Table I. Values of $\Delta\mu_A$ for MLCT Transitions of Several Tris(diimine)ruthenium(II) Complexes Determined by Stark Effect Spectroscopy

complex[a]	λ (nm)	ν (cm^{-1})	$\lvert\Delta\mu_A\rvert$ (D)[b]
$Ru(bpy)_3^{2+}$	454	22026	$(8.8 \pm 0.7)/f$
	420	23810	$(5.3 \pm 0.4)/f$
$Ru(bpy)_2(biq)^{2+}$	532	18797	$(5.7 \pm 0.4)/f$
	441	22676	$(4.8 \pm 0.3)/f$
$Ru(biq)_3^{2+}$	510	19608	$(6.3 \pm 0.9)/f$

[a] All complexes are salts of PF_6^- in poly(vinyl alcohol) at 77 K. [b] $\chi = 54.74°$; $F_{ext} \simeq 6.5 \times 10^5$ V/cm; f is the local field correction;[5] D = Debye (3.34×10^{-30} C·m).

in Figure 1. Large features resembling a second derivative line shape, increasing quadratically with applied electric field, and corresponding to transitions assigned to singlet MLCT states ($^1A_1 \rightarrow {}^1E$),[6,7] appear in the Stark effect spectrum (Figure 1B). If contributions to ΔA from overlapping bands in the spectrum are neglected, the apparent $|\Delta\mu_A|$ for the dominant band at 22026 cm^{-1} (454 nm) is $(8.8 \pm 0.7)/f$ D, where f is the local field correction.[5,8] This value represents the excited-state dipole moment if the ground state possesses true D_3 symmetry and thus no permanent dipole moment;[9] $|\Delta\mu_A|$ then corresponds to separation of a full charge by $1.83/f$ Å. The distance from the metal to the geometric center of a bipyridine ligand is 2.82 Å[10] and allows an estimate of $(65/f)$% of full charge-transfer character. Such a large value of $|\Delta\mu_A|$ is most consistent with work which indicated that the initially prepared ^{1}MLCT state is highly dipolar.[2] The transition at 23 810 cm^{-1} (420 nm) also possesses a significant Stark effect, though comparison with the second derivative spectrum (Figure 1C) shows that the $|\Delta\mu_A|$ associated with this transition is smaller than that for the 22 026-cm^{-1} transition. Direct excitation to the lowest triplet MLCT state of the complex results in the weak shoulder on the low-energy side of the main MLCT absorption band;[6] from the positive feature in the Stark effect spectrum at 17606 cm^{-1} (568 nm), we estimate $|\Delta\mu_A| \simeq 10/f$ D.[11] No significant Stark effect appears between 26 000 and 29 000 cm^{-1}, indicating that the excited states in this region are not highly dipolar.

The presence of only two bands in the visible region of the Stark effect spectrum due to large $|\Delta\mu_A|$ is consistent with the assignments of Ceulemans and Vanquickenborne, who predicted that only two of the four possible spin- and symmetry-allowed MLCT transitions to the lowest π^* orbitals of the complex should possess significant CT intensity.[7] Other work has suggested that three singlet MLCT transitions occur in the visible region.[12,13] The second derivative of the absorption spectrum does show an additional feature at ~21 600 cm^{-1} (463 nm) which is absent in the Stark effect spectrum. While second derivative spectra with good signal-to-noise are difficult to obtain for the broad absorption bands found in these complexes, the 21 600-cm^{-1} feature is reproducible and may reflect an electronic transition with significant oscillator strength but a relatively small excited state dipole moment. Alternatively, a third ^{1}MLCT band may lie too close in energy to the 22 026-cm^{-1} band to be resolved in the Stark effect spectrum.

