

Figure 1. Stereochemistry of $\text{Rh}_2(\text{PF}_3)_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$.

that complexes containing unsymmetrically disubstituted acetylenes should have three nonequivalent PF_3 groups (see inset, Figure 2); two of these become equivalent when the acetylene is symmetrically disubstituted. At room temperature, the high-resolution ^{19}F nmr spectrum of all the compounds in CFCl_3 consists of a doublet with separation about 1400 Hz, due to $^1J_{\text{PF}}$ and $^3J_{\text{PF}}$. Each peak is broad and without fine structure, presumably because of the large number of coupled nuclei with $I = 1/2$. On lowering the temperature, each peak broadens and then separates into two or three peaks which sharpen on further cooling. As expected, complexes containing symmetrically disubstituted acetylenes give two peaks (ratio $\sim 2:1$), whereas those containing unsymmetrically disubstituted acetylenes give three peaks (ratio $\sim 1:1:1$) (Figure 2);¹² the changes are reversible with temperature. These observations, and the fact that the spectra are unaffected by the presence of free PF_3 ,¹³ are consistent only with intramolecular exchange of coordinated PF_3 groups; *i.e.*, the molecules are stereochemically nonrigid. This exchange is fast on the nmr time scale at room temperature and slow at low temperatures (-50 to -147°). The magnitude of the barrier to exchange depends critically on the acetylene substituents and varies from $\text{CF}_3\text{C}_2\text{CF}_3$ [ΔG^\ddagger (-56°) ~ 10 kcal/mol] to $n\text{-C}_4\text{H}_9\text{C}_2\text{H}$ [ΔG^\ddagger (-138°) ~ 6 kcal/mol] in the complexes so far studied. In contrast, even at -90° , the carbonyl ^{13}C nmr spectrum of $\text{Co}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$ is a relatively sharp singlet, suggesting that at this temperature the intramolecular exchange of CO groups is still rapid on the nmr time scale.

The stereochemical nonrigidity of these rhodium complexes can be explained by assuming a propeller-like rotation of the PF_3 ligands about the Rh-Rh bond with the acetylene remaining stationary. Alternatively, or in addition, there could be a concerted rotation of the $\text{Rh}_2(\text{PF}_3)_6$ unit with respect to the acetylene. These possibilities, and the effect of acetylene substituents on the activation barrier, will be discussed in detail in a forthcoming publication.

(12) The ratio is only approximately 1:1:1 owing to overlap of the separate resonances arising from the complex spin system. We have recently found that the ^{31}P -decoupled ^{19}F nmr spectra of $\text{Rh}_2(\text{PF}_3)_6(\text{CH}_3\text{C}_2\text{-}n\text{-C}_6\text{H}_7)$ in CHF_2Cl at -142° and of $\text{Rh}_2(\text{PF}_3)_6(p\text{-NO}_2\text{C}_6\text{H}_4\text{C}_2\text{-CO}_2\text{C}_2\text{H}_5)$ in CHF_2Cl at -103° consist of three singlets of equal intensity which coalesce to a singlet as the temperature is raised.

(13) We thank a referee for pointing out that CO exchange with the analogous $\text{Co}_2(\text{CO})_8(\text{ac})$ complexes is also very slow [G. Cetini, O. Gambino, P. L. Stanghellini, and G. A. Vaglio, *Inorg. Chem.*, **6**, 1225 (1967)].

