10.35), $H^b$ ($\delta$ 4.72), $H^c$ ($\delta$ 2.65), and $H^d$ ($\delta$ −0.02) resonate at a gradually increasing field. Since the chemical shifts are well apart and the coupling constants relatively small (0.8–9.0 Hz), a first order ddd splitting pattern may be expected in a fully coupled four-component system, as indeed was observed [$J$(ab) = 6.2, $J$(ac) = 1.2, $J$(ad) = 0.8, $J$(bc) = 6.9 (cis), $J$(bd) = 9.0 (trans), and $J$(cd) = 2.8 Hz (geminal)]. In the spectrum of **4**, the absence of $H^b$ gives rise to a dd splitting pattern [$J$(ac) = 1.6, $J$(ad) = 0.75, and $J$(cd) = 2.5 Hz (geminal)] with the respective coupling constants being similar to those found for **3**. In the $^{13}C$ NMR (90 MHz) spectrum of **3**, the parent $\mu$-$\eta^1$,$\eta^3$-allylidene carbon nuclei resonate at $\delta$ 152.82 [$C^\alpha$; $J(\alpha{-}a)$ = 98.5 Hz], 79.12 [$C^\beta$; $J(\beta{-}b)$ = 51.5 Hz], and 39.58 [$C^\gamma$; $J(\gamma{-}c)$ = 6.6 Hz and $J(\gamma{-}d)$ = 30.1 Hz].

According to available $^1H$ and $^{13}C$ NMR spectral information[3,4] on ($\sigma$-alkyl)-, ($\eta^1$-allyl)-, and ($\eta^3$-allyl)metal complexes, neither **6** nor **7** are expected to display any extraordinarily strong deshielding effects at the $C^\alpha(H^a)$ position. On the other hand, low-field resonances are rather characteristic of coordinated carbenes.[4] In this regards, the $H^a(C^\alpha)$ shifts ($\delta$) in **3** [10.35 (152.82)] can be compared with those reported for other M–CH(R)–M-containing complexes such as $[Ru_2(\mu\text{-CHMe})(\mu\text{-CMe}_2)(\eta^5\text{-C}_5H_5)_2]$ [9.40 (135.3)][5] and a series of rhodium complexes of the type of $[Rh_2(CO)_2(\mu\text{-CHR})(\eta^5\text{-C}_5H_5)_2]$ [R = H, 5.97 (111.36); R = Me, 7.09; R = COOEt, 5.78].[6] Terminally coordinated carbenes (M=CHR) resonate [$\delta$, $^1H$ ($^{13}C$)] at a lower field as is exemplified from the spectra of $[Fe(CO)(L)(CHPh)(\eta^5\text{-C}_5H_5)]^+PF_6^-$ [L = CO, 16.86 (342.4); L = $Ph_3P$, 17.43 (341.2)],[7] $[Fe(Ph_2PCH_2CH_2PPh_2)(CH_2)(\eta^5\text{-C}_5H_5)]^+PF_6^-$ [13.89 and 17.29 (317.5)],[8] $[W(CO)_5(CHPh)]$ [17.21],[9] and $[Re(CH_2)(PPh_3)(NO)(\eta^5\text{-C}_5H_5)]^+PF_6$ [15.67].[10] Among the terminally coordinated carbene complexes of tantalum and niobium,[11] the downfield shifts are in general less extreme as compared with the above cited examples.

Preliminary studies on various substituted $\eta^3$-allyl derivatives of **2** have suggested the generality of this allyl to allylidene transformation.[11] Attempts to evaluate the mechanistic aspects of this transformation were made difficult by the heterogeneous experimental conditions utilized in these reactions.

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**Registry No. 2** (R = H), isomer 1, 77983-17-6; **2** (R = H), isomer 2, 77983-18-7; **2** (R = Me), isomer 1, 77933-78-9; **2** (R = Me), isomer 2, 78037-33-9; **3**, 82182-14-7; 4, 82182-13-6.

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# Ring Expansion of Dimetallacyclopropanes. A Straightforward Route to Sulfene Complexes[1]

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*Summary:* Insertion of sulfur dioxide into the three-membered framework of the dimetallacyclopropane-type methylene complex $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5Me_5)Rh(CO)]_2$ cleanly yields the first example of coordinated sulfene, $CH_2{=}SO_2$, in the course of a three- to four-membered ring expansion reaction.