Data for $Ru(biq)_3^{2+}$ and $Ru(bpy)_2(biq)^{2+}$ (biq = 2,2′-biquinoline) have also been obtained for the principal ^{1}MLCT transitions (Table I). The ^{1}MLCT bands of $Ru(biq)_3^{2+}$ give smaller observed values of $|\Delta\mu_A|$ than those for $Ru(bpy)_3^{2+}$. This result presumably reflects the slightly greater metal-to-ligand distance in $Ru(biq)_3^{2+}$,[14] which diminishes overlap of metal and ligand orbitals, reducing CT and the magnitude of the excited state dipole. $Ru(bpy)_2(biq)^{2+}$ has C_2 molecular point symmetry and is of interest because transitions corresponding to CT to each type of ligand are distinguishable in the absorption spectrum.[15] Interestingly, $|\Delta\mu_A|$ measured for transitions to the bpy ligands (22676 cm^{-1}) are smaller than those for $Ru(bpy)_3^{2+}$. Possibly, a steric interaction between bpy and biq ligands suffices to diminish bpy overlap with metal orbitals relative to $Ru(bpy)_3^{2+}$.

Stark effect spectroscopy should be generally applicable to quantitatively characterizing the excited states of a wide range of transition-metal complexes. Even at a qualitative level variations in the degree of CT character associated with different transitions are immediately evident from the Stark spectra. Extensions of these measurements to the photochemically interesting emitting states of these complexes will be reported shortly.

Acknowledgment. This work was supported in part by a grant from the Gas Research Institute and a Presidential Young Investigator Award to S.G.B. D.H.O. is an MSTP trainee supported by Grant GM07365 from NIGMS. We thank Professor V. Balzani for providing samples of $Ru(bpy)_2(biq)^{2+}$ and $Ru(biq)_3^{2+}$.

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(8) Crude deconvolution of the absorption spectrum into a sum of Gaussian bands shows that, while the band centered at 23810 cm^{-1} contributes little to the absorption at 22026 cm^{-1}, the bands overlap where the curvature is large, contributing some uncertainty in the values of the second derivative and $|\Delta\mu_A|$ at this energy.

(9) The ground state is most likely only approximately D_3 due to static distortions of the complex in the PVA matrix and the influence of the PF_6^- counterions. For qualitative arguments, we assume that the ground-state dipole is negligible compared to the excited-state dipole.

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Synthesis and Reactivity of the First Structurally Characterized Heterobimetallic Complex Containing an Unsupported Bridging Sulfur Atom

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Studies of the reactivity of complexes containing sulfur atoms bridging two inequivalent transition metals are important in both biological[1] and heterogeneous catalytic (e.g., hydrodesulfurization[2]) systems. Although many bimetallic complexes and clusters containing double sulfido bridging units are known,[3] there is

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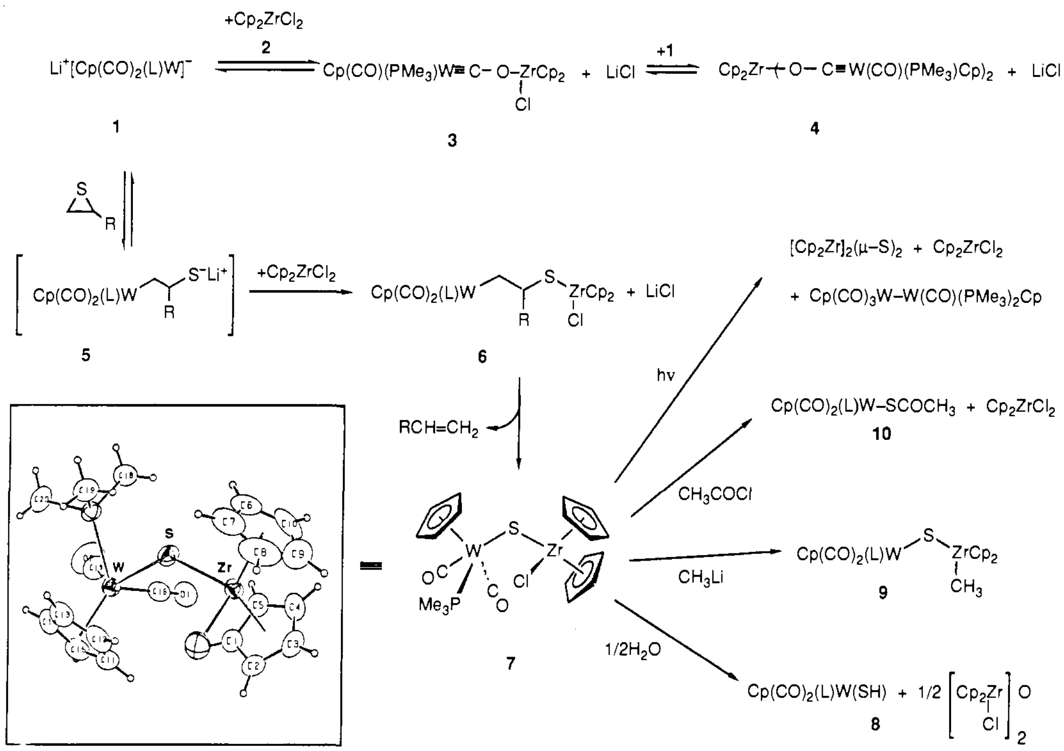
Scheme I