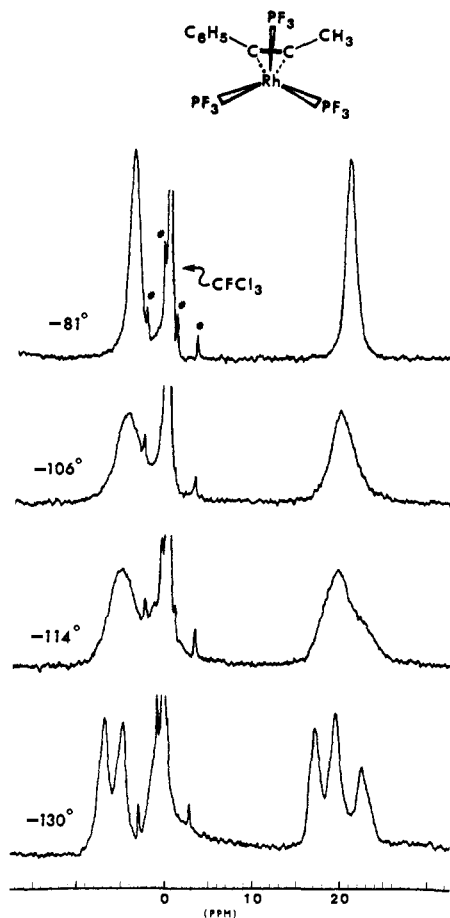


Figure 2. Variable-temperature ^{19}F nmr spectra of $\text{Rh}_2(\text{PF}_3)_6(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$ in CFCl_3 measured at 56.45 MHz. At -130° one peak is obscured by the CFCl_3 resonance. The inset is a projection of the molecule along the Rh-Rh bond not including the eclipsed Rh and PF_3 groups. (#) indicates spinning side bands of CFCl_3 and $^{13}\text{CFCl}_3$ resonances.

Acknowledgment. We thank Johnson-Matthey Co., England, for a generous loan of rhodium.

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Received May 19, 1972

9-Thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide

Sir:

The 1,4 cycloaddition of SO_2 to 1,3-dienes is a well-known reaction.¹ Cyclooctatetraene sulfone **4**, however, is not formed from **1** in liquid SO_2 even after 30 days at 20° . Paquette, *et al.*, have prepared derivatives of **4** by a bishomoconjugative Ramberg-Bäcklund rearrangement of thiapropellane dioxides.²

We found that on treatment of **1** in liquid SO_2 at -70° with 1.0 equiv of antimony pentafluoride in SO_2 , evaporation of the solvent, and work-up with dichloromethane-water, the colorless leaflets of the sulfone **4**, mp $192.5\text{--}193^\circ$ dec, were obtained in 95% yield; ir

(1) S. D. Turk and R. L. Cobb in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 13.

(2) L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *J. Amer. Chem. Soc.*, **93**, 1047 (1971).

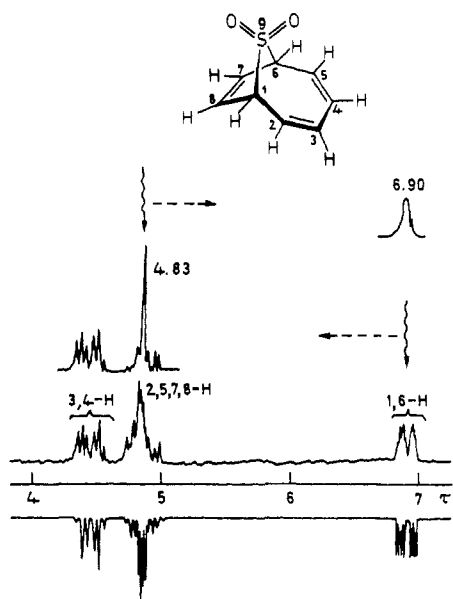
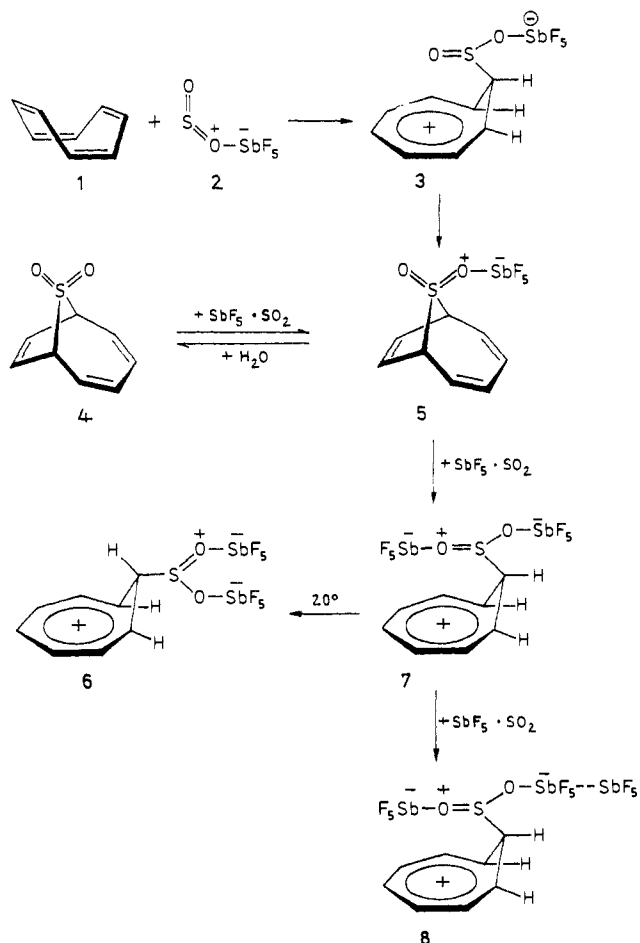


