4070 Organometallics 1991, 10, 4070–4073

$Mo)(S_2CH)(S_2CH_2)(MoCp^*)]I$, 136630-22-3; $[(Cp^*Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]CF_3SO_3$, 136630-24-5; $[Cp^*Mo(\mu\text{-}S)]_2S_2CH_2$, 124944-97-4; CH_2Cl_2, 75-09-2.

Supplementary Material Available: Complete listings of crystallographic data, bond distances and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for 1 (9 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

C–H Cleavage versus N–N Cleavage in μ_3-η^2-Azoalkane Ligands on the $M_3(CO)_9$ Clusters of Iron, Ruthenium, and Osmium

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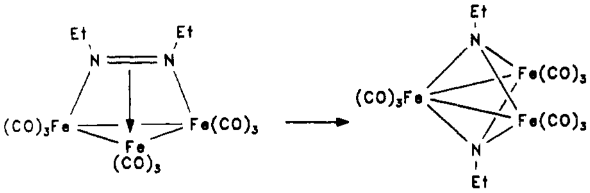
Summary: While thermal treatment of the cluster $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}N_2Et_2)$ leads to N–N cleavage and formation of the isomeric cluster $Fe_3(CO)_9(\mu_3\text{-}NEt)_2$, the new ruthenium cluster $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}N_2Et_2)$ undergoes a different thermal rearrangement. One hydrogen atom of an *N*-ethyl group is transferred to the metal core, and the isomeric cluster $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}EtN{-}N{=}CH{-}CH_3)$ containing a hydrazone-type ligand is formed. Both isomeric ruthenium clusters can be hydrogenated to yield $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}EtN\text{-}NHEt)$ containing a hydrazine-type ligand. $Os_3(CO)_{12}$ and azoethane yield only the hydrazone derivative $HOs_3(CO)_9(\mu_3\text{-}\eta^2\text{-}EtN{-}N{=}CH{-}CH_3)$. The crystal structures of the Os_3–hydrazone and of the Ru_3–hydrazine-type clusters have been determined.

If clusters are to become synthons in preparative chemistry it will have to be demonstrated that they can activate organic substrates efficiently and in a new fashion. Accordingly, ligand sphere reactivity of organometallic clusters is of current interest.[1] A prominent substrate for investigations of this kind is the alkyne ligand.[2] Less well investigated objects for such studies are the related ligand systems with C–N and N–N multiple bonds (nitriles,[3] isonitriles,[4] azoalkanes[5]).

We have demonstrated isoelectronic relations between clusters with face-bridging alkyne, nitrile, and azoalkane ligands,[6] and we have used cluster expansion methods for the synthesis of all three compound types.[7] For reactivity investigations we have focused on the cluster-bound azoalkane ligand. We could show that it can behave like an alkyne ligand in its N–N cleavage reaction[8] as well as in its combination with other organic fragments to form organic products.[9] We have now tried to extend these investigations, previously done on the $Fe_3(CO)_9$ cluster, to corresponding ruthenium and osmium clusters with azoalkane ligands. This paper reports our first results of these studies.

Prior to us Bruce[10] and Gladfelter[11] had shown that azoarenes in contact with ruthenium carbonyls are cleaved to form nitrene-bridged clusters, similar to the azoalkane → nitrene cleavage 1 → 2 observed by us on the iron cluster.[8] This cleavage occurs so easily that azoalkane- or azoarene-bridged ruthenium clusters were unknown until recently.[7] It was therefore not unexpected for us to find that the azoethane Ru_3 cluster 3 is rather labile. However, to our surprise, the lability of 3, is not due to its N-N cleavage but to alternative C–H cleavage, and so far we have not been able to make the ethylnitrene-bridged ruthenium cluster analogous to 2.