apparently no example in the literature of a fully characterized molecule containing a simple unsupported M–S–M′ linkage.[4] We wish to report the synthesis of such a complex, by an unusual route involving the simultaneous use of these reactants, along with its structure, reactivity, and preliminary studies of the mechanism of its formation.

The tungsten–zirconium complex [*cis*-(η^5-C_5H_5)(CO)$_2$(PMe$_3$)W](μ-S)[Zr(Cl)(η^5-C_5H_5)$_2$] (**7**; cf. Scheme I) was synthesized by introducing 1 equiv of propylene sulfide into a mixture of tungsten anion[5] **1** (L = PMe$_3$) and zirconium dichloride complex **2**. One equivalent of propylene is evolved, and a single sulfur atom is transferred to form a bridge between the two different metals involved in this reaction. No homonuclear products (e.g., [(η^5-C_5H_5)(CO)$_2$(PMe$_3$)W]$_2$(μ-S)[6] or [(η^5-C_5H_5)$_2$Zr]$_2$(μ-S)$_2$[7]) are observed.

Dinuclear μ-sulfido complex **7** was isolated from a rigorously O_2/H_2O-free toluene/hexane (1:1 v/v) solution in the dark, and fully characterized.[8] IR and ^{13}C NMR data were consistent with a normal piano stool geometry[9] about the tungsten center in a cis configuration.[10] ^{31}P NMR analysis supported retainment of the tungsten-bound PMe$_3$ ligand. The electronic spectrum[11] of **7** in C_6H_6 displays a band at λ_{max} = 400 nm. Single crystals of the complex were obtained by diffusion of *n*-hexane into a toluene solution, and the structure of the complex was solved by X-ray diffraction.[12]

As illustrated in the ORTEP diagram shown in Scheme I, the diffraction study confirms that a single S atom occupies a bridge position in complex **7**. The W–Zr separation of 4.52 Å indicates that there is no direct interaction between the metals. The W–S–Zr bridge angle in **7** (132.42 (4)°) is strongly bent relative to the corresponding W–O–Zr angle (175.7 (2)°) in the oxo analogue[13] [(η^5-C_5H_5)(CO)$_3$W](μ-O)[Zr(Cl)(η^5-C_5H_5)$_2$]. The W–S distance (2.526 (1) Å) in **7** is in close agreement with the corresponding average distance (2.530 Å) in the homometallic dimer [(η^5-C_5H_5)(CO)$_3$W]$_2$(μ-S).[4f] There is no direct interaction between the tungsten-bound CO (C(16)–O(1)) and the electron-deficient Zr center as demonstrated by the O(1)···Zr separation (>3.0 Å). The Zr–S distance (2.418 (1) Å) in **7** is extremely short relative to others reported in the literature[7,14] and most closely compares with that of the terminally-bound S-Bu^t of [Zr$_3$(μ_3-SBu^t)(μ_3-S)(μ-SBu^t)$_3$(SBu^t)$_6$].[14b]

