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 ^1H 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 ^1H 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.

[16] Posner, G. H.; Rogers, D. Z. *J. Am. Chem. Soc.* **1977**, *99*, 8214.

[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 ^1H 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 $(\eta^5\text{-Cyclohexadienyl})_2Fe_2(CO)_4$ in the Presence of $2e^-$ Donor Ligands: Isolation and Characterization of $(\eta^4\text{-}C,C'\text{-}(\text{Cyclohexadiene})_2)Fe_2(CO)_4L_2$

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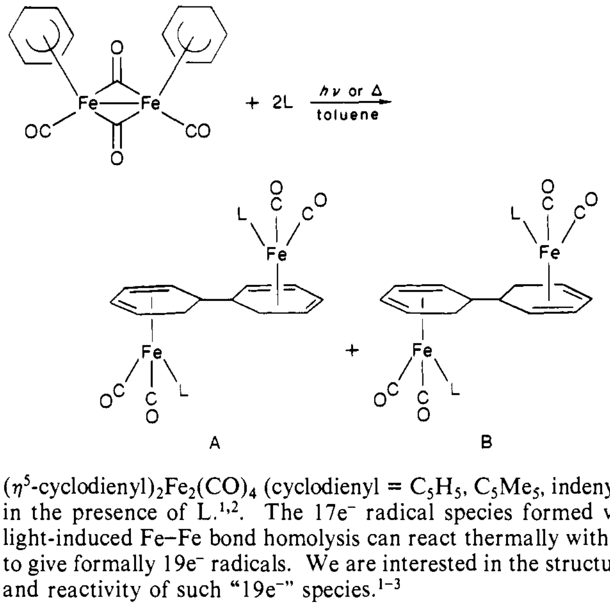
We wish to report thermal and photochemical reactions of $(\eta^5\text{-cyclohexadienyl})_2Fe_2(CO)_4$ in the presence of a $2e^-$ donor ligand L to give the ring–ring coupling products $(\eta^4\text{-}C,C'\text{-}(\text{cyclohexadiene})_2)Fe_2(CO)_4L_2$ ($L = CO$, PPh_3) (eq 1). We have recently established the photochemistry of complexes of the type $(\eta^5\text{-cyclodienyl})_2Fe_2(CO)_4$ (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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[*] Address correspondence to this author.

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Data so far indicate the "19e⁻" (cyclodienyl)Fe(CO)$_2$L to be an Fe-centered radical for cyclodienyl = indenyl, based on EPR,[2] but radical coupling chemistry for cyclodienyl = C_5H_5,[1] C_5Me_5,[1] or indenyl[4] suggests the odd e⁻ is at least partially delocalized onto the cyclodienyl ligands. Despite our attentiveness to possible formation of ring–ring coupled products from coupling of ring-centered radicals from irradiation of (η^5-cyclodienyl)$_2$Fe$_2$(CO)$_4$ in the presence of L, we have found no such coupling chemistry. Similar ring–ring coupling chemistry for some redox generated 19e⁻ cyclodienyl complexes, however, has been observed,[5,6a] including coupling of (cyclohexadienyl)Fe(CO)$_3$.[6] Our new results summarized by eq 1 show that the "19e⁻" species (cyclohexadienyl)Fe(CO)$_2$L do have substantial radical character in the hydrocarbon ligand.

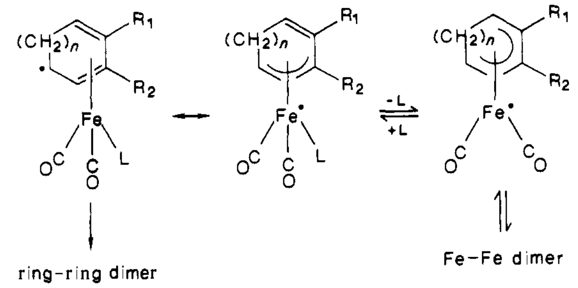
The Fe–Fe bond of (η^5-cyclohexadienyl)$_2$Fe$_2$(CO)$_4$[7] is weak, as evidenced by reaction with BzBr at 298 K to give the Br atom abstraction product, eq 2. Presumably, reaction occurs via the 17e⁻ radical present in a pre-equilibrium as shown in eq 3. In pure toluene containing (η^5-cyclohexadienyl)$_2$Fe$_2$(CO)$_4$ we find a very weak EPR signal (g = 2.0455)[8] attributed to (cyclohexadienyl)Fe(CO)$_2$, which has no detectable H-hyperfine, in contrast to the 17e⁻ (η^3-C_3H_5)Fe(CO)$_3$.[9] This signal declines in intensity upon lowering the temperature, consistent with a shift in the equilibrium (to the Fe–Fe bonded species) shown in eq 3.

