thenacycle **3** and dihydrogen (path a). Another possible route to **3** (path b) would involve a reductive coupling of the two vinyl ligands to yield the diruthenium-1,3-butadiene complex B. Rotation of the coordinated butadiene and activation of C–H bonds at the terminal carbons of the butadiene followed by reductive elimination would give the ruthenacycle **3**.

While an example of the reductive elimination of 1,3-butadiene from a monomeric ruthenium divinyl complex has been reported,[9] path b could be excluded on the basis of the result of a control experiment. Thermolysis of **2** in benzene even in the presence of a 10-fold excess of isoprene exclusively afforded **3**, and the formation of a 2-methylated ruthenacyclopentadiene was not observed. Furthermore, an intermediary hydride species observed at δ −9.32 as a singlet by monitoring the reaction by means of ^{1}H NMR spectroscopy suggests the validity of path a.[10]

Further reactivity studies of **3** and mechanistic studies pertaining to the formation of **3** will be reported in due course.

Acknowledgment. Support from Ministry of Education, Science and Culture of the Japanese government (No. 63550618) is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates, interatomic distances and angles, and thermal parameters (18 pages); a listing of calculated and observed structure factors (29 pages). Ordering information is given on any current masthead page.

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[9] (a) Czisch, P.; Erker, G.; Korth, H.-G.; Sustmann, R. *Organometallics* **1984**, *3*, 945. (b) Chang, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4298.

[10] The reaction was carried out in C_6D_6 (c = 0.33 M) at 65 °C and was monitored by means of ^{1}H NMR spectroscopy. After the mixture was heated for 30 min, resonance signals due to the intermediary hydride species were observed at δ −9.32 (s, Ru-*H*) and 2.06 (s, C_5Me_5) in the intensity ratio of 2:15 together with signals for **2** and **3**. One of the resonances for C_5Me_5 ligands of intermediate might overlap that of **2**. The molar ratio of the intermediate, **2**, and the ruthenacycle **3** was 3:40:1. The ratio changed to 1.5:8:1 after heating for 2 h.

Synthesis and Characterization of $[HgAu(CH_2SPPh_2CH_2)_2]PF_6$, the First Example of Structurally Characterized Carbene Double Insertions into Metal–Sulfur Bonds

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Summary: The reaction of CH_2N_2 with the heterobimetallic complex $HgAu(SPPh_2CH_2)_2PF_6$, **1**, in THF/diethyl ether at 0 °C yields a novel complex, $HgAu(CH_2SPPh_2CH_2)_2PF_6$, **2**, in 40% yield. **2** is the result of methylene group double insertions into the Au–S bonds in **1**. The structure of **2** was determined by single-crystal X-ray diffraction. **2** crystallizes in the monoclinic space group $P2_1/c$ with a = 11.218 (4) Å, b = 24.59 (2) Å, c = 12.598 (7) Å, and β = 109.42 (4)°. **2** is the first example of CH_2 insertion into metal–sulfur bonds.

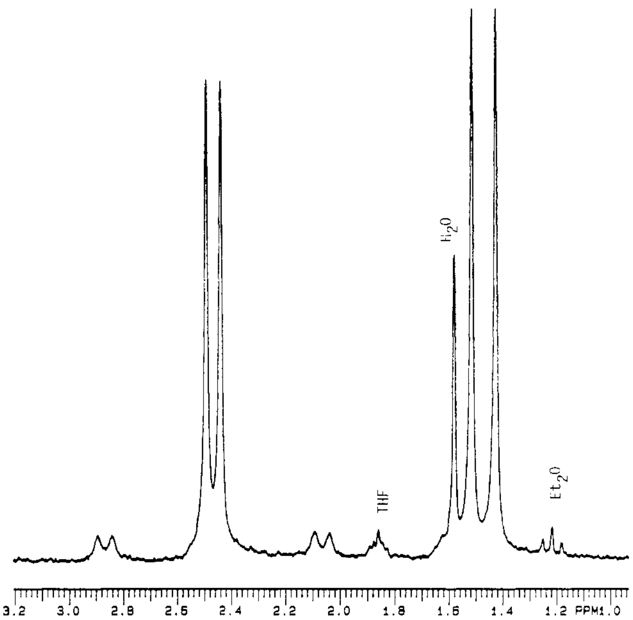

Figure 1. ^{1}H NMR spectrum of **2** in $CDCl_3$.