Much effort has been dedicated toward the development of effective synthetic routes to $\mu$-methylene transition-metal complexes since the time this class of compounds was discovered.[3] The pivotal intermediacy of surface-bound methylene functionalities in the chain-growth sequence of the Fischer–Tropsch process[4] has added another stimulating aspect to the synthesis of dimetallacyclopropanes and, at the same time, has initiated many laboratories' interest in reactivity studies of suitable model compounds as well.[3] The most intruiging reactions that have so far been observed with $\mu$-methylene complexes include the proton-induced ring opening of $\overline{\mathrm{M{-}CH_2{-}M}}$ frameworks with the possibility of synthesizing halomethyl[5a] and $\mu$-methylidyne derivatives,[5a,b] the conversion of bridging methylene moieties to ketenylidene groups (methylene carbonylation),[5d–f] the migration of $\mu$-alkylidene chains along a dinuclear metal frame,[5c] and the insertion of carbon disulfide[5g] as well as the Wittig-type methylene transfer to organic substrates.[3,5h] In this paper we wish to disclose our observations on an unexpectedly facile three- to four-membered ring expansion as a synthetically useful and methodologically fundamental type of reaction in the chemistry of the $\mu$-methylene series.

The thermally and photochemically exceedingly stable ($\mu$-methylene)rhodium complex **1** cleanly reacts with dry sulfur dioxide (**2**) in the temperature range −80 to +25 °C (THF solution) with concomitant formation of a novel complex, **3** (isolated yield 93%), of composition $C_{23}H_{32}O_4Rh_2S$ (eq 1).[6] The following spectroscopic data yield

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[1] Communication 31 of the series "Transition Metal Methylene Complexes". This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Degussa Hanau. Dr. B. E. Mann (University of Sheffield/England) is acknowledged for having recorded 400-MHz NMR spectra. Communication 30: Herrmann, W. A.; Huggins, J. M.; Bauer, Ch.; Smischek, M.; Pfisterer, H.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *226*, C59.

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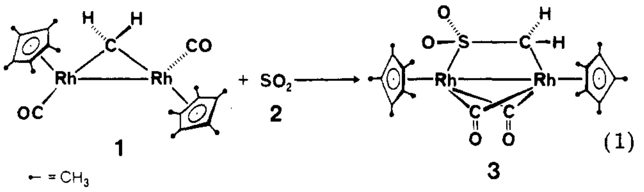

unambiguous proof that compound **3** represents a $C_s$ symmetrical $\mu$-$\eta^2$-sulfene complex that originates from electrophilic insertion of sulfur dioxide into the three-membered backbone of the precursor compound **1**.

(1) The IR spectra (KBr)[6] exhibit a very strong absorption at 1807 cm$^{-1}$. Both the position of this band and its observed long-wave shift occurring upon $^{13}$CO labeling of **3** (1776 cm$^{-1}$)[7] underline its assignment to carbon monoxide bridges, the presence of which latter groups being once more evident from a characteristic low-field triplet in the $^{13}$C NMR spectrum ($\delta$(CO) 228.0 ($^1J$(Rh–C) = 40 Hz)).[6]

(2) Convincing proof of loss of the dimetallacyclopropane geometry of compound **1** upon reaction with sulfur dioxide comes from $^1$H NMR spectroscopy: as a result of $SO_2$ insertion into one of the rhodium–methylene bonds, the methylene protons give rise to a $A_2X$ system centered at $\delta$ 2.96 (relative intensity 2 H; $CDCl_3$, 25 °C, 400 MHz), with the observed coupling constant ($^2J$(Rh–H) = 3.5 Hz) being typical of Rh–$CH_x$ functionalities ($x$ = 1–3).[5a,8] In addition, the methylene carbon resonance is no longer found within the shift range of $\mu$-methylene complexes[3b,c] but is rather close to that of metal alkyls ($\delta$($CH_2$) 68.8 (d)); again, the corresponding coupling constant ($^1J$(Rh–C) = 28 Hz) is in the order commonly observed for alkylrhodium complexes.[5a,8] The positions of two intense IR absorptions found at 1197 cm$^{-1}$ [$\nu_{as}$($SO_2$), KBr] and 1063 cm$^{-1}$ [$\nu_s$($SO_2$), KBr] are diagnostic of *S*-sulfinato derivatives that are structurally closely related to the methylenesulfene bridge of compound **3**.[9,10]

(3) The unequal chemical environment of the metal centers arising from C,S coordination of the sulfene ligand across the dimetal frame accounts for the appearance of separate, well-resolved signals for each set of the methyl protons as well as the ring carbon atoms in the $^1$H and $^{13}$C NMR spectra, respectively.[6] Based upon the well-documented structural details of triply bridged ($\eta^5$-$C_5Me_5$)Rh–Rh($\eta^5$-$C_5Me_5$) dimetal fragments, we should expect both $C_5Me_5$ ligands to be oriented perpendicular to the metal-to-metal vector and also parallel to each other.[3c,11,12]

