104–105 °C dec) which was isolated by precipitation from the reaction mixture by addition of hexanes and was purified by recrystallization from THF/hexane solution at −80 °C. The powder obtained is formulated as Cp*Ir(2,5-Me_2T)·4MeO_2CC≡CCO_2Me on the basis of its ^{1}H NMR spectrum [Cp* (δ 1.96 (15 H), 2,5-Me_2T (δ 7.69 (d, 1 H), 7.52 (d, 1 H), 2.02 (s, 3 H), 1.86 (s, 3 H)), and MeO_2CC≡CCO_2Me (δ 3.87–3.49 (m, 24 (H))], mass spectrum (m/e 1008 (M^+)), and elemental analyses (Calcd for $C_{40}H_{47}O_{16}SIr$: C, 47.66; H, 4.70. Found: C, 47.87; H, 4.98). We were unable to grow crystals of this compound for an X-ray study; so the structure is not known.

Acknowledgment. We thank Dr. Lee M. Daniels for the crystal structure determination of complex **3**. The

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[14] (a) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4580. (b) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.

[15] Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708.

[16] Glavee, G. N.; Su, Y.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chim. Acta* **1989**, *157*, 73 and references therein.

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

diffractometer was funded in part by the National Science Foundation [Grant No. CHE-8520787). The loan of $IrCl_3$ from Johnson Matthey, Inc., is greatly appreciated. We thank David Miller for preparing the thiaalkynes.

Registry No. 1, 122424-96-8; 2, 132462-17-0; 3, 138180-44-6; 4, 138180-45-7; MeSC≡CSMe, 59507-56-1; MeSC≡CMe, 22174-51-2.

Supplementary Material Available: Tables of additional bond angles, displacement parameters, and least-squares planes (4 pages); a listing of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

Titanium/Magnesium Complexes: Intermediates in the Reduction of Titanocene Dichloride by Magnesium

Douglas W. Stephan

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

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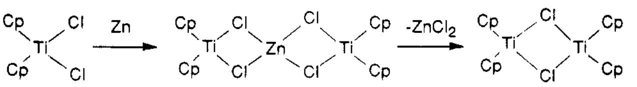
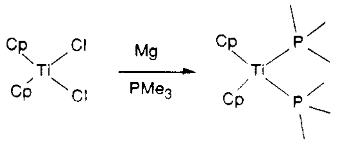
Summary: $(Cp_2Ti(\mu\text{-}Cl)_2)_2Mg(THF)_2$ (**1**) and $(Cp_2Ti(\mu\text{-}Cl)_2Mg(THF)_2(\mu\text{-}Cl)_2)_2$ (**2**) have been isolated from the reaction of Cp_2TiCl_2 with Mg in THF and in the presence of P donors. A more convenient synthesis of **1** is derived from the reaction of $(Cp_2Ti(\mu\text{-}Cl))_2$ with anhydrous $MgCl_2$. These species have been structurally characterized. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with a = 8.104 (2) Å, b = 11.371 (4) Å, c = 16.282 (9) Å, β = 91.53 (3)°, Z = 2, and V = 1500 (1) Å^3, while compound **2** crystallizes in the tetragonal space group $I4_1/a$ with a = 24.018 (6) Å, c = 14.927 (7) Å, Z = 8, and V = 8611 (5) Å^3. These species react with PMe_3 to yield the Ti(III) species $Cp_2Ti(PMe_3)Cl$ (**3**) and $MgCl_2$. The species **3** reacts further with Mg in the presence of PMe_3 to give the "stabilized titanocene" $Cp_2Ti(PMe_3)_2$. These observations support the notion that Ti(III)/Mg compounds such as **1** and **2** are intermediates in the reduction of Cp_2TiCl_2 to Ti(II).

The reduction of Cp_2TiCl_2 to $[Cp_2Ti(\mu\text{-}Cl)]_2$ can be effected by a number of metallic reagents, including Zn, Na, Al, Na/Hg, Li/Hg, and K.[1] In addition, organolithium, organoaluminum, and Grignard reagents and metal hydrides such as MgH_2, $NaBH_4$, and $LiAlH_4$ have been employed to obtain Ti(III) species.[1] Electrochemical[2] and photochemical[3] procedures have also been studied. In some cases, intermediate adducts are observed. For example, Zn reduction affords the well-characterized intermediate $(Cp_2Ti(\mu\text{-}Cl)_2)_2$ Zn, which degrades to $[Cp_2Ti(\mu\text{-}Cl)]_2$ and $ZnCl_2$ in a donor solvent (eq 1).[4,5] Alternatively, borohydride reductions afford complexes of the form $Cp_2Ti((\mu\text{-}H)_2BH_2)$.[6] Reduction of Cp_2TiCl_2 to the Ti(II) species $Cp_2Ti(CO)_2$ was first achieved with Mg in the presence of CO.[7] Similarly, Rausch and co-workers[8] have developed a convenient, high-yield route to stabilize "titanocene" employing Mg reduction of Cp_2TiCl_2 in the presence of phosphine ligands, which affords complexes such as $Cp_2Ti(PMe_3)_2$ (eq 2). This work has prompted numerous studies in which titanocene is employed to effect organic transformations.[9-14] Such applications have been recently reviewed.[1]