Figure 1. Proton nmr spectrum (100 MHz/sec) of the sulfone **4** in hexadeuteriobenzene with TMS as internal standard. The lower spectrum was calculated with the computer program LAMB (C. W. Haigh, *Annu. Rep. Nucl. Magn. Resonance Spectrosc.*, **4**, 311 (1971)).

sulfone absorptions at 1115 and 1300 cm^{-1} (see Scheme I).

Scheme I



Double resonance experiments on the ^1H nmr spectrum (Figure 1) confirmed structure **4** and excluded an

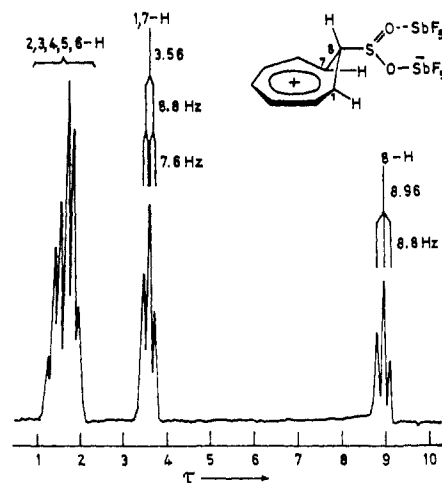


Figure 2. ^1H nmr spectrum (60 MHz/sec) of the *exo*-8-homotropylium sulfinate complex **6** in SO_2 at -40° .

episulfone as well as a cyclic sulfinate ester structure. Spin decoupling of the allylic protons at τ 6.90 left the signals of H-3 and H-4 unchanged while the total vinylic region was converted to an AA'BB' spectrum plus a singlet at τ 4.83 for H-7 and H-8. Irradiation at the frequency region of the four vinylic protons produced a singlet for H-1 and H-6 and established their equivalence. The calculated spectrum, which agrees well with the experimental one, is based on the coupling constants that were observed for the structurally analogous 9-phenyl-9-phosphabicyclo[4.2.0]nonatriene.⁸

On treatment of **4** in SO_2 with 1 equiv of SbF_5 , the signal of H-1 and H-6 was shifted from τ 5.88 to 5.14 while the τ values of the vinylic protons remained nearly unchanged. This behavior suggests the formation of the complex **5**. However, after introduction of a second equivalent of SbF_5 at -40° the ^1H nmr spectrum of the *endo*-8-substituted homotropylium species **7** (see below: τ 1.0–2.0 (m, 5), 3.63 (m, 3). Reaction of **1** with 2 equiv of SbF_5 in SO_2 at -40° likewise produced **7**.