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[4] Even homonuclear transition-metal dimers containing unsupported single (μ-S) bridges are relatively rare. Examples of structurally characterized M(μ-S)M systems: (a) Mukherjee, R. N.; Stack, T. D. P.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 1850. (b) Skapski, A. C.; Troughton, T. G. H. *J. Chem. Soc. A* **1969**, 2772. (c) Drew, M. G. B.; Mitchell, P. C. H.; Pygall, C. F. *J. Chem. Soc., Dalton Trans.* **1979**, 1213. (d) Goh, L. Y.; Hambly, T. W.; Robertson, G. B. *J. Chem. Soc., Chem. Commun.* **1983**, 1458. (e) Dorfman, J. R.; Girard, J.-J.; Simhon, E. D.; Stack, T. D. P.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 4407. (f) Kubas, G. J.; Wasserman, H. J.; Ryan, R. R. *Organometallics* **1985**, *4*, 419. (g) Brennan, J. G.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1986**, *25*, 1761. The only previously reported heterobimetallic M(μ-S)M′ system [(η^5-C_5H_5)(CO)$_3$W](μ-S)[Cr(CO)$_3$(η^5-C_5H_5)] is thermally unstable and exists in equilibrium with the corresponding homonuclear dimers [(η^5-C_5H_5)(CO)$_3$W]$_2$(μ-S)[4f] and [(η^5-C_5H_5)(CO)$_3$Cr]$_2$(μ-S). (h) Fischer, R. A.; Herrmann, W. A. *J. Organomet. Chem.* **1987**, *330*, 377.

[5] Li[Cp(CO)$_2$(PMe$_3$)W] (**1**) was synthesized by deprotonation of Cp(CO)$_2$(PMe$_3$)W(H) (Bainbridge, A.; Craig, P. J.; Green, M. *J. Chem. Soc. A* **1968**, 2715) with LiN(i-Pr)$_2$ in THF solution. Experimental details of the synthesis of **1** are provided as Supplementary Material.

[6] [(η^5-C_5H_5)(CO)$_2$(PMe$_3$)W]$_2$(μ-S), the PMe$_3$ derivative of [(η^5-C_5H_5)(CO)$_3$W]$_2$(μ-S),[4f] has not been reported; however, we detect no resonances attributable to this material in reactions of **1** and **2** monitored by ^{1}H NMR.

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[8] Full experimental, spectroscopic, and analytical data are provided in the Supplementary Material.

[9] Kubacek, P.; Hoffman, R.; Havias, Z. *Organometallics* **1982**, *1*, 180.

[10] IR (C_6D_6) 1932 (s), 1840 (s) cm^{-1}. Two inequivalent CO resonances are observed in the ^{13}C{^{1}H} NMR (THF; δ 249.2 (d, J = 22 Hz), 237.7 (d, 8.2 Hz)) which correspond to CO's trans and cis to PMe$_3$, respectively.

[11] In solution, complex **7** rapidly ($t_{1/2} \sim$ 20 min) converts to monomeric products (vide infra) upon exposure to light produced by the UV-vis lamp in the region λ = 310–420 nm. It was therefore not possible to determine the extinction coefficient of the observed (λ_{max} = 400 nm) absorption band, which is most likely a S to Zr(IV) charge-transfer band.

[12] The crystal structure reported in this paper was determined by Dr. F. J. Hollander of the U.C. Berkeley College of Chemistry X-ray Diffraction Facility (CHEXRAY). Complex **7** crystallizes in the monoclinic space group $P2_1/n$ with a = 12.38 (1) Å, b = 17.14 (2) Å, c = 12.36 (1) Å, β = 119.34 (8)°, and V = 2286.9 (9) Å^3. With use of 2986 unique data (3° ≤ 2θ ≥ 45°, $I \geq 3\sigma(I)$) the structure was refined to $R(R_w)$ = 3.64 (2.10)%. Details of the structure are provided as Supplementary Material.