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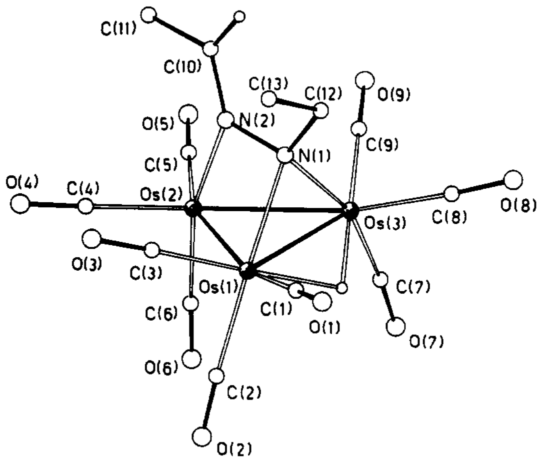

Figure 1. Molecular structure of 4. Important bond lengths (Å): Os1–Os2 2.764 (1), Os1–Os3 2.794 (1), Os2–Os3 2.768 (1), Os1–N1 2.15 (1), Os2–N2 2.12 (1), Os3–N1 2.18 (1), N1–N2 1.41 (2), N1–C12 1.48 (2), N2–C10 1.29 (2), C10–C11 1.48 (2), C12–C13 1.50 (3).

Cluster 3 was obtained by irradiation of $Ru_3(CO)_{12}$ with N_2Et_2 in moderate yield and was identified by its IR and NMR data, which are analogous to those of 1.[8] Thermal treatment of 3 in refluxing toluene resulted mostly in decomposition, but the major isolable product was 5. Lower reaction temperatures or attempts to induce rearrangement by irradiation or oxidative treatment did not improve the yield of 5 or any other product. Attempts to produce the osmium analogue of 3 from $Os_3(CO)_{12}$, $Os_3(CO)_{10}(CH_3CN)_2$, or $H_2Os_3(CO)_{10}$ failed. However the high-temperature reaction of $Os_3(CO)_{12}$ with N_2Et_2 led directly to small yields of 4, the osmium analogue of 5. The capping ligand in the clusters 4 and 5 can be derived from a hydrazone. Actually, Süss-Fink has recently prepared analogous Ru_3 clusters from $Ru_3(CO)_{12}$ and hydrazones.[12]

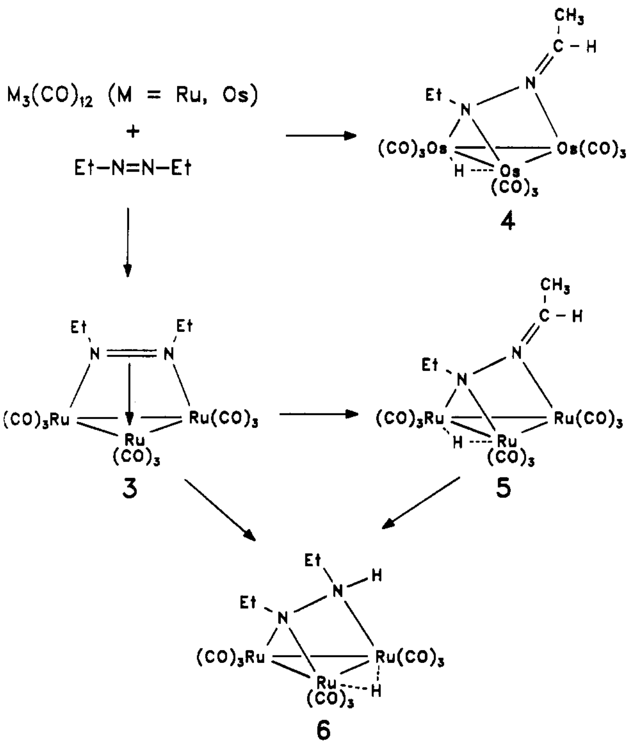

Table I. Experimental Data for the X-ray Diffraction Study on the Complexes 4 and 6