After the SO_2 solution was allowed to stand 1 hr at room temperature, a new nmr spectrum at -40° (Figure 2) revealed that **7** had undergone quantitative inversion to the *exo*-8-homotropylium sulfinate complex **6**. The spectra of **6** and **7** corresponded to those of *endo*- and *exo*-8-chlorohomotropylium salts; the $\Delta\tau$ (*endo*-H-8 minus *exo*-H-8) amounts to 5.3 ppm (*cf.* 5.7 for chlorohomotropylium ions).⁴

The ^{19}F nmr spectrum of **4** in the presence of 4 equiv of SbF_5 in SO_2 at -80° ⁵ provided evidence for the homotropylium complexes **7** and **8** as well as the complex **2**; complexes of the type $\text{RF}\cdot\text{Sb}_2\text{F}_{10}$ and their ^{19}F nmr spectra have been described.^{6,7}

By which pathway is the sulfone **4** formed? It is plausible that the electrophilic 1:1 complex **2** of SO_2

(3) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *ibid.*, **88**, 3832 (1966).

(4) G. Boche, W. Hechtel, H. Huber, and R. Huisgen, *J. Amer. Chem. Soc.*, **89**, 3344 (1967).

(5) At -70° the absorptions were still broad due to exchange processes. The supercooling of the SO_2 solution to -80° was successful in the presence of 4 equiv of SbF_5 .

(6) A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2929 (1969).

(7) P. A. W. Dean and R. J. Gillespie, *ibid.*, **91**, 7260 (1969).

and SbF_5 (^{19}F nmr and X-ray⁸) attacks **1** from the endo side.⁹ The hypothetical homotropylium species **3** undergoes ring closure to form **5**. After complexation with the second mole of SbF_5 , the excellent stabilization of the anionic portion allows the ring opening to **7**.

The addition of SO_2 to 1,3-dienes can take a concerted pathway as a cheletropic reaction.^{10,11} With cyclooctatetraene, however, the lack of a planar diene system probably prevents a concerted SO_2 cycloaddition. There is an analogy to the 1,4 addition of SO_2 to **1** in the formation of the *N*-chlorosulfonyl isocyanate adduct of **1**, a reaction which is also assumed to proceed *via* a homotropylium zwitterion.¹²

The sulfone **4** dissociates quantitatively to **1** and SO_2 in the injection block of a gas chromatograph at 345°.

(8) J. W. Moore, H. W. Baird, and H. B. Miller, *J. Amer. Chem. Soc.*, **90**, 1358 (1968).

(9) R. Huisgen, G. Boche, and H. Huber, *ibid.*, **89**, 3345 (1967).

(10) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(11) W. L. Mock, *J. Amer. Chem. Soc.*, **91**, 5682 (1969); **92**, 3807 (1970).

(12) L. A. Paquette, J. R. Malpass, and T. R. Barton, *ibid.*, **91**, 4714 (1969).

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Received June 5, 1972

Reaction of Metal-Carbene Complexes with Wittig Reagents. A New Vinyl Ether Synthesis

Sir:

Since stable metal-carbene complexes were first synthesized and characterized by Fischer¹ in 1964, attempts to use these complexes as synthetic carbene or carbenoid sources have met with only limited success. Neither thermal,² photochemical,³ nor pyridine-induced⁴ decomposition of metal-carbene complexes in the presence of alkene have led to cyclopropanes. Oxidation of carbene complexes with pyridine *N*-oxide or with ceric ion in the presence of alkenes failed to give cyclopropanes and led only to the corresponding esters.^{5,6} The only successful use of a stable metal-carbene complex in cyclopropane synthesis is the recently reported stereospecific reaction of $\text{Ph}(\text{CH}_3\text{O})\text{CCr}(\text{CO})_5$ with *trans*-methyl crotonate which gave a mixture of two cyclopropanes in 60% yield.³

Rather than viewing metal-carbene complexes as carbenoid sources, we have now centered our attention on the M^--C^+ ylide nature of the metal-carbene bond in developing new approaches to the use of metal-carbene complexes in synthesis. Nucleophiles such as amines⁷ and thiols⁸ attack the electropositive carbene carbon atom to give substitution products. Here

(1) E. O. Fischer and A. Maasböl, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964); E. O. Fischer and A. Maasböl, *Chem. Ber.*, **100**, 2445 (1967).

(2) E. O. Fischer, B. Heckel, K. H. Dötz, J. Müller, and H. Werner, *J. Organometal. Chem.*, **16**, P29 (1969).

(3) E. O. Fischer and K. H. Dötz, *Chem. Ber.*, **102**, 1273 (1970).

