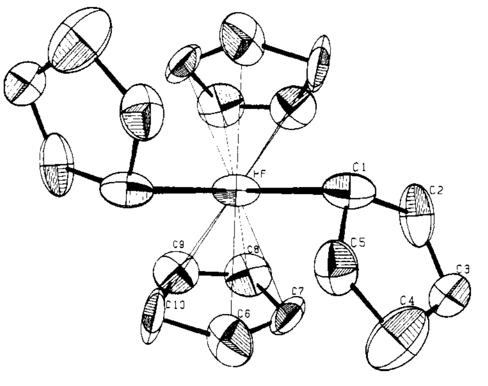

Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Hf(\eta^1\text{-}C_5H_5)_2$ with the atoms represented by their 50% probability ellipsoids for thermal motion. The hafnium atom resides on a crystallographic twofold axis.

Tetracyclopentadienylhafnium was prepared by the reaction of $(\eta^5\text{-}C_5H_5)_2HfCl_2$ with NaC_5H_5 in diethyl ether. Crystals appropriate for the X-ray diffraction study were grown by the slow cooling of a toluene solution. A yellow crystal of the compound was sealed under a N_2 atmosphere in a thin-walled capillary, and contrary to a previous report no decomposition in the X-ray beam was observed.[6]

The Hf-C(σ) bond length, 2.38 (2) Å, is considerably larger than the 2.24 (1) Å value found for the sp^3 carbon in $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$.[7] It is, however, significantly shorter than that found in $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$: 2.447 (6) Å. The contraction can be ascribed either to steric considerations or to the 16- vs. 18-electron configurations in $(C_5H_5)_4Hf$ and $(C_5H_5)_4Zr$, respectively.[8] The Hf-C bond vector makes an angle of 66° with the plane of the $\eta^1\text{-}C_5H_5$ ring.

The Hf-C(π) distances range from 2.48 (3) to 2.57 (3) Å. The 2.50 (4) Å average is slightly larger than normal but is of no consequence because of the high esd's. More important, the ligand is planar to within 0.02 Å. (The σ-bonded cyclopentadienyl ligand is planar to 0.03 Å.)

Bond angles which involve the ring centroids and the σ-bonded carbon atoms agree rather well with those found in $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$: centroid-Hf-centroid′ = 130° (129.9° for the Ti analogue), centroid-Hf-C(1)′ = 108° average (108°), and C(1)-Hf-C(1)′ = 88 (1)° (86.3°).

Acknowledgment. We are grateful to the National Science Foundation for support of this research program.

Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, thermal parameters, and observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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(6) The unit cell parameters are $a = 9.790$ (5), $c = 16.211$ (8) Å; $D_c = 1.88$ g cm^{-3} for $Z = 4$. Least-squares refinement based on 531 observed reflections led to a final R value of 0.040. Hydrogen atoms were included with fixed contributions, and all nonhydrogen atoms were refined with anisotropic thermal parameters.

(7) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Inorg. Chem.*, in press.

(8) The formulation of $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$ as an 18-electron situation has been noted by Lauher and Hoffmann: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

Manifestations of Sulfur to Sulfur Through-Bond Interactions in Complex Ion Spectra

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In a previous communication,[1] through-space electronic delocalization in mixed-valence complexes of ruthenium ammines with 1,5-dithiocane as bridging ligand was demonstrated. We now report results for a ligand in which the character of the molecular orbitals is exclusively σ, but in which the sulfur lone pairs do not overlap directly.

