(allyl)Pd chloride (2.2 mg, 0.01 mmol of Pd), and crotyl chloride (118 μL, 1.2 mmol) were dissolved in dry air-free THF. Maleic anhydride (5 mg, 0.05 mmol) was added, and the reaction mixture was warmed to +50 °C. After 12 h, products recovered by evaporative distillation were analyzed by gas chromatography (2-methyl-2,6-octadiene, 40%; 2,6-octadiene, 10%; 2,7-dimethyl-2,6-octadiene, 27%). Other results given in Table II show that regiochemistries for cross-coupling are identical with those noted in stoichiometric procedures.

The use of allylic tin reagents in conjunction with maleic anhydride to intercept reactive bis(allyl)Pd intermediates has enabled us to broaden in scope C–C bond formation processes via these species and complements results obtained by another route in the absence of this ligand.[9] We are currently studying other metal allyl involved reaction procedures to further demonstrate the use of this interception technique.

Acknowledgment. We acknowledge support for this work given by the National Institutes of Health and the National Science Foundation.

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[9] Stille has recently reported the synthesis of diallylic ketones from allylic halides and allylic tin reagents (without allylic transposition), catalyzed by Pd(0) in the presence of CO, a species which *may* serve to induce eliminations from an (allylic)(acyl)Pd(II) intermediate: Merrifeld, J. H.; Godschalx, J. P.; Stille, J. K. *Organometallics* 1984, *3*, 1108.

[10] Prepared by trimethyltin hydride addition to ethyl 3,5-hexadienoate initiated by AIBN.

New Metal–Sulfur Complexes from SO_2 Reduction by $(\eta^5\text{-}C_5R_5)W(CO)_3H$ (R = H, Me): Structures of $[CpW(CO)_3]_2(\mu\text{-}S)$ and $[Cp^*W(CO)_2(\mu\text{-}S\cdot SO_2)]_2$, a Complex with Strong SO_2–Sulfide Bonding

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Summary: The title complexes are produced by direct reaction of $CpW(CO)_3H$ or $Cp^*W(CO)_3H$ with SO_2 (Cp^* = C_5Me_5). X-ray structures reveal that $[CpW(CO)_3]_2S$ possesses a bent, unsupported sulfide bridge, while $[Cp^*W(CO)_2(\mu\text{-}S\cdot SO_2)]_2$ contains the first structurally characterized example of a metal sulfide–SO_2 Lewis acid–base interaction.

We have been investigating the reduction of SO_2 by a variety of transition-metal hydride complexes in order to determine the fundamental steps involved in these reactions. Recently we have found that the solution reactions of $CpM(CO)_3H$ and $Cp^*M(CO)_3H$ [M = Mo, W; Cp^* = $C_5(CH_3)_5$] with SO_2 result in a large variety of products depending upon the complex and the reaction conditions.[1] In all cases, complexes resulting from insertion of SO_2 into the metal–hydride bond form initially, and complexes such as $CpMo(CO)_3(SO_2H)$ have been isolated.[1] These "insertion" products, which are the first examples of complexes containing the SO_2H ligand, undergo further reaction, either in the solid or in solution, in which the ultimate fate of the SO_2 is water and metal sulfide complexes.[1] We report here the isolation and characterization of two new dinuclear tungsten sulfide complexes.

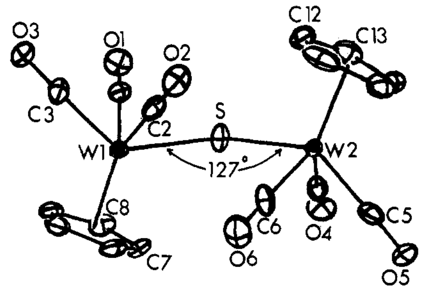

Figure 1. Molecular geometry of $[CpW(CO)_3]_2(S)$ (ORTEPII diagram, 30% ellipsoids).