	4	6
mol formula	$C_{13}H_{10}N_2O_9Os_3$	$C_{13}H_{12}N_2O_9Ru_3$
mol wt	908.83	643.46
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
λ (graphite-monochromated Mo Kα radiation), Å	0.71073	0.71073
a, Å	9.104 (3)	8.004 (4)
b, Å	14.932 (5)	15.496 (7)
c, Å	15.266 (5)	15.889 (6)
β, deg	103.84 (1)	100.31 (2)
V, Å^3	2015 (1)	1939 (1)
Z	4	4
D_{calcd}, g cm^{-3}	2.996	2.204
F(000)	1608	1232
cryst dimens, mm	0.25 × 0.28 × 0.32	0.17 × 0.22 × 0.28
linear abs, cm^{-1}	189.45	23.11
diffractometer	CAD 4 Enraf-Nonius	Philips PW 1100
scan type	ω/2θ	ω/2θ
scan speed, θ, deg/min	<3.3	3–12
2θ range, deg	6–50	6–54
no. of reflns measured	±h,k,l	±h,k,l
no. of std reflns	one measd after 200 reflns	one measd after 50 reflns
no. of unique total data	3735	4350
no. of unique obsd data [$I > 2\sigma(I)$]	1973	3555
R	0.0291	0.0361
R_w	0.0344	0.0460

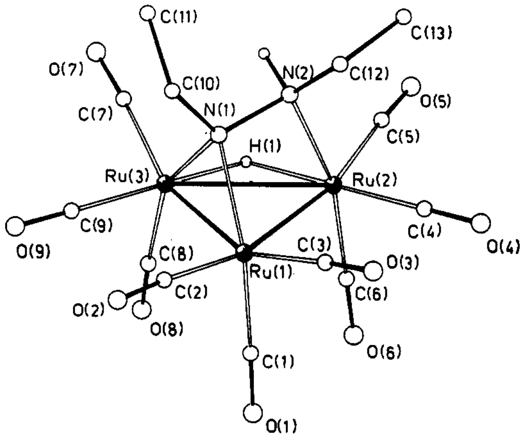

Figure 2. Molecular structure of 6. Important bond lengths (Å): Ru1–Ru2 2.737 (1), Ru1–Ru3 2.655 (1), Ru2–Ru3 2.897 (1), Ru1–N1 2.115 (4), Ru2–N2 2.177 (4), Ru3–N1 2.130 (4), N1–N2 1.473 (5), N1–C10 1.485 (6), N2–C12 1.488 (7), C10–C11 1.513 (7), C12–C13 1.502 (7).

During attempts to enforce N–N cleavage in the cluster 5, we also used hydrogen under pressure. By doing this under 50 bar of H_2 at 95 °C in the presence of Pd/C catalyst, we observed hydrogenation of the C=N bond and formation of 6 in moderate yield. It then turned out that 6 can be obtained in much better yield under the same conditions directly from 3. The capping ligand in 6 is a hydrazine derivative, and again similar compounds were obtained by Süss-Fink from $Ru_3(CO)_{12}$ and organic hydrazines.[12]

The structures of 4–6 were deduced from their spectra and proved by crystal structure determinations of 4 and 6, as documented in the supplementary material. Table I lists the basic crystallographic information. Figures 1 and 2 give the structures with the pertinent bond length

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information. The N-H, Ru-H, and Os-H hydrogen atoms were located and refinend in both molecules, but as usual for such heavy-atom structures their positions bear some degree of uncertainty.

In both **4** and **6** the orientation of the N_2 unit with respect to the metal triangle has changed compared to that in **1** or **3**. There is no longer a N-N π-bond interaction with one metal atom since the N-N bond, now part of a hydrazine derivative, is no longer a double bond (N-N bond lengths 1.39 Å in **1**,[8] 1.41 Å in **4**, and 1.47 Å in **6**). Instead, the NEt unit of the N_2 ligand behaves as a three-electron μ_2 ligand like an amide in both cases. A simple related compound is $HRu_3(CO)_{10}(\mu\text{-NH-CH}_2Ph)$[13] with similar Ru-N distances (2.09 and 2.11 Å). In both clusters the hydride ligand bridges the longest metal-metal bond, as usual. It is noticeable, however, that only in **4** this metal-metal bond is also bridged by the μ_2 nitrogen.