Studies of the syntheses, characterization, and reactivity of carbene ligands and their metal complexes are among the most attractive and active areas of investigation in organometallic chemistry in the last two decades.[1] The important application of metal carbene complexes in organic syntheses has given rise to many studies of the reactions of carbene complexes with organic substrates. Nucleophilic and electrophilic substitution reactions on the carbene ligands have been the well-studied topics of numerous papers.[1] In contrast, carbene insertion reactions into metal–ligand bonds, reactions which play a critical role in organic syntheses, have been recognized and investigated only relatively recently.[2] Although there are numerous examples of carbene insertions into metal–carbon bonds,[2,3] very little is known about carbene insertions into M–X bonds where X is a main group element such as O, S, P, or halide.[4] Our interest in studying the interactions of the methylene group with bimetallic complexes caused investigation of the reaction of CH_2N_2 with the heterobimetallic compound[5] $[HgAu(SPPh_2CH_2)_2]PF_6$, **1**. A novel complex with the formula of $[HgAu(CH_2SPPh_2CH_2)_2]PF_6$, **2**, resulted from the carbene double insertion into Au–S bonds in **1**. This is the first example of a structurally characterized complex produced from carbene insertions into metal–sulfur bonds. We report here the synthesis and characterization of this remarkable product.

The reaction[6,7] of CH_2N_2 with **1** in the mixed solvents THF/diethyl ether at 0 °C yielded the air-stable colorless compound **2** as a major product. **2** was isolated in crys-

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[1] (a) Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99. (b) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. (c) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (d) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

[2] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, University Science Books: Mill Valley, CA, 1987; p 119–134, 379–381.

[3] (a) Kleitzein, H.; Werner, H.; Serhadli, P.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46. (b) Jernakott, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3026. (c) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.

[4] (a) Seyferth, D. *Chem. Rev.* **1955**, *55*, 1155 and references therein. (b) McCrindle, R.; Arsenault, G. J.; Farwaha, R. *J. Organomet. Chem.* **1985**, *296*, C51. (c) Hubbard, J. L.; McVicar, W. K. *J. Am. Chem. Soc.* **1986**, *108*, 6422.

[5] Wang, S.; Fackler, J. P., Jr. *Organometallics* **1988**, *7*, 2415.

[6] CH_2N_2 was generated from the reagent 1-methyl-3-nitro-1-nitrosoguanidine (MNNG) purchased from Aldrich by using the method reported in literature.[7]

[7] Black, T. H. *Aldrichim. Acta* **1983**, *16*, 3.

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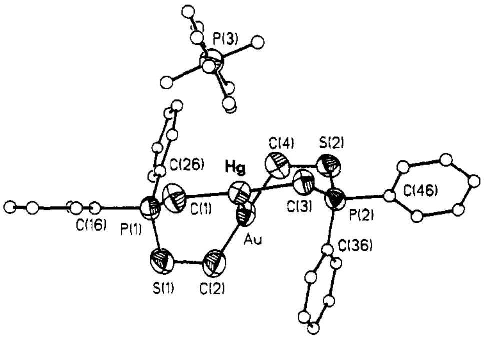
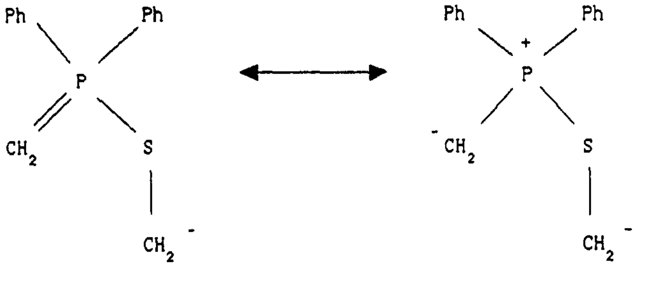