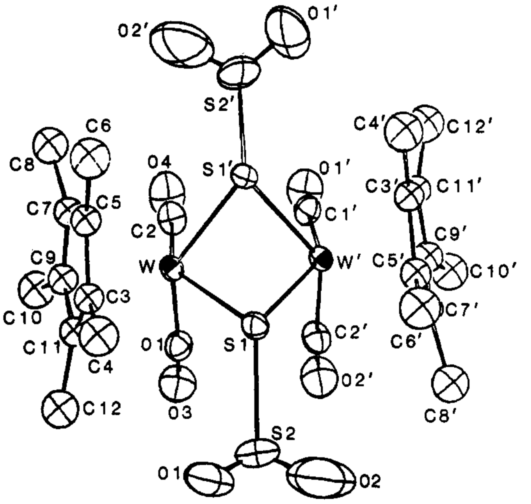

Figure 2. The molecular structure of $[Cp^*W(CO)_2(S\cdot SO_2)]_2$. Atoms labeled without primes (′) constitute the crystallographic asymmetric unit; those with primes are related to those without by a twofold axis of symmetry.

The overnight reaction of $CpW(CO)_3H$ with SO_2 (2:1) in acetonitrile results in a crystalline mixture containing primarily $[CpW(CO)_3]_2$ and $[CpW(CO)_3]_2S$, 1.[2] The latter may be isolated as dark green, air-stable microcrystals[3] in 32% yield by extraction with SO_2-saturated CH_3CN, volume reduction, and precipitation using methanol. The Mo analogue[3] is prepared in similar manner except that reaction and isolation temperature is 0 to −20 °C because of high solution instability. 1 also decomposes in solution slowly (rapidly at 70 °C). The structure[4] of 1 is shown in Figure 1. The molecule consists of two $CpW(CO)_3$ moieties bridged by a single sulfur atom through equivalent distances of W(1)–S = 2.528 (6) and W(2)–S = 2.533 (9)

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[1] Kubas, G. J.; Ryan, R. R.; Wasserman, H. J., submitted for publication in *J. Am. Chem. Soc.*

[2] $[CpW(CO)_3]_2S$ has previously been reported by us (Kubas, G. J.; Ryan, R. R. Abstracts of Papers, 38th Southwest and 6th Rocky Mountain Combined Regional Meeting of the American Chemical Society, Dec 1982, El Paso, TX, 1982; p 74) and has independently been prepared (Herberhold, M.; Jillen, W.; Murray, H. H. *J. Organomet. Chem.* 1984, *270*, 65.

[3] 1: IR ν(CO) (Nujol mull) 2006, 1993, 1951, 1935, 1921, 1897 cm^{-1}; ^1H NMR (C_6D_6) δ 4.75, ($Me_2SO\text{-}d_6$) δ 5.64, (CS_2) δ 5.37. Anal. Calcd for $C_{16}H_{10}O_6SW_2$: C, 27.53; H, 1.44; W, 52.68; O, 13.75. Found: C, 26.38; H, 1.57; W, 52.44; O, 14.35. $[CpMo(CO)_3]_2S$: IR ν(CO) 2005, 1997, 1959, 1947, 1931, 1909 cm^{-1}; ^1H NMR ($Me_2SO\text{-}d_6$) δ 5.56.

[4] $C_{16}H_{10}O_6S\,W_2$: M_r = 642.1, monoclinic, space group $P2_1/c$, a = 6.8473 (8) Å, b = 15.715 (1) Å, c = 16.056 (1) Å, β = 84.51 (1)°, V = 1719.7 $Å^3$, ρ(calcd) = 2.48 g cm^{-3}, Z = 4, μ(Mo Kα) = 137.8 cm^{-1}; $R(F)$ = 0.046, $R_w(F)$ = 0.053 for 1980 absorption corrected data with $I > 3.0\sigma(I)$. Full-matrix least-squares refinement included anisotropic thermal parameters for non-hydrogen atoms, fixed, isotropic contributions from hydrogen atoms, and a correction for secondary extinction.

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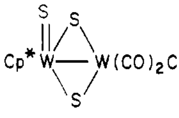
Å. These bond lengths are indicative of tungsten–sulfur single bonds, in contrast with two previous M–(μ-S)–M systems, $[(Cp)Cr(CO)_2]_2S$[5a] and $[(CN)_6MoSMo(CN)_6]^{6-}$,[5b] in which multiple metal–sulfur bonding is clearly evident. Note that in these previous structures, the metals are almost linearly disposed about the sulfur atom [Cr–S–Cr(av) = 174.4 (2)°; Mo–S–Mo = 169.5 (2)°], while in the present example, the W(1)–S–W(2) angle is 127.0 (2)°. Thus, **1** apparently represents the first example of a complex with a single, bent, unsupported sulfide bridge.