The major difference between **4** and **6** lies in the "rear" part of the N_2 ligand with its terminally bonded nitrogen atom. In **6** the NHEt unit contains a roughly tetrahedral nitrogen with a C—N single bond (1.49 Å), while in **4** the N=CHMe unit contains a roughly trigonally planar nitrogen with a C—N double bond (1.29 Å). Corresponding, the N—C—C angles at the N-bound carbon atoms in **4** reflect the sp^2 situation at C10 (121°) and the sp^3 situation at C12 (116°). A similar cluster containing an imide-type ligand is $HRu_3(CO)_{10}(\mu\text{-N=CHPh})$ (C=N 1.27 Å).[14] The parent cluster of **6**, $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-NH-NH}_2)$, prepared from hydrazine, has been found by Süss-Fink[12] to contain a Ru_3N_2 skeleton very similar to that in **6**. In summary, it can be stated that the molecular geometries of **4** and **6** confirm their formulation as hydrazone and hydrazine derivatives, respectively.

The hydrogen transfer in the **3** → **5** interconversion or in the formation of **4** represents an unusual type of C-H activation.[15] It is intramolecular, but the carbon atom remaining after the hydrogen has been removed from it is not connected to a metal atom. Thus this reaction cannot be placed in the normal context of β-eliminations[16] or ortho-metalations.[17] Instead, it is something like the reversal of a metal-catalyzed hydrogenation of a double bond. The C=N bonded system remaining after hydrogen transfer is part of a five-electron hydrazone-yl ligand which results from a reorientation of its predecessor, the six-electron azoalkane ligand. The electron count for the metal atoms is balanced by the attachment of the hydrogen atom. Thereby the stabilizing factor for this new type of β-activation is the adaptability of the $M_3(CO)_9$ cluster "surface" to various types of $\mu_m\text{-}\eta^n$ bonding. A similar type of reaction and ligand attachment is observed in the formation of $HOs_3(CO)_{10}(CHCH{=}NEt_2)$ from $Os_3(CO)_{10}(MeCN)_2$ and NEt_3.[18]

The differences in energy responsible for the different reaction pathways (N-N cleavage for **1** → **2**, C-H cleavage for **3** → **5**) must be small since the reaction conditions for both interconversions are almost the same. It is however well-established that ruthenium or osmium have a higher affinity for hydrogen than iron. It can therefore be concluded that the loss of bonding in the starting materials is better compensated by new metal-nitrogen bonding in the case of Fe and by new metal-hydrogen bonding in the case of Ru and Os.

The hydrogenation of **3** or **5** to form **6** is another demonstration of the adaptability of the $M_3(CO)_9$ cluster. The bonding mode of the substrate changes from **3** to **6** just as it changes from **3** to **5**, i.e. a six-electron N_2 ligand is converted to a five-electron N_2 ligand. Accordingly, the bonding mode does not change in the **5** → **6** transformation. Although a catalyst (Pd/C) is needed for both hydrogenations, it is likely that the presence of ruthenium in the cluster supports the ligand hydrogenation, just as it does in the conversion of Ph—CN to μ-N=CHPh and μ-NH—CH_2Ph ligands in the presence of $Ru_3(CO)_{12}$ and H_2.[19]

Experimental Section

The general experimental procedures and the synthesis of the starting materials were as described before.[8]

$Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}N_2Et_2)$ (3). The reaction was performed in an irradiation vessel in which the reaction mixture was allowed to circulate. An immersed water-cooled 150-W high-pressure mercury lamp was used. To a petroleum ether (100 mL) solution of azoethane (138 mg, 1.6 mmol) was added $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol). The solution was irradiated for 1.5 h at 15 °C, during which time the color changed from orange to red. The solvent was removed under vacuum, and the residue was chromatographed on silica gel with petroleum ether/CH_2Cl_2 (9:1) as eluent. The first yellow band was $Ru_3(CO)_{12}$ (4 mg), which was followed by an orange band of **3** (32 mg, 31%). IR (hexane): $\nu(CO)$ = 2081 (w), 2041 (vs), 1995 (s), 1987 (m), 1979 (m) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 4.12$ (dq, $^2J = 13.8$ Hz, $^3J = 6.8$ Hz, 2 H_a, CH_aH_b), 3.49 (dq, $^2J = 13.8$ Hz, $^3J = 7.3$ Hz, 2 H_b, CH_aH_b), 1.52 (d, $J = 6.8$ Hz, 3 H, CH_3), 1.49 (d, $J = 7.3$ Hz, 3 H, CH_3). Anal. Calcd for $C_{13}H_{10}N_2O_9Ru_3$: C, 24.34; H, 1.57; N, 4.37. Found: C, 24.65; H, 1.47; N, 4.39.

$HOs_3(CO)_9(\mu_3\text{-}\eta^2\text{-EtN—N=CHMe})$ (4). A 50-mL autoclave was charged with 150 mg (0.166 mmol) of $Os_3(CO)_{12}$, 25 mL of *n*-octane, and 143 mg (1.66 mmol) of N_2Et_2 and was heated under N_2 at 140 °C for 2 h. After cooling, 86 mg of unreacted $Os_3(CO)_{12}$ was separated as a yellow crystalline precipitate. The yellow solution was dried under vacuum, and the residue was picked up in a minimum amount of CH_2Cl_2 and was chromatographed by silica on a TLC plate with petroleum ether/CH_2Cl_2 (8:2) as eluent. This yielded 16 mg of a yellow, not yet identified osmium hydride complex and 9 mg (14%, based on the amount of $Os_3(CO)_{12}$ consumed) of **4** as a yellow band. IR (hexane): $\nu(CO)$ = 2086 (w), 2060 (m), 2031 (m), 1996 (vs), 1985 (vw, sh), 1976 (s), 1959 (vw), 1946 (w) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.81$ (q, $J = 5.2$ Hz, 1 H, CH), 3.13 (q, $J = 7.3$ Hz, 2 H, CH_2), 2.09 (d, $J = 5.2$ Hz, 3 H, CH_3), 0.98 (t, $J = 7.3$ Hz, 3 H, CH_3), −14.31 (s, 1 H, OsH). Anal. Calcd for $C_{13}H_{10}N_2O_9Os_3$: C, 17.18; H, 1.11; N, 3.08. Found: C, 17.34; H. 1.10; N, 3.08.

$HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-EtN—N=CHMe})$ (5). **3** (50 mg, 0.078 mmol) was dissolved in toluene (20 mL), and the solution was refluxed for 40 min. After the solution was filtered through silica gel, the solvent was removed under vacuum. The residue was chromatographed on a silica TLC plate with petroleum ether/CH_2Cl_2 (8:2) as eluent. The first yellow band contained $Ru_3(CO)_{12}$ (traces) followed by a brown band of $Ru_4(CO)_{12}(N_2Et_2)$ (4 mg). The third yellow band contained **5** (8 mg, 16%). IR (hexane): $\nu(CO)$ = 2081 (m), 2050 (vs), 2027 (vs), 1991 (vs), 1961 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): $\delta = 7.08$ (q, $J = 5.5$ Hz, 1 H, HC=N), 3.11 (q, $J = 6.9$ Hz, 2 H, CH_2), 1.99 (d, $J = 5.5$ Hz, 3 H, CH_3), 1.09 (t, $J = 6.9$ Hz, 3 H, CH_3), −13.06 (s, RuH). Anal. Calcd for $C_{13}H_{10}N_2O_9Ru_3$: C, 24.34; H, 1.57; N, 4.37. Found: C, 24.53; H, 1.50; N, 4.41.