$$(\eta^5\text{-cyclohexadienyl})_2\mathrm{Fe_2(CO)_4} \xrightarrow[\text{toluene, } t_{1/2} \sim 30 \text{ min}]{0.5 \text{ M BzBr, 298 K}} 2(\eta^5\text{-cyclohexadienyl})\mathrm{Fe(CO)_2Br} \quad (2)$$

$$(\eta^5\text{-cyclohexadienyl})_2\mathrm{Fe_2(CO)_4} \rightleftarrows (\text{cyclohexadienyl})\mathrm{Fe(CO)_2} \quad (3)$$

Addition of CO to a 298 K toluene solution containing 2 mM (η^5-cyclohexadienyl)$_2$Fe$_2$(CO)$_4$ results in a diminution of the EPR signal, consistent with reaction of the 17e⁻ species with CO. An isolable product slowly ($t_{1/2}$ ~ 1.5 h) forms, as revealed by IR spectral changes, at the expense of the starting material. The same IR spectral changes (Figure 1) occur when the (η^5-cyclohexadienyl)$_2$Fe$_2$(CO)$_4$ is irradiated (λ > 500 nm) in toluene at 298 K under ~1 atm of CO, but the rate of reaction can be much faster depending on the light intensity. Under the conditions used the photoreaction at 298 K can be effected in <10 min. Photoexcitation of (η^5-cyclohexadienyl)$_2$Fe$_2$(CO)$_4$ results in formation of the 17e⁻ radical and effectively drives the equilibrium shown in eq 3 to the radical species.

Scheme I



Products from thermal or photochemical reaction of (η^5-cyclohexadienyl)$_2$Fe$_2$(CO)$_4$ with CO are the same and have been isolated by chromatography on Al_2O_3 eluting with hexanes. The isomeric products formed in about a 1:1 ratio are shown in eq 1 and have been characterized by ^{1}H and ^{13}C NMR,[10] IR, and X-ray crystallography.[11] Upon slow evaporation of the alkane solvent containing the products a pale-yellow solid of two crystal morphologies results: small needles (too small for X-ray structure determination) and plates suitable for X-ray structure determination. The crystals were separated manually under a microscope and the plates yielded the structure shown in Figure 2,[11] corresponding to isomer A in eq 1. The two (cyclohexadienyl)Fe(CO)$_3$ fragments are coupled in an exo–exo manner via the cyclohexadienyl ligands in accord with an intermolecular coupling process. The needles and plates give remarkably similar, but different, NMR spectral features[10] consistent with the conclusion that the needles are isomer B and the plates are isomer A. Variable-temperature ^{1}H NMR from 25 to 105 °C shows no sign of interconversion between A and B, consistent with the conclusion that A and B are not conformational isomers. The IR in the CO region is typical of (η^4-diene)Fe(CO)$_3$.[12] The ring–ring coupled species fully characterized here have been claimed to form via reduction of (η^5-cyclohexadienyl)Fe(CO)$_3^+$.[6] Similar to results upon reaction with CO, we find that thermal or photochemical reaction of (η^5-cyclohexadienyl)$_2$Fe$_2$(CO)$_4$ with PPh$_3$ yields two ring–ring coupled isomers.[13] For both L = PPh$_3$ and L = CO the chemistry represented in eq 1 is essentially quantitative. We do not find thermal or photochemical (λ > 500 nm) substitution of CO by PPh$_3$, as might be expected from results for other (η^5-cyclodienyl)$_2$Fe$_2$(CO)$_4$ complexes.[14]

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[10] Varian 300 MHz FT-NMR spectrometer. ^{1}H NMR (C_6D_6): isomer A, δ 4.49–4.64 (m, 4 H), 2.49 (m, 4 H), ~1.40 (m, 4 H), 0.49 (d, 2 H); isomer B, δ 4.49–4.64 (m, 4 H), 2.35–2.52 (m, 4 H), 1.32–1.62 (m, 4 H), 0.64 (d, 2 H). ^{13}C NMR (C_6D_6): isomer A, δ 212.5, 85.3, 85.0, 65.3, 60.0, 45.8, 28.0; isomer B, δ 212.5, 85.3, 85.0, 64.8, 59.8, 45.5, 27.6.