The reaction of $Cp^*W(CO)_3H$ with SO_2 proceeds differently. Allowing an SO_2-saturated solution of $Cp^*W(CO)_3H$ in $CH_3CN–Et_2O$ to stand for several days in a closed flask gives a 32% yield of sparingly soluble deep green crystals of a complex, **2**, with the composition $Cp^*W(CO)_2S_2O_2$.[6] A crystal structure analysis of this complex was performed as well.

The molecular geometry[7] of what is actually $[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$, in which SO_2 bonds as a Lewis acid to a bridging sulfide group, is shown in Figure 2. The molecule exhibits precise, i.e., crystallographically imposed, C_2 symmetry. The W–W′ separation of 2.992 (1) Å suggests a substantial interaction between the metal atoms, although a slightly shorter distance has been observed in a di-μ-sulfido complex of W(V).[8] The acute angles at the bridging sulfur atoms, W–S(1)–W′ = 75.9 (1)°, further substantiate the presence of a metal–metal bond. The sulfides form symmetrical bridges across the tungsten–tungsten vector with W–S(1) = 2.431 (3) and W–S(1′) = 2.434 (3) Å. The hinged W_2S_2 unit produces a dihedral angle of 95.4° between the W–S(1)–W′ and W–S(1′)–W′ planes; note that the nonbonded S(1)–S(1′) distance is 2.836 (5) Å (sum of van der Waals radii = 3.6 Å). The SO_2 molecules coordinate to the bridging sulfide ligands through distances of S(1)–S(2) = 2.408 (5) Å. A slightly larger sulfur–sulfur separation of 2.530 (5) Å has been observed[9] in $Cu(PPh_2Me)_3(SPh)(SO_2)$, a molecule in which SO_2 binds as a Lewis acid to a *mercaptide* sulfur. Although disorder[7] has impaired the precision with which the SO_2 groups were located, the geometry of the $S{\cdot}SO_2$ is pyramidal, with S(1)–S(2)–O(1) = 98 (2)°, S(1)–S(2)–O(2) = 106 (2)°, and O(1)–S(2)–O(2) = 107 (2)°.

The observation of a *sulfide*–SO_2 adduct in **2**, the first structurally characterized example of which we are aware,[10] prompted us to examine the reaction of **1** with SO_2. Compound **1** and its Mo congener react reversibly with SO_2 resulting in a change in solution color from green to red. A solid material[11] is obtained in which the SO_2 appears to be bound to the bridging sulfur atom, since the observed ν(SO) are not inconsistent with sulfide–SO_2 binding[12] and are similar to those for **2**. However, the difference in stability between **2** and $\mathbf{1}{\cdot}SO_2$ is marked. Whereas $\mathbf{1}{\cdot}SO_2$ must be isolated in an SO_2 atmosphere and reversibly loses SO_2 quantitatively at room temperature, **2** is stable in air for at least 45 days, requires heating to >100 °C to drive off SO_2, and decomposes upon SO_2 loss even under mild conditions (solution, 40 °C). Thermogravimetric data (5 °C/min) indicate that **1** loses 2 mol of CO at 100–140 °C, followed by loss of remaining CO at 140–400 °C. However, **2** loses all volatiles (22% weight loss) at 110–150 °C. In both cases, at least five different Cp or Cp* proton resonances are identified in the NMR of the residues, even after partial decomposition. Analysis of the gases evolved upon heating **2** (0.06 mmol) in vacuo for 30 min at 150 °C shows, in addition to CO, the presence of 0.025 mmol of CO_2 and COS and only 0.08 mmol (theory, 0.12 mmol) of SO_2, presumably as a result of reaction of SO_2 and CO. Since the gases were trapped at −196 °C immediately after being formed, it is unlikely that CO–SO_2 reaction occurs after their evolution from the solid phase. The known complex[13]



and oxo-containing complexes (ν(W=O) 912, 921 cm^{-1}) are products of the decomposition of **2** in both solution and solid states.

The appearance on heating **2** of CO_2 and COS simultaneously with the W_2S_3 cluster and the associated oxo species suggests an oxygen transfer mechanism. One of the SO_2 atoms may shift from the sulfide bridge to the metal center, possibly replacing a CO ligand, followed by transfer of two oxygens to two CO's to form CO_2 and the W_2S_3 dimer. Also, a second process involving transfer of an oxygen and a sulfur atom to two CO's to form COS and CO_2 plus the oxo complexes may be occurring.