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$HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}EtN\text{–}NHEt)$ (6). (a) **5** (50 mg, 0.078 mmol) was dissolved in ethyl acetate (20 mL), and Pd/C catalyst (10% Pd) was added. The solution was placed into an autoclave that was pressurized with 50 bar of H_2 and stirred for 24 h at 95 °C. After the solution was filtered through silica gel, the solvent was removed by evaporation under vacuum. The residue was chromatographed on a silica TLC plate with petroleum ether/CH_2Cl_2 (9:1) as eluent. The first fraction was a yellow band of $Ru_3(CO)_{12}$ (traces) followed by a yellow fraction of unreacted **5** (13 mg, 26%). The third yellow band contained **6** (12 mg, 24%). IR (hexane): $\nu(CO)$ = 2081 (m), 2050 (s), 2027 (vs), 1983 (vs), 1956 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.81–3.63 (m, 2 H, NH and H_a overlapping), 3.17–3.07 (m, 1 H, H_a), 2.20–2.03 (m, 1 H, H_b), 1.81 (dq, ^2J = 14.5 Hz, ^3J = 7.3 Hz, 1 H, H_b), 1.12–1.01 (m, 6 H, 2 CH_3), −12.61 (s, RuH). Anal. Calcd for $C_{13}H_{12}N_2O_9Ru_3$: C, 24.27; H, 1.88; N, 4.35. Found: C, 24.22; H, 1.87; N, 4.36.

(b) **3** (100 mg, 0.16 mmol) was dissolved in ethyl acetate (40 mL), and Pd/C catalyst (10% Pd) was added. The solution was placed into an autoclave that was pressurized with 50 bar of H_2 and stirred for 1 h at 95 °C. After the solution was filtered through silica gel, the solvent was removed under vacuum. The residue was chromatographed on silica gel with petroleum ether/CH_2Cl_2 (8:2) as eluent. The first yellow band contained $Ru_3(CO)_{12}$ (traces), which was followed by a yellow band of **6** (73 mg, 71%).

Crystal Structure Determinations. Crystals of **4** and **6** for single-crystal X-ray diffraction were obtained by slow evaporation from benzene/hexane mixtures. The crystallographic data are summarized in Table I. Unit cell parameters were determined from the θ values of 30 (**4**) and 25 (**6**) carefully centered reflections, having $12.3 < \theta < 16.8°$ (**4**) and $14.1 < \theta < 19.8°$ (**6**). Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects; a correction for absorption[20] was applied to **4** (maximum and minimum values for the transmission factors were 1.2685 and 0.7713). Only the observed reflections were used in the structure solution and refinement.

The structures were solved by Patterson and Fourier methods and refined first by full-matrix least squares with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms H(1) and H(10) (**4**) and H(1) and H(2) (**6**) were clearly localized in the final difference Fourier maps and refined isotropically; all other hydrogen atoms were placed at their geometrically calculated positions (C–H = 1.00 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 260 (**4**) and 262 (**6**) variables. In the final cycle of refinement a weighting scheme, $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the g values were 0.0008 (**4**) and 0.0053 (**6**). The atomic scattering factors, corrected for anomalous dispersion, were taken from ref 21. For the computations the SHELX-76 and SHELX-86 systems of crystallographic computer programs were used.[22]

Acknowledgment. This work was supported by the European Community (Grant ST2J-0437-C) and the Volkswagen-Stiftung.

Registry No. **3**, 121788-61-2; **4**, 136804-56-3; **5**, 136804-57-4; **6**, 136804-58-5; $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{12}$, 15696-40-9; Et_2N_2, 821-14-7; EtNN═CHMe, 136804-55-2.

Supplementary Material Available: Listings of atomic coordinates including hydrogen atoms, of anisotropic thermal parameters, and of all atomic distances and angles for the X-ray diffraction analyses of 4 and 6 (8 pages); tables of observed and calculated structure factors for 4 and 6 (31 pages). Ordering information is given on any current masthead page.

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