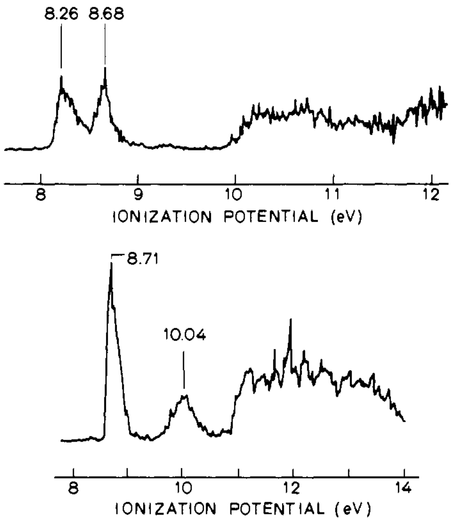
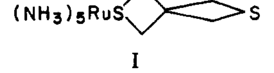


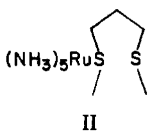
Figure 1. He I photoelectron spectra of 1,5-dithiocane (top) and 2,6-dithiaspiro[3.3]heptane.

2,6-Dithiaspiro[3·3]heptane was synthesized by the method of Backer:[2] mp 31-32 °C (lit;[2] 31.5 °C); ^1H NMR (CCl_4) δ 3.3 (s, 8 H), ^{13}C NMR ($CDCl_3$) δ 52.32 (s), 40.54, 39.77, 39.00 (t) (Me_4Si = 0 ppm). (The triplet was obtained by irradiation near 0 ppm in the ^1H spectrum and corresponds to the disubstituted carbon. The singlet corresponds to the tetrasubstituted carbon.)[3]

Pentaammine(2,6-dithiaspiro[3·3]heptane)ruthenium(II), I, and pentaammine(2,6-dithiaheptane)ruthenium(II), II (included for purposes of comparison), were synthesized by reaction of a 10-fold excess of ligand with 200 mg of $[(NH_3)_5RuH_2O](PF_6)_2$[4] in 5 mL of deaerated acetone and were worked up as previously described.[1]



I



II

The binuclear species were produced by the reaction of the mononuclear species with a 5% excess of $[(NH_3)_5RuH_2O](PF_6)_2$ in the minimum volume of acetone needed to provide for a homogeneous reaction system. μ-(2,6-Dithiaspiro[3·3]heptane)-bis-[*trans*-(isonicotinamide)tetraammineruthenium(II)], III, was synthesized by combining 200 mg of *trans*-$[isn(NH_3)_4RuSO_4]Cl$[5] and 200 mg of the ligand in a minimum of argon-deaerated 0.10 M HCl and adding acetone dropwise until the cloud point. A few pieces of Zn/Hg amalgam were then added, and after 3 h in the dark under continuous argon flow, the mixture was filtered and solid NH_4PF_6 added. The orange solid was collected by filtration, washed with ethanol and ether, and purified by reprecipitation from a minimum of 0.10 M HCl. A single product with the elution characteristics of a tetrapositive ion was found on chromatography on Dowex 50W-X2 ion exchange resin. The overall yield was ~20%.

Analyses were performed on the hexafluorophosphate salts containing ruthenium(II). Anal. Calcd for $[(NH_3)_5Ru(C_5H_8S_2)(PF_6)_2$: C, 9.87; H, 3.81; H, 11.51; S, 10.54; Ru, 16.62; F, 37.47. Found: C, 9.54; H, 3.77; N, 11.17; S, 10.28; Ru, 16.4; F, 36.9. Calcd for $[(NH_3)_5Ru(C_5H_{12}S_2)](PF_6)_2$: C, 9.81; H, 4.44; N, 11.44; S, 10.47; Ru, 16.51; F, 37.22. Found: C, 8.58; H, 4.26; N, 11.58; 10.89; Ru, 16.6; F, 37.6. Calcd for $[((NH_3)_5Ru)_2$-

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(1) Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1978**, *100*, 1635.

(2) Backer, H. J. *Recr. Trav. Chim. Pays-Bas* **1933**, *502.*

(3) We thank L. Durham for this measurement.

(4) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

(5) Isied, S. S. Ph.D. Dissertation, Stanford University, 1972.