The Lewis acid bonding of SO_2 to the μ-S ligands in **2** is remarkably strong compared to that for $\mathbf{1}{\cdot}SO_2$. Other group 6 sulfide complexes, such as $Cp_2^*W_2(CO)_2S_3$[13] and $[Cp^*MoS(\mu\text{-}S)]_2$,[14] do not yield stable SO_2 adducts at 20 °C. The anomalously high basicity of the bridging sulfur atoms in **2** suggests further study in light of the interesting reaction of initially sulfide-bound SO_2 and metal-bound CO. Sulfide basicity is also quite relevant to industrial

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[5] (a) Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3543. Goh, L. Y.; Hambley, T. W.; Robertson, G. B. *J. Chem. Soc., Chem. Commun.* **1983**, 1458. (b) Drew, M. G. B.; Mitchell, P. C. H.; Pygall, C. F. *J. Chem. Soc., Dalton Trans.* **1979**, 1213.

[6] **2**: IR (Nujol mull) ν(CO) 2027, 1972, ν(SO) 1198, 1053 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20, (C_6H_6) δ 1.80. Anal. Calcd for $C_{24}H_{30}O_8S_4W_2$: C, 30.59; H, 3.21; S, 13.61; O, 13.58. Found: C, 30.84; H, 3.28; S, 13.67; O, 13.87. A small amount of impurities, including $Cp_2^*W_2(CO)_2S_3$,[13] cocrystallized with **2** but these were removed either mechanically and/or by washing **2** with benzene.

[7] $[(\eta^5\text{-}C_5Me_5)W(CO)_2(S)(SO_2)]$ crystallizes in the noncentrosymmetric orthorhombic space group *F2dd* $\{C_{2v}^{19}$; No. 43$\}$, with a = 8.389 (1) Å, b = 18.896 (2) Å, c = 37.229 (4) Å, V = 5901.3 Å^3, and ρ(calcd) = 2.12 g cm^{-3} for Z = 8 and mol wt 942.4. Intensity data ($1.5° \leq \theta \leq 25.0°$) were collected with use of an Enraf-Nonius CAD4 diffractomer operating in the ω-scan mode with Mo Kα radiation (λ = 0.71069 Å). A total of 1341 unique, absorption corrected (μ = 82.7 cm^{-1}) data having $I > 2.0\sigma(I)$ were used to refine the structure. Anisotropic thermal parameters were used for all non-hydrogen atoms save those of the pentamethylcyclopentadienyl ligand. Oxygen atoms in the single unique SO_2 group are disordered. Attempts to resolve the disorder were unsuccessful; the electron density in the resulting model is described by artificially large, extremely anisotropic thermal ellipsoids. An isotropic secondary extinction parameter was also refined, giving a total of 122 parameters. The final residuals were R_F = 2.4% and R_{wF} = 3.0%. The correct chirality for the crystal examined was determined by performing a refinement in which the signs of the $\Delta F''$ terms were reversed.

[8] Bino, A.; Cotton, F. A.; Dori, Z.; Sekutowski, J. C. *Inorg. Chem.* 1978, *17*, 2946.

[9] Eller, P. G.; Kubas, G. J. *J. Am. Chem. Soc.* **1977**, *99*, 4346.

[10] Nonstructurally characterized complexes containing relatively robust sulfide–SO_2 interactions have been reported: (a) Ugo, R.; La Monica, G.; Cenini, S. *J. Chem. Soc. A* **1971**, 522. See also: Gukathasan, R. R.; Morris, R. H., Walker, A. *Can. J. Chem.* **1983**, *61*, 2490. (b) Kubas, G. J.; Vergamini, P. J. *Inorg. Chem.* **1981**, *20*, 2667.

[11] $1{\cdot}SO_2$: IR (Nujol mull) ν(CO) 2044, 1995 br, 1970 br sh, 1954 br, 1912, 1897, ν(SO) 1213, 1074, 1054 cm^{-1}; ^1H NMR (C_6D_6, SO_2 saturated) δ 5.04. The complex was prepared by reacting a slurry of **1** in 4:1 heptane–ether with excess SO_2, filtering off the resulting red solid, and drying in a SO_2 stream.