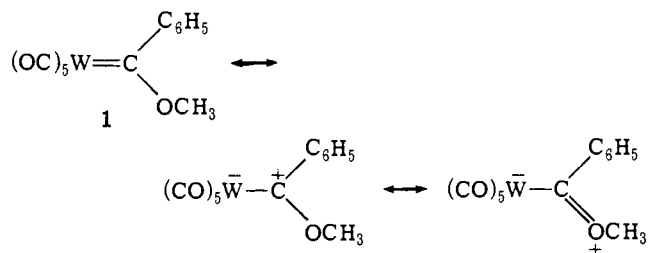
(4) E. O. Fischer and A. Maasböl, *J. Organometal. Chem.*, **12**, P15 (1968).

(5) C. P. Casey, R. Boggs, and T. J. Burkhardt, unpublished results.

(6) F. A. Cotton and C. M. Lukehart, *J. Amer. Chem. Soc.*, **93**, 2672 (1971).

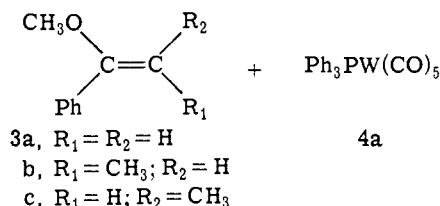
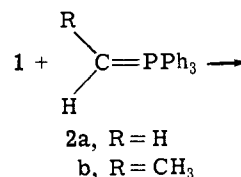
(7) J. A. Connor and E. O. Fischer, *Chem. Commun.*, 1024 (1970).

(8) E. O. Fischer and V. Keiner, *Angew. Chem., Int. Ed. Engl.*, **6**, 961 (1967).



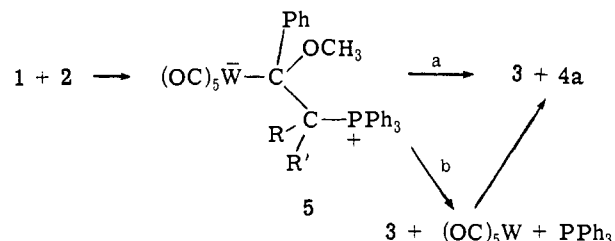
we report the reaction of a carbon nucleophile with a metal-carbene complex which leads to the removal of the carbene ligand from the metal in a synthetically useful way.

Phenylmethoxycarbenepentacarbonyltungsten(0) undergoes facile reactions with Wittig reagents to give enol ethers in high yields. Addition of methylenetriphenylphosphorane (**2a**) to a solution of **1** in ether



at room temperature resulted in a rapid reaction giving methyl 1-phenylvinyl ether and pentacarbonyltriphenylphosphinetungsten(0) (**4a**, 40% yield). **3a** was identified by comparison of its ir and nmr spectra and gas chromatographic retention time with those of an authentic sample⁹ and by conversion to acetophenone on treatment with dilute hydrochloric acid (82% yield from **1**). **4a** was identified by comparison of its infrared and mass spectra and its R_f on thin-layer chromatography with those of an authentic sample.¹⁰ Similarly ethylenetriphenylphosphorane (**2b**) reacted with **1** in diethyl ether to give **4a** (47% yield) and an approximately 1:1 mixture of methyl *cis*- and *trans*-1-phenylpropenyl ether **3b** and **3c**.¹¹ The vinyl ethers **3b** and **3c** were converted to propiophenone (98% yield from **1**) by treatment with dilute hydrochloric acid.

The reaction can be envisioned as proceeding *via* nucleophilic attack by the phosphorane carbon atom upon the electron-deficient carbene carbon atom to form a betaine-like intermediate **5** which subsequently frag-



(9) V. H. Lüssi, *Makromol. Chem.*, **103**, 68 (1967); S. Winstein and L. L. Ingraham, *J. Amer. Chem. Soc.*, **77**, 1738 (1955).

(10) T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *ibid.*, **83**, 3200 (1961).

(11) R. C. Fahey and C. Schubert, *ibid.*, **87**, 5172 (1965).