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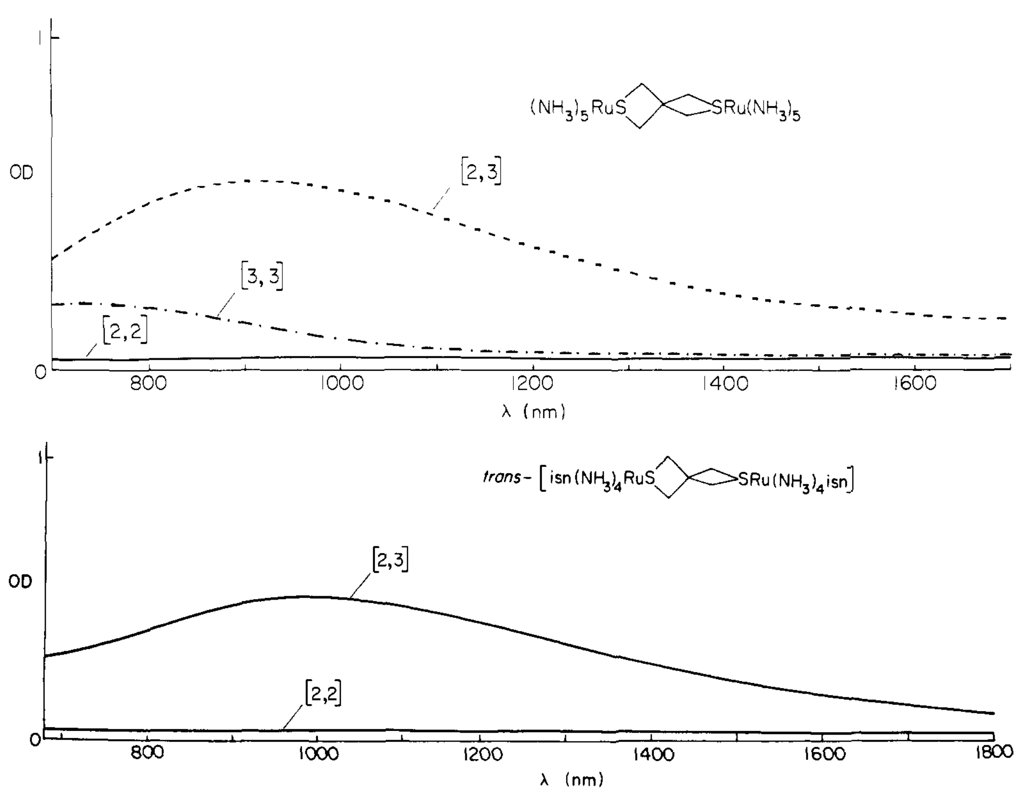

Figure 2. Near-Infrared spectra for binuclear complexes. For pentaammine complex: 0.24 M DCl, 2-cm quartz cells, 25 °C, [Ru] = 5.81 × 10^{-3} M. For the *trans*-isnoctaammine complex: 0.24 M DCl, 2-cm quartz cells, 25 °C, [Ru] = 5.20 × 10^{-3} M. The [3.3] species is not included due to its rapid decomposition into highly colored products.

$(C_5H_8S_2)](PF_6)_4$: C, 5.53; H, 3.53; N, 12.96; S, 5.91; Ru 18.63. Found: C, 6.21; H, 3.64; N, 12.18; S, 6.44; Ru, 18.9. Calcd for $[((NH_3)_5Ru)_2(C_5H_{12}S_2)](PF_6)_4$: C, 5.51; H, 3.89; N, 12.91; S, 5.89; Ru, 18.56; F 41.86. Found: C, 5.19; H, 3.80; N, 12.41; S, 5.69; Ru, 18.13; F, 41.1. Calcd for $[((NH_3)_5Ru)_2(C_{17}H_{20}N_2S_2O_2)](PF_6)_4$: C, 15.77; H, 3.43; N, 12.98; S, 4.95; Ru, 15.61; F, 35.21. Found: C, 15.63; H, 3.45; N, 12.54; S, 5.25; Ru, 15.3; F, 34.85.