The reactivity of the dimetallacyclopropane **1** is in marked contrast to related systems that display a metal–metal double bond in addition to a methylene bridge. Thus, the cobalt derivative ($\mu$-$CH_2$)($\mu$-CO)[($\eta^5$-$C_5Me_5$)Co]$_2$ instantaneously reacts with sulfur dioxide even at low temperatures to give the triply bridged species ($\mu$-$CH_2$)($\mu$-CO)($\mu$-$SO_2$)[($\eta^5$-$C_5Me_5$)CO]$_2$.[1] Furthermore, both electronic and structural details seem to decidedly govern $SO_2$-induced reaction pathways of dimetallacyclopropanes: for example, the $\mu$-diphenylmethylene derivative of the parent compound **1** undergoes ring opening instead of ring expansion, with the single product formed in this particular case being the diphenylcarbene complex of composition ($\mu$-$SO_2$)[($\eta^5$-$C_5Me_5$)$_2$Rh$_2$(CO){C($C_6H_5$)$_2$}].[13]

This paper demonstrates for the first time the feasibility of electrophilic $SO_2$ insertion into methylene bridges with concomitant metal-centered formation of the parent sulfene, $CH_2{=}SO_2$. This latter species—a highly reactive formal analogue of ketene[14]—has to the best of our knowledge escaped all previous attempts of stabilization through metal coordination. We are presently in the process of applying this promising straightforward synthetic method to related dimetallacyclopropanes.

**Registry No.** 1, 76545-02-3; 2, 7446-09-5; 3, 82264-78-6; Rh, 7440-16-6.

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[6] Procedure. A magnetically stirred solution of 273 mg (0.5 mmol) of **1** in 50 mL of rigorously dried tetrahydrofuran is treated at −78 °C (dry ice/acetone) with a vigorous stream of high-quality dry $SO_2$ gas for ca. 3 min (100-mL Schlenk tube). The Schlenk tube is then connected with a mercury-filled pressure relief valve, and the solution is allowed to slowly warm up to room temperature. After the color change from deep red to brownish yellow has gone to completion (30–60 min at ca. 25 °C), the solvent is stripped off in a water aspirator. The remaining brown residue is first washed with *n*-pentane and subsequently with diethyl ether. Product **3** is finally crystallized from a nearly saturated solution in acetone/diethyl ether (+25 to −35 °C) to give brownish red lustrous crystals: yield 283 mg (93%); mp 100 °C (sealed capillary). The compound is air stable both in solution and in the solid state, very soluble in benzene, methylene chloride, acetone, and tetrahydrofuran, and insoluble in *n*-pentane and diethyl ether. Anal. Calcd for $C_{23}H_{32}O_4Rh_2S$ (610.38): C, 45.26, H, 5.28 Rh, 33.71, S, 5.25. Found: C, 45.33, H, 5.58, Rh, 33.81, S, 5.29; mol wt, 610 (field desorption mass spectrometry). Spectroscopic data of **3**: IR (KBr) 1807 (vs) ($\nu$($^{12}$CO)), 1776 ($\nu$($^{13}$CO)); 1197 (vs) [$\nu_{as}$($SO_2$)], 1063 (vs) [$\nu_s$($SO_2$)]; further typical bands: 2912 (m), 2899 (m), 1003 (s), 727 (s); IR (THF) 1813 (vs) ($\nu$($^{12}$CO)), 1784 ($\nu$($^{13}$CO)); $^1$H NMR (90 MHz, $CDCl_3$, 25 °C, internal $Me_4Si$) $\delta$($CH_3$) 1.83 (d, 15 H, $^3J$(Rh–H) = 0.6 Hz), $\delta$($CH_3$) 1.80 (d, 15 H; $^3J$(Rh–H) = 0.7 Hz), $\delta$($CH_2$) 2.96 (d, 2 H, $^2J$(Rh–H) = 3.5 Hz); $^{13}$C {$^1$H} NMR (67.88 MHz, $CDCl_3$, 28 °C, internal $Me_4Si$) $\delta$(CO) 228.0 (t, $^1J$(Rh–C) = 40 Hz), $\delta$($CH_3$) 8.7 (s), $\delta$($C_5Me_5$) 105.0 (s) and 103.9 (s), $\delta$($CH_2$) 68.8 (d, $^1J$(Rh–C) = 28 Hz). The $CH_2$ signal expectedly appears as a doublet of triplets in the off-resonance decoupled $^{13}$C NMR spectrum. Systematic nomenclature: [$\mu$-$\eta^2$(*C,S*)-sulfene]bis[($\mu$-carbonyl)($\eta^5$-pentamethylcyclopentadienyl)rhodium](*Rh–Rh*).

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# Hydrosilane-Induced Reductive Coupling of Carbon Monoxide

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*Summary:* A remarkable acceleration by hydrosilanes of the transition-metal-catalyzed reduction of carbon monoxide to compounds containing methoxy and 1,2-ethanedioxy groups has been discovered.

We wish to report the remarkable acceleration by a hydrosilane of the transition-metal-catalyzed reduction of carbon monoxide to compounds containing methoxy and

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