Figure 2. The molecular structure of 2 showing 50% thermal ellipsoids with labeling scheme of atoms' positions. Selected bond lengths and angles: Hg-Au = 2.934 (1), Hg-C(1) = 2.111 (16), Hg-C(3) = 2.123 (16), Au-C(2) = 2.095 (24), Au-C(4) = 2.084 (23), S(1)-P(1) = 2.025 (8), S(2)-P(2) = 2.045 (7), S(1)-C(2) = 1.887 (20), S(2)-C(4) = 1.845 (19), P(1)-C(1) = 1.800 (18), P(2)-C(3) = 1.826 (15) Å; C(2)-Au-C(4) = 175.5 (7)°, C(1)-Hg-C(3) = 164.0 (6)°, P(1)-S(1)-C(2) = 110.6 (8)°, P(2)-S(2)-C(4) = 106.1 (6)°, S(1)-P(1)-C(1) = 114.6 (7)°, S(2)-P(2)-C(3) = 113.0 (6)°, Au-C(2)-S(1) = 117.7 (11)°, Au-C(4)-S(2) = 118.6 (10)°, Hg-C(1)-P(1) = 115.8 (8)°, Hg-C(3)-P(2) = 115.4 (8)°.

talline form[8] in 40% yield. The ^1H NMR spectrum of 2 in $CDCl_3$ shows two groupings of CH_2 resonances (Figure 1). The doublet at 2.45 ppm has a coupling constant of 11 Hz that is assigned to the $^2J_{P-H}$ coupling since it is similar to those $^2J_{P-H}$ coupling constants found in [5,9a] $Hg(CH_2PPh_2S)_2$, $[HgAu(SPPh_2CH_2)_2]PF_6$, $Au_2(CH_2PPh_2CH_2)_2$, and [9b] $Au_2(SPPh_2CH_2)_2$. The mercury satellite and the J_{Hg-H} coupling constant of ($^2J_{Hg-H}$ = 155 Hz), suggesting this methylene group is bonded to the Hg atom and the P atom as well. The doublet at 1.46 ppm does not show any mercury satellite but has an unusually large J_{P-H} coupling constant of 18 Hz. It was recognized nearly 20 years ago[10] that the sulfur linkage increases the $^3J_{P-H}$ coupling constant in $R_2P-S-CH_x$, $X = 1-3$ such that $^3J_{P-H}$ is larger than $^2J_{P-H}$. Hence the methylene group with the chemical shift at 1.46 ppm appears bound to the sulfur and Au atoms. In order to confirm this a single-crystal X-ray diffraction analysis was performed on 2.

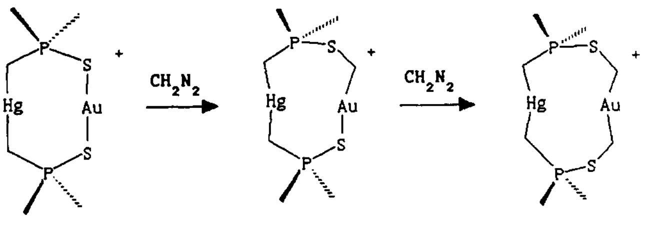
The molecular structure of 2 is shown in Figure 2. As expected, the Hg atom bonds linearly to two carbon atoms as found[5] in 1. The Au atom originally bonded to two S atoms[5] in 1 is coordinated linearly to two carbon atoms with typical Au-C bond lengths, 2.08 (2) and 2.10 (2) Å. The sulfur atoms are bonded to phosphorus and carbon atoms with normal bond distances. The Hg-Au separation of 2.934 (1) Å is much shorter than found in 1 (3.088 Å) or the sum[12] of metallic radii of Hg and Au (3.099 Å), indicating the presence of some Hg-Au interactions. The six-membered ring, PCHgAuCS, is puckered. The PF_6 anion is crystallographically disordered. Two sets of F atoms were observed on the equatorial plane. The occupancy factors were refined to 53% and 47% for each set, respectively.