A ^1H NMR spectrum of the mononuclear complex I in acetone-d_6 demonstrated that the singlet at 3.15 ppm vs. Me_4Si observed in the ligand spectrum had shifted to 3.45 ppm and had become an unsymmetrical doublet ($J \simeq 1$ Hz). The cis and trans ammonia protons registered as broad singlets at 2.45 and 1.85 ppm in a 4:1 ratio. A single reversible wave at +575 mV vs. NHE (0.1 M HCl, 25 °C) was observed by cyclic voltammetry. Oxidation of I to a 3+ ion by 1 equiv of Ce(IV) in 0.2 M HCl produced a single, symmetric ligand-to-metal charge-transfer band at 458 nm (ϵ 2.2 × 10^2 M^{-1} cm^{-1}). A band in this region is also observed in a similarly oxidized solution of $[(NH_3)_5RuS(CH_3)_2]^{3+}$,[6] λ_{max} 452 nm (ϵ 3.0 × 10^2 M^{-1} cm^{-1}). The existence of a single visible transition in the spectrum of the dithioether implies that there is minimal direct sulfur lone-pair ground-state overlap and that the transition originates from a nonbonding pair.[1] This is confirmed by comparison of the He I photoelectron spectra of 2,6-dithiaspiro[3·3]heptane and 1,5-dithiocane (Figure 1).[7] For the latter, the ratio of band width to height indicates[8] that the two equal intensity bands of similar shape at 8.26 and 8.68 eV originate, respectively, from ionizations of the antisymmetric and symmetric combinations of sulfur lone pair orbitals. In the former, only a single ionization (8.71 eV) in the expected energy regions is seen.

When I is converted to the binuclear species, the resultant complex shows a single broad cyclic voltammetric wave with an abnormally large peak-to-peak separation (20 mV greater than for $Ru(NH_3)_6^{3+/2+}$ under the same conditions). This kind of profile shows that the successive redox stages are governed by values of E_f which differ only slightly. The superposition of two such waves results in an abnormal peak-to-peak separation. The value of the comproportionation constant[9] is likely of the order of 10. In a half-oxidized sample of the [2.2], where the concentration of the [2.3] is at a maximum, a single band appears in the visible region (λ_{max} 452 nm (ϵ 2.6 × 10^2 M^{-1} cm^{-1})) and a band appears in the near-infrared region (λ_{max} 910 nm (ϵ based on total ruthenium 43 ± 2 M^{-1} cm^{-1}; $f = 1.40 \pm 0.1 \times 10^{-3}$) which slowly decreased in intensity with time (Figure 2a). For the mixed-valence ion based on III (E_f = +800 mV vs. NHE, $K_{com} \sim 10$), a band in the near-infrared occurs at λ_{max} 1008 nm (ϵ 48 M^{-1} cm^{-1}) (movement of the band energy to lower values on trans substitution by π acids has also been observed for pyrazine as a bridging ligand).[10] For both complexes, adding a second oxidizing equivalent does not cause absorption in the near-IR to vanish entirely, but a small non-Gaussian band appears at ~ 700 nm. Formation of decomposition products with similar absorption characteristics (λ_{max} 700 nme is common to the ions $(NH_3)_5Ru(thiocyclobutane)^{3+}$,[11] $(NH_3)_5Ru(1,3\text{-dithietane})^{3+}$,[12] and I.

For the binuclear complex based on II, which contains the same number of carbon steps between the thioethers as does the binuclear based on I, a band in the near-IR was observed at λ_{max} 755 nm (ϵ 5 M^{-1} cm^{-1}), $f = 0.1 \times 10^{-3}$, $K_{com} \leq 10$.

As to the mechanism of electron delocalization, through-bond interactions must be considered if through-space interactions are discounted, as seems appropriate, owing to the large metal-to-metal separation, estimated as about 9 Å. When combinations of Walsh orbitals are taken and the MO shapes and energies calculated for spiro[2·2]pentane[14] (also of D_{2d} symmetry) are used, the highest

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(6) Stein, C. A.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1168.