[12] (a) Kubas, G. J. *Inorg. Chem.* **1979**, *18*, 182. (b) Ryan, R. R.; Kubas, G. J.; Moody, D. C.; Eller, P. G. *Struct. Bonding (Berlin)* **1981**, *46*, 47.

[13] Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1982**, *1*, 1107.

[14] Rakowski Dubois, M.; DuBois, D. L.; Van Derveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064. We have found that the disulfide-bridged isomer, $Cp_2^*Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)$,[13] forms an SO_2 adduct, but the bonding site has not been established.

metal sulfide catalysts where reactivity at sulfur is apparently critical to their function. Efforts to isolate 2 without the SO_2 groups and to determine the reactivity of the μ_2-S ligands are underway.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences.

Registry No. 1, 92468-48-9; $1{\cdot}SO_2$, 94024-80-3; 2, 94024-81-4; $CpMo(CO)_3(SO_2H)$, 94024-82-5; $[CpW(CO)_3]_2$, 12091-65-5; $[CpMo(CO)_3]_2S$, 94024-83-6; $Cp^*{}_2W_2(CO)_2S_3$, 94024-84-7; $CpW(CO)_3H$, 12128-26-6; $CpMo(CO)_3H$, 12176-06-6; $Cp^*W(CO)_3H$, 32839-62-6; SO_2, 7446-09-5.

Supplementary Material Available: Lists of structure factor amplitudes, positional and thermal parameters, and distances and angles (16 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of a Rhodacyclobutene Complex Formed by Addition of Two $F_3CC{\equiv}CCF_3$ Molecules to a Rh–η^2-CS_2 Moiety

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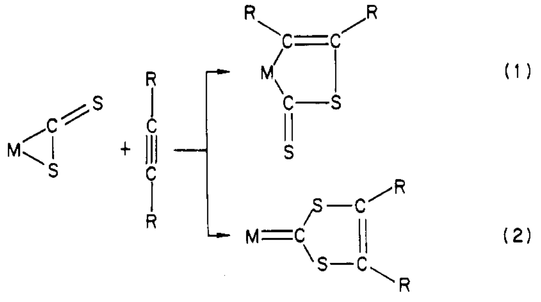
Received September 20, 1984

Summary: The complex (triphos)RhCl(η^2-CS_2) [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane] reacts with two molecules of $F_3CC{\equiv}CCF_3$, to give the rhodacyclobutene complex (triphos)ClRhC(CF_3)=C(CF_3)CSC(CF_3)=C(CF_3)S whose structure has been established by X-ray methods.

Acetylenes with electron-withdrawing substituents are known to react with η^2-CS_2 metal complexes. Generally, one molecule of activated acetylene adds to the metal–η^2-CS_2 moiety. The nature of the metal fragment and of the coligands determine whether heterocyclic five-membered metalla ring complexes (eq 1)[1,2] or 1,3-dithiol-2-ylidene derivatives (eq 2)[2,3] are formed.



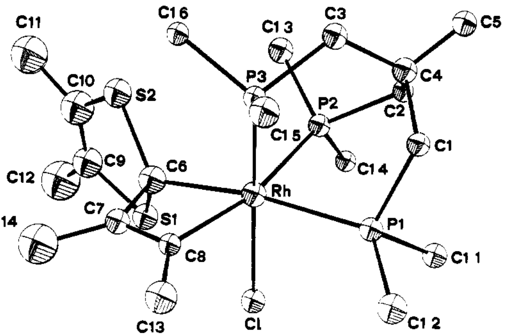
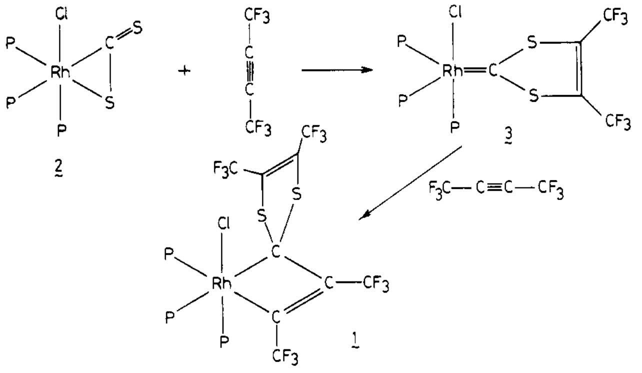