(1)



(2)

Despite the convenience of employing Cp_2TiCl_2/Mg as a source of titanocene species, little is known about intermediates in the reduction process. In this paper, we describe two Ti/Mg complexes obtained from reactions of Cp_2TiCl_2 with Mg. These species react with PMe_3 to yield the Ti(III) species $Cp_2Ti(PMe_3)Cl$ and $MgCl_2$, suggesting that these Ti/Mg compounds are intermediates in the Mg reduction of Cp_2TiCl_2 and that further reduction of such Ti(III) species in the presence of PMe_3 affords the "stabilized titanocene" $Cp_2Ti(PMe_3)_2$.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing a Vacuum Atmospheres inter-atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N_2 and degassed by the freeze–thaw method at least three times prior to use. EPR spectra were recorded using a Varian E-12 EPR spectrometer employing DPPH as the external reference. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Laboratories, Woodside, NY. Cp_2TiCl_2, Mg, P_4, and $MgCl_2$ were purchased from the Aldrich Chemical Co., while $PhPH_2$ and $CyPH_2$ were purchased from Pressure Chemical. $(Cp_2Ti(\mu\text{-}Cl))_2$ was prepared by the literature method.[15]

Synthesis of $(Cp_2Ti(\mu\text{-}Cl)_2)_2Mg(THF)_2$ (1). (i) Cp_2TiCl_2 (100 mg, 0.403 mmol) was dissolved in 5 mL of THF. Fivefold molar excesses of fine Mg turnings and P_4 were added. The mixture stood for 18 h and was filtered, and hexane (1–2 mL) was added. Small green crystals of 1 formed on standing for 24–48 h; yield 5%.

(ii) $(Cp_2Ti(\mu\text{-}Cl))_2$ (100 mg, 0.235 mmol) and $MgCl_2$ (22.3 mg, 0.235 mmol) were suspended in 5 mL of toluene, and 1 mL of THF

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(1) This subject has been recently reviewed and is well referenced in: Dang, Y.; Geise, H. J. *J. Organomet. Chem.* **1991**, *405*, 1.

(2) Samuel, E.; Vedel, J. *Organometallics* **1989**, *8*, 237.

(3) Bhide, V. V.; Farona, M. F.; Djebli, A.; Youngs, W. J. *Organometallics* **1990**, *9*, 1766.

(4) Jungst, R.; Sekutowski, D.; Stucky, G. *J. Am. Chem. Soc.* **1974**, *96*, 8108.

(5) Vonk, C. G. *J. Cryst. Mol. Struct.* **1973**, *3*, 201.

(6) Noth, H.; Hartwimmer, R. *Chem. Ber.* **1960**, *93*, 2246.

(7) This chemistry has been reviewed in: Sikora, D. J.; Macomber, D. W.; Rausch, M. D. *Adv. Organomet. Chem.* **1986**, *25*, 317.

(8) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 394.

(9) Scott, F.; Raubenheimer, H. G.; Pretorius, G.; Hamese, A. M. *J. Organomet. Chem.* **1990**, *384*, C17.

(10) Schobert, R. *Angew Chem., Int. Ed. Engl.* **1988**, *27*, 855.

(11) Rao, S. A.; Periasamy, M. *J. Organomet. Chem.* **1988**, *352*, 125.

(12) Rao, S. A.; Periasamy, M. *J. Organomet. Chem.* **1988**, *342*, 15.

(13) Nelsen, T. R.; Tufariello, J. J. *J. Org. Chem.* **1975**, *40*, 3159.

(14) Shur, V. B.; Berkovich, E. G.; Volpin, M. E. *J. Organomet. Chem.* **1982**, *228*, C36.

(15) Manzer, L. E. *J. Organomet. Chem.* **1976**, *110*, 291.

0276-7333/92/2311-0996$03.00/0