(7) We are grateful to Professor D. C. Frost and N. P. C. Westwood, University of British Columbia, for these measurements.

(8) Bock, H.; Ramsey, B. G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 734 and references.

(9) Richardson, D. E.; Taube, H. *Inorg. Chem.*, submitted for publication.

(10) Tom, G. M. Ph.D. Dissertation, Stanford University, 1975.

(11) Stein, C. A.; Lewis, N., work in progress.

(12) Stein, C. A.; Block, E.; Taube, H., to be submitted to *Inorg. Chem.*

(13) Jorgenson, W. L.; Salem, L. "The Organic Chemists Book of Orbitals"; Academic Press: New York, 1973; p 168.

(14) Hoffmann, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, 93, 5699.

bonding orbital (b_2) is delocalized (and may account for the peak in the PES at 10.07 eV). This orbital can interact with the πd orbital of the metal; it and its antibonding counterpart may play some role in the delocalization of electron density. If the contribution of the bonding level dominated, III would be expected to show a more intense band than II, because isonicotinamide, by making Ru(III) more oxidizing, would cause a stronger admixture of the Ru(III)·L^+·Ru(III) state into the ground state.

Since a significant fraction of the nominally [2.3] species is present in the isovalent forms, the extinction coefficient of the mixed-valence molecule may be as high as 60 or 70, suggesting that elecron transfer within the molecule, while nonadiabatic, is not markedly so.[15]

Acknowledgment. Support for this work through Grant GM13638-14 from the National Institutes of Health is gratefully acknowledged.

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[15] Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

Photochemistry of Transition-Metal Polyhydrides: Dimerization of $ReH_5(PMe_2Ph)_3$ Following Photodissociation of Phosphine†

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Among low-valent metals, those at the center of the transition series (groups 6, 7, and 8) constitute a group where the effective atomic number concept rules most firmly. Moreover, within a group it appears that the heavier representatives have the greatest aversion to coordinative unsaturation. It is thus predictable that monomeric 16-electron rhenium complexes should be (1) difficult to produce and, once formed, (2) highly reactive. We report here the photoassisted production of $H_5Re(PMe_2Ph)_2$ by an unprecedented photoextrusion of phosphine in preference to dihydrogen. We demonstrate a regioselective and catalytic activation of arene C–H bonds by 16-electron $H_5Re(PMe_2Ph)_2$ and also the efficient condensation of this fragment to a new class of rhenium polyhydride dimers.

Photolysis[1] of a benzene solution of colorless $H_5Re(PMe_2Ph)_3$[2] results in rapid appearance of a dark red color due to a new polyhydride dimer of formula $H_6Re_2P_5$ ($P \equiv PMe_2Ph$). In a closed vessel of limited head space, H_7ReP_2[2,3,4a] is also a detectable product, but it, unlike $H_6Re_2P_5$, is rather photosensitive (see below).

We have sought to establish the primary chemical product of irradiation, although the existing literature[5,6] indicates that L_mMH_n ($n \geq 2$) complexes generally undergo photoextrusion of dihydrogen. We consider the two processes shown in eq 1 and 2. Irradiation

$$H_5ReP_3 \overset{h\nu}{\rightleftharpoons} H_3ReP_3 + H_2 \tag{1}$$

$$H_5ReP_3 \overset{h\nu}{\rightleftharpoons} H_5ReP_2 + P \tag{2}$$

of a benzene solution of H_5ReP_3 in the presence of 3 equiv of PMe_2Ph completely quenches dimerization; no change is evident in the solution composition after irradiation. Additionally, irradiation of a C_6D_6 solution of D_5ReP_3 containing excess free PMe_2Ph under a purge of H_2 results in no incorporation of protium bound directly to rhenium. Finally, irradiation of a benzene solution of $H_5Re(PMe_2Ph)_3$ containing 6 equiv of PEt_2Ph shows (^{31}P NMR) production of all possible species of the type $H_5Re(PMe_2Ph)_{3-n}(PEt_2Ph)_n$, along with free PMe_2Ph. This photoinduced[7] phosphine exchange,[8] along with the preceding two experiments, indicates that irradiation effects dissociation of phosphine (eq 2). Photoextrusion of hydrogen (eq 1) is not viable even as a second, independent photodecay pathway. This result is highly significant in that the photoproduct thus conserves the inherently more interesting hydride ligand.