[11] Isomer A in eq 1, L = CO, crystallizes out in a monoclinic crystal system, space group $C2/c$, with Z = 8 in a unit cell of dimensions a = 23.998 (3) Å, b = 7.088 (1) Å, c = 21.038 (7) Å, β = 105.24 (2)°, V = 3453 (2) Å^3. Data, in the range 3.0° < 2θ < 55.0°, were collected at 23 °C on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation. Final residual indices were R_1 = 0.044 and R_2 = 0.045 in the final cycle of a full-matrix least-squares refinement of the data.

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[13] (η^5-Cyclohexadienyl)$_2$Fe$_2$(CO)$_4$ (0.1 g) and PPh$_3$ (0.15 g) were dissolved in 25 mL of dry toluene and irradiated with >500-nm light. The reaction was complete within 15 min and the red solution became yellow. The solution was concentrated under vacuum to ~3 mL and chromatographed on Al_2O_3. Elution with hexanes removed excess PPh$_3$, and subsequent elution with ether/hexanes (1:2) gave a orange-yellow band which was collected. The solvent was removed in vacuo yielding pale-yellow crystals identified by ^{1}H NMR to be the ether adduct (η^4-C,C'-(cyclohexadiene)$_2$)Fe$_2$(CO)$_4$(PPh$_3$)$_2$·Et$_2$O. Pure product was obtained by dissolving the ether adduct in a small quantity of chloroform and removing the solvent under vacuum. IR in hexanes: 1976, 1923 cm^{-1}. NMR shows two species to be present, A and B of eq 1: ^{1}H NMR (CDCl$_3$): δ 7.38 (m, 30 H), 4.72 (m, 4 H), 2.09–2.50 (m, 4 H), 1.60–1.90 (m, 4 H), 0.90 (m, 2 H). ^{13}C NMR (CDCl$_3$): two isomers, δ 219.9, 219.6, 219.2, 219.0, 136.5, 136.0, 133.1, 133.0, 129.5, 128.2, 128.1, 84.8/84.5, 84.3/84.0, 77.2/64.1, 59.2/58.4, 46.9/46.2, 29.1/28.7.

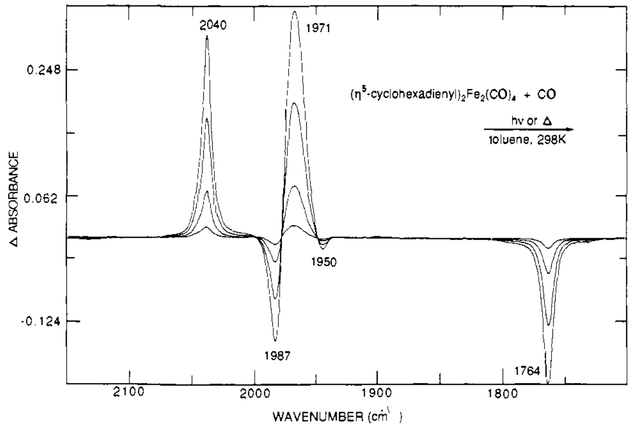

Figure 1. IR spectral changes accompanying near-UV irradiation of 2 mM (η^5-cyclohexadienyl)$_2$Fe$_2$(CO)$_4$ in a CO-saturated toluene solution at 298 K. The negative peaks indicate the consumption of starting material, while the positive peaks at 2040, 1971 cm^{-1} correspond to formation of (η^4-C,C′-(cyclohexadiene)$_2$)Fe$_2$(CO)$_6$ (eq 1).

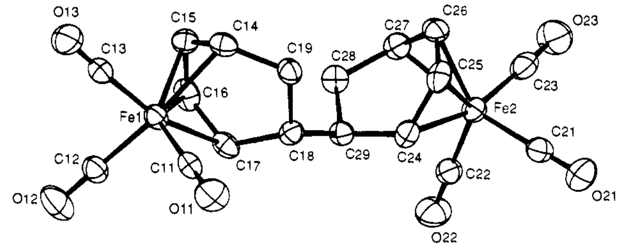

Figure 2. ORTEP diagram of isomer A of eq 1, showing the atom labeling scheme and 40% probability ellipsoids. Selected bond distances (Å): Fe1–C11 = 1.795 (6); Fe1–C12 = 1.786 (6); Fe1–C13 = 1.780 (7); Fe1–C14 = 2.109 (5); Fe1–C15 = 2.033 (6); Fe1–C16 = 2.057 (6); Fe1–C17 = 2.134 (6); C11–O11 = 1.125 (7); C12–O12 = 1.144 (6); C13–O13 = 1.148 (7); C14–C15 = 1.414 (8); C14–C19 = 1.517 (8); C15–C16 = 1.400 (8); C16–C17 = 1.411 (8), C17–C18 = 1.528 (7); C18–C19 = 1.534 (7); C18–C29 = 1.542 (7). The dihedral angle between the C24–C25–C26–C27 plane and the C24–C29–C28–C27 plane is 37.91°.