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Episulfides are frequently used as a source of sulfur in the synthesis of transition-metal sulfides. However, the mechanism of sulfur-atom transfer from these reagents to metals has not yet been examined. Accordingly, we have carried out experiments designed to provide some preliminary information on the mechanism of this reaction. First, both transition-metal complexes **1** and **2** are required for S abstraction; no detectable reaction occurs between the tungsten anion and propylene sulfide in the absence of zirconium halide. In contrast, complexes **1** and **2** do react independently: in the absence of organic sulfide, they give CO-bridged complex **3**, which affords bis-oxycarbyne bridged complex **4** in a subsequent step.[15] Despite this, however, reaction of **1** with **2** does not appear to be the initial step in the formation of **7**. The formation of **3** and **4** is reversible; these species can be driven back quantitatively to a mixture of **1** and **2** by addition of soluble chloride ion. Rates measured in the presence of excess concentrations of **2** and episulfides show some dependence on the concentration of Li^+ (as might be expected for a nucleophilic ring opening raction[16]), but in the presence of constant $[Li^+]$ the reaction is first order in tungsten complex **1** and episulfide but zero order in zirconium complex **2**. As a working hypothesis, therefore, we suggest that the reaction proceeds by an endoergic initial step leading to transient intermediate **5** (L = PMe_3, R = CH_3), and this species is rapidly trapped by Cp_2ZrCl_2 to give complex **6** (L = PMe_3, R = CH_3). Elimination of alkene from this material[13] leads to **7**.

Further information regarding the course of the reaction was obtained by varying the ligands or substituents on the tungsten center and the episulfide. When ethylene sulfide rather than propylene sulfide was used, and the process was monitored carefully by ^{1}H NMR spectrometry, the unsubstituted μ-alkylsulfido-bridged complex **6** (L = PMe_3, R = H) was detected as a fleeting intermediate in the formation of **7**. The stability of **6** can be increased further by adjusting the ligands at the tungsten center. Thus $[(\eta^5\text{-}C_5H_5)(CO)_3W]^-$ (**1**, L = CO) reacted with **2** and ethylene sulfide to form $[(\eta^5\text{-}C_5H_5)(CO)_3W](\mu\text{-}CH_2CH_2\text{-}S)[Zr(Cl)(\eta^5\text{-}C_5H_5)_2]$ (**6**, L = CO; R = H)[17] which is stable enough to isolate and partially purify; this complex can be shown by conventional spectrometric analysis to contain an intact μ-CH_2CH_2-S bridge.[18]

Heterodinuclear complex **7** is quite reactive. The material is extremely sensitive to water, undergoing immediate conversion at room temperature to mononuclear tungsten hydrosulfide $(\eta^5\text{-}C_5H_5)(CO)_2(PMe_3)W(SH)$ (**8**, 24% isolated) and homobimetallic $[Cp_2Zr(Cl)]_2(\mu\text{-}O)$.[19] Complex **8** appears to be more stable than the previously reported[20] CO analogue $(\eta^5\text{-}C_5H_5)(CO)_3W(SH)$. Ultraviolet irradiation induces smooth conversion (NMR analysis) of **7** to homonuclear dimers $[Cp_2Zr]_2(\mu\text{-}S)_2$,[7] $[(\eta^5\text{-}C_5H_5)(CO)_3W][W(CO)(PMe_3)_2(\eta^5\text{-}C_5H_5)]$,[21] and Cp_2ZrCl_2. In analogy to the behavior of the corresponding μ-oxo complex, reaction with acetyl chloride rapidly gives **2** and thioacetate **10** (81% by NMR); once again it is the heteroatom–zirconium, rather than the heteroatom–tungsten, bond that is broken in this reaction. Treatment of **7** with methyllithium gives **9**, contaminated with ca. 5–20% Cp_2ZrMe_2.[22] We have not yet been able to observe reactivity with alkenes and alkynes; efforts to achieve this are continuing.

Acknowledgment. We are grateful for financial support of this work from the National Science Foundation (Grant CHE-872201). J.A.K. acknowledges the award of a President's Fellowship from the University of California.