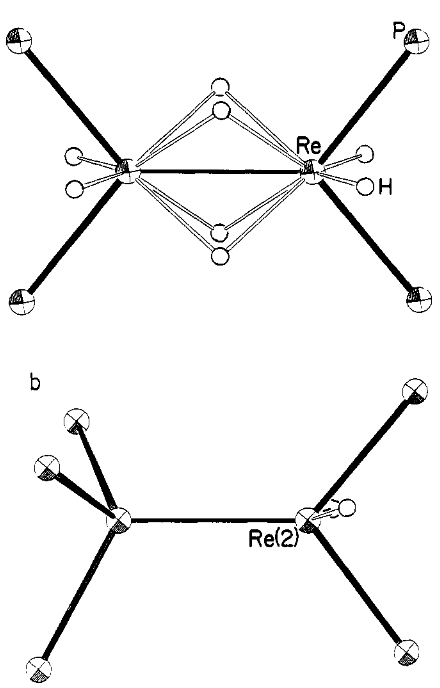
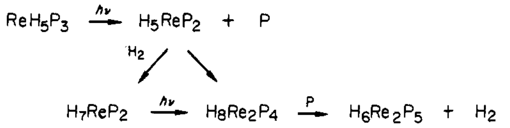


Figure 1. ORTEP drawings of the inner coordination spheres of (a) $H_8Re_2(PEt_2Ph)_4$[4] and (b) $H_6Re_2(PMe_2Ph)_5$, oriented to show the structural relationship between the two.[16] Note that only two of the six metal-bound hydrogens have been located in $H_6Re_2(PMe_2Ph)_5$. These yield a terminal ligand environment about Re(2) which closely mimics that in $H_8Re_2(PEt_2Ph)_4$.

Scheme I



The photodimerization (eq 3) which occurs in the absence of added phosphine is enhanced in rate when carried out under a

$$2H_5ReP_3 \xrightarrow{h\nu} H_6Re_2P_5 + 2H_2 + P \tag{3}$$

purge of H_2. Under these conditions, H_7ReP_2 achieves considerably higher concentrations at intermediate stages of the photolysis. Conversely, an argon purge during photolysis slows (but does not completely prevent) dimer formation; this establishes the existence of a direct path from H_5ReP_2 to the dimer. We interpret these results in terms of Scheme I, which invokes both a direct route to dimer from H_5ReP_2 and also dimerization of H_7ReL_2 by a secondary photolysis.[9] If irradiation is carried out in hexane,

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† Contribution No. 3552.

[1] Hanovia 550-W medium-pressure Hg lamp, through Pyrex glass.

[2] Douglas, P. G.; Shaw, B. L. *Inorg. Synth.* **1977**, *17*, 64.

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[7] This same solution held at 80 °C for 3 h showed no evidence (^{31}P NMR) for phosphine exchange.

[8] We view this experiment as equivalent to an isotopic exchange. It is essentially entropically driven: when the mixture of complexes $H_5Re(PMe_2Ph)_{3-n}(PEt_2Ph)_n$, separated from free PEt_2Ph, is irradiated in the presence of added PMe_2Ph, complete regeneration of $H_5Re(PMe_2Ph)_3$ is effected.

[9] H_7ReP_2 is thermally stable to dimerization under our photochemical reaction conditions. The photodimerization of H_7ReP_2 has been verified independently.

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