Figure 1. ORTEP drawing of the (triphos)ClRhC(CF_3)=C(CF_3)CSC(CF_3)=C(CF_3)S molecule. For the sake of clarity the phenyl rings (except for the connecting C atoms) and the F atoms of the trifluoromethyl groups are not shown. Some relevant bond lengths (Å) and angles (deg) are as follows: Rh–Cl = 2.427 (9); Rh–P1 = 2.446 (8); Rh–P2 = 2.454 (10); Rh–P3 = 2.305 (9); Rh–C6 = 2.15 (3); Rh–C8 = 2.09 (3); S1–C6 = 1.83 (3); S2–C6 = 1.85 (3); C6–C7 = 1.50 (4); C7–C8 = 1.30 (4); C9–C10 = 1.36 (5). C6–Rh–C8 = 64 (1); S1–C6–C2 = 105 (2).

Scheme I



Herein we report the synthesis and the crystal structure of the rhodacyclobutene complex (triphos)ClRhC(CF_3)=C(CF_3)CSC(CF_3)=C(CF_3)S (1) [triphos = 1,1,1-tris(diphenylphosphino)methyl)ethane], which is obtained by the unprecedented addition of two molecules of $F_3CC{\equiv}CCF_3$ to the Rh–η^2-CS_2 moiety of (triphos)RhCl(η^2-CS_2)[4] (2). Yellow crystals of 1[5] are formed in 90% yield by reacting at room temperature a twofold excess of hexafluorobut-2-yne with a methylene chloride solution of 2.[6] The crystal structure of 1[7] consists of mononuclear units where the rhodium atom has a pseudooctahedral coordination given by the three phosphorus atoms of triphos, one chlorine atom, and two carbon atoms from the chelating ligand SC(CF_3)C(CF_3)SCC(CF_3)C(CF_3), which is formed in situ (Figure 1). The latter ligand contains the five-membered

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[1] Wakatsuki, Y.; Yamazaki, H.; Iwasaki, H. *J. Am. Chem. Soc.* **1973**, *95*, 5781.

[2] Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *Inorg. Chem.* **1981**, *20*, 2486.

[3] (a) Le Marouille, J. Y.; Lelay, C.; Benoit, A.; Grandjean, D.; Touchard, D.; Le Bozec, H.; Dixneuf, P. *J. Organomet. Chem.* **1980**, *191*, 133. (b) Frazier, C. C.; Magnussen, N. D.; Osuji, L. H.; Parker, K. O. *Organometallics* **1982**, *1*, 903. (c) Schenk, W. A.; Schwietzke, T.; Müller, H. *J. Organomet. Chem.* **1982**, *232*, C41. (d) Bianchini, C.; Meli, A. *J. Chem. Soc., Chem. Commun.* **1983**, 1309. (e) Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics*, in press.

[4] Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.*, in press.

[5] IR (Nujol mulls): ν(C=C) 1625, 1605 cm^{-1}, ν(CF) 1270, 1240, 1170, 1130 cm^{-1}. Anal. Calcd: C, 51.62; H, 3.37; Rh, 8.84; S, 5.51. Found: C, 51.43; H, 3.48; Rh, 8.79; S, 5.46.

[6] When equimolecular amounts of hexafluorobut-2-yne and **2** are reacted, yellow crystals of 1 are obtained in ca. 40% yield. Unreacted **2** can be recovered in almost the same yield from the reaction mixture.

[7] Crystallographic data for 1: hexagonal, a = 23.425 (6) Å, c = 18.982 (5) Å, space group $P6_1$, $Z = 6$, $d_{calcd} = 1.28$ g/cm³, μ(Mo Kα) = 5.33 cm^{-1}. Intensity data were collected by standard methods in this institute. The structure was solved by Patterson and Fourier techniques using the SHELX76 program package.[8] Refinement converged at $R = 0.064$ and $R_w = 0.061$ for 1339 absorption corrected reflections with $I > 3\sigma(I)$ measured on a Philips PW 1100 diffractometer with Mo Kα radiation ($2.5 < \theta < 25°$). The fluorine atoms of one of the hexafluorobut-2-yne molecules were found disordered. The phenyl rings were treated as rigid groups of the D_{3h} symmetry.

[8] Sheldrick, G. M., SHELX76, Program for Crystal Structure Determinations, University of Cambridge, Cambridge, England, 1976.

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