Supplementary Material Available: Spectroscopic and analytical data for complexes **1**, **3**, **4**, **6**, **7**, and **8**-**10** and details of the structure determination of complex **7**, including experimental description, ORTEP drawing, crystal and data collection parameters, temperature factor expressions (*B*'s), and positional parameters and their estimated standard deviations (17 pages); tables of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

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[15] Complex **3** could not be isolated in pure form but was identified by ^{1}H NMR spectrometry in a mixture containing **3**, **4**, and **2** (see Supplementary Material). In C_6D_6 solution, **4** (isolated and fully characterized) displays a characteristic low-energy CO stretch at 1526 cm^{-1} which, by analogy to the previously reported $Cp(CO)_2W(\mu\text{-}CO)Zr(Me)Cp_2$ (Longato, B.; Martin, B. D.; Norton, J. R.; Anderson, O. P. *Inorg. Chem.* **1985**, *24*, 1389), has been assigned to a reduced bridging CO ligand with oxycarbyne character.

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[17] $[(\eta^5\text{-}C_5H_5)(CO)_3W](\mu\text{-}CH_2CH_2\text{-}S)[Zr(Cl)(\eta^5\text{-}C_5H_5)_2]$ (**6**, L = CO, R = H) is both photochemically and thermally labile; it exhibits two complex sets of multiplets in the ^{1}H NMR spectrum (C_6D_6) at δ 3.53, 2.72 ppm which are assigned to the methylene groups in the bridging chain.

[18] We have not been able to convert **6** (R = H, L = CO) to **7** (L = CO); ethylene is extruded from the bridge of **6** (P = H, L = CO) under photochemical and thermal conditions, but only decomposition products attributable to the transient formation of **7** (vide infra) are observed. We assume that the conditions necessary to decompose **6** (R = H, L = CO) are a bit too stringent to allow **7** (L = CO) to survive.

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Thermal and Photochemical Reactions of $(\eta^5$-Cyclohexadienyl$)_2Fe_2(CO)_4$ in the Presence of 2e$^-$ Donor Ligands: Isolation and Characterization of $(\eta^4$-*C*,*C*′-(Cyclohexadiene$)_2)Fe_2(CO)_4L_2$

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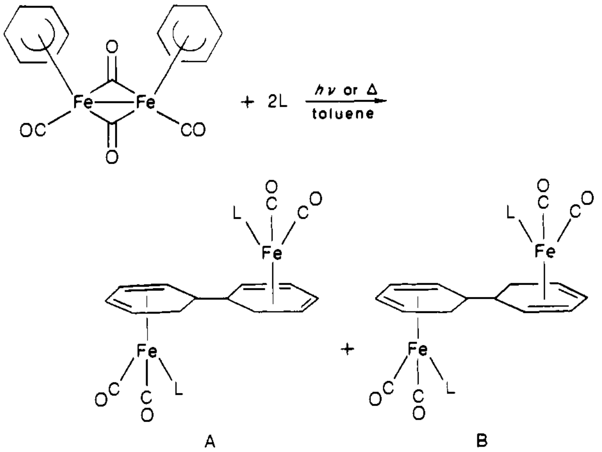
We wish to report thermal and photochemical reactions of $(\eta^5$-cyclohexadienyl$)_2Fe_2(CO)_4$ in the presence of a 2e$^-$ donor ligand L to give the ring–ring coupling products $(\eta^4$-*C*,*C*′-(cyclohexadiene$)_2)Fe_2(CO)_4L_2$ (L = CO, PPh_3) (eq 1). We have recently established the photochemistry of complexes of the type $(\eta^5$-cyclodienyl$)_2Fe_2(CO)_4$ (cyclodienyl = C_5H_5, C_5Me_5, indenyl) in the presence of L.[1,2] The 17e$^-$ radical species formed via light-induced Fe–Fe bond homolysis can react thermally with L to give formally 19e$^-$ radicals. We are interested in the structure and reactivity of such "19e$^-$" species.[1-3]



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[1] Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

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