Scheme I summarizes our current understanding of the chemistry reported here. The ring–ring coupling products signal radical character in the hydrocarbon ligand of the "19e$^-$" (cyclohexadienyl)Fe(CO)$_2$L species. The lack of ring–ring coupled products from other (cyclodienyl)Fe(CO)$_2$L systems studied[1,2] presumably stems from the fact that these species are mainly Fe-centered radicals. Further studies are in progress to establish factors controlling whether 19e$^-$ radicals are metal- or ligand-centered, because it is appreciated that the coupling chemistry does not necessarily characterize the electron distribution of the radicals.[3e,f]

Acknowledgment. We thank the National Science Foundation for support of this research. We also thank Dr. William Davis for collecting the data and for helping to solve the X-ray structure.

Supplementary Material Available: Listing of experimental details of the X-ray study of Fe$_2$(CO)$_6$(C$_{12}$H$_{14}$), final positional parameters, thermal parameters, interatomic distances, and angles (10 pages). Ordering information is given on any current masthead page.

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The Tetramethyleneethane Radical Cation. An ESR and ENDOR Study[1]

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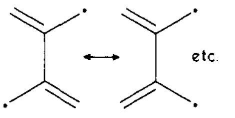
Tetramethyleneethane (**1**) is an intriguing alternant π-system of eight carbon centers for which a Kekulé formula with less than two unpaired electrons cannot be drawn.[2] The radical anion **1**$^{\bullet-}$ was prepared from 1,2-dimethylenebutane (**2**) in liquid ammonia some time ago.[3] More recently, an ESR study of the neutral **1**, using the azo precursor **3**, has clearly established that this molecule is a ground-state triplet (**1**$^{\bullet\bullet}$).[2] Here, we report on the still missing third member of the series, the radical cation **1**$^{\bullet+}$, which is obtained by opening of the two rings in the radical cation of bicyclopropylidene (**4**).[4]



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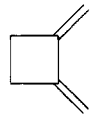

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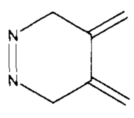

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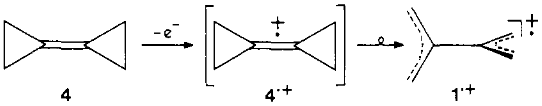

4 **4**$^{\bullet+}$ **1**$^{\bullet+}$

Upon γ-irradiation of **4** in a CF$_3$CCl$_3$ matrix at 77 K,[5] an ESR spectrum was observed which consisted of nine broad hyperfine components spaced by ca. 0.75 mT (g = 2.0029 ± 0.0002). Figure 1 shows this spectrum taken at a higher temperature, 140 K, required to achieve a better resolution. Additional information was provided by ENDOR spectroscopy, of which the use for radical cations in freon matrices has recently been initiated by the Basel research group.[1] In the present study, the corresponding proton ENDOR spectrum exhibited two essentially isotropic signals at 25.83 and 24.58 MHz, i.e., at positions given by $\nu_H + |a/2|$, where ν_H and $a/2$ stand for the free proton frequency (14.56 MHz) and half the coupling constant (in MHz), respectively.[6] These signals are reproduced at the top of Figure 1; their low-frequency counterparts, positioned at $\nu_H - |a/2|$, were too weak to be detected in our ENDOR experiment.

The ESR and ENDOR spectra are readily analyzed in terms of two isotropic coupling constants of 0.805 ± 0.010 and 0.716 ± 0.010 mT, each due to a set of four equivalent protons. These hyperfine data cannot be attributed to the primary radical cation **4**$^{\bullet+}$ which represents a tetraalkyl-substituted ethene that is ionized by an electron removal from the π-system of the double bond.[7]

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† Universität Basel.

‡ Universität Hamburg.

(1) This communication is part 3 of "Applications of ENDOR Spectroscopy to Radical Cations in Freon Matrices". Part 2: Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* **1988**, *71*, 1498. Part 1: Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* **1988**, *71*, 1065.

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