A

Figure 3.

Scheme I



1 2

The CH_2 insertions into Au-S bonds resulted in the formation of the new ylide ligand A (Figure 3). Complexes with this ligand A are previously unknown.

Although the mechanism of the formation of 2 is not understood yet, one possible explanation is that the CH_2N_2 attacks the Au atom at first to form a Au-C bond. The sulfur atom then attacks the carbon center—a typical reaction for a Fischer carbene[1,2]—to form a S-C bond (Scheme I). Although Seyferth described the carbene insertion reactions into M-O bonds 30 years ago[4a] and a few examples of carbene insertions into metal-halide bonds[4b,c] are known, to our knowledge direct carbene insertion reactions into metal-sulfur bonds have not been reported previously. Herrmann and Herberhold et al. have reported that reactions of CH_2N_2 with[13a] $(\mu\text{-}S)[CpW(CO)_3]_2$ or[13b,c] $(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_5(\mu\text{-}S_2)$ yield $\mu_3\text{-}\eta^2$-thioformaldehyde complexes. However, no CH_2 insertions into metal-sulfur bonds have been established in these reactions.

The reaction of CH_2N_2 with 1 appears to be solvent-dependent. If the reaction is carried out in diethyl ether only, the reaction is slow and 2 is obtained as the only product. If the reaction is done in THF only, other new compounds are obtained along with 2 as a minor product. Characterizations of these compounds may shed light on the carbene insertion reaction into Au-S bonds in this system. These efforts are underway in our laboratory.

Acknowledgment. We thank the Welch Foundation and National Science Foundation (CHE 8708625) for financial support.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and data collection parameters (9 pages); a table of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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[8] Elemental Anal. Calcd for $C_{28}H_{28}HgAuS_2P_3F_6$ (2): C, 32.43; H, 2.72. Found: C, 32.66; H, 2.74.

[9] (a) Basil, J. D.; Murray, H. H.; Fackler, J. P., Jr.; Tocher, J.; Mazany, A. M.; Trzcinka-Bancroft, B.; Knachel, H.; Dudis, D.; Delord, T. J.; Marler, D. O. *J. Am. Chem. Soc.* **1985**, *107*, 6908. (b) Mazany, A. M.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 801.

[10] Burg, A. B.; Kang, D. K. *J. Am. Chem. Soc.* **1970**, *92*, 1901.

[11] Crystal data. $C_{28}H_{28}HgAuS_2P_3F_6$; space group $P2_1/c$; $a = 11.218$ (4) Å, $b = 24.59$ (2) Å, $c = 12.598$ (7) Å, $\beta = 109.42$ (4), $V = 3278$ (3) Å^3, $Z = 4$. Convergence to the final R values of $R = 4.56\%$ and $R_w = 5.55\%$ was achieved by using 2657 reflections ($F_o^2 \geq 3\sigma(F_o^2)$) and 239 least-square parameters. Data were collected on a Nicolet R3m/E diffractometer and processed on a Data General S140 computer using SHELXTL software (version 5.1). The structure was solved by direct methods.

[12] Sanderson, R. T. *Chemical Periodicity*; Reinhold: New York, 1962.

[13] (a) Herberhold, M.; Jellen, W.; Murray, H. H. *J. Organomet. Chem.* **1984**, *270*, 65. (b) Herrmann, W. A.; Rohrmann, J.; Schäfer, A. *J. Organomet. Chem.* **1984**, *265*, C1. (c) Herrmann, W. A.; Rohrmann, J.; Nöth, H.; Nanila, Ch. K.; Bernal, I.; Draux, M. *J. Organomet. Chem.* **1985**, *284*, 189.