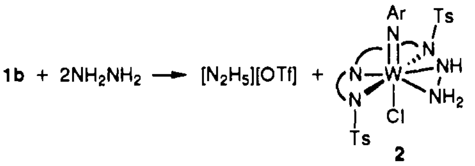
quartet for the methylene protons, which suggests that no mirror plane passes through the methylene carbon atoms. However, the aryl ring must not be able to rotate rapidly, since two types of isopropyl methyl groups are observed by NMR.

The reaction between **1b** and 2 equiv of hydrazine yields W(NAr)[N(NTs)$_2$](η^2-NHNH$_2$)Cl (**2**) (eq 3) in 49% yield. We propose that the reaction proceeds via a hydrazine adduct (see **3** below), which is subsequently deprotonated rapidly by hydrazine. The structure of **2**, as determined in an X-ray crystallography study, is shown in Figure 1.[5] The core of the molecule can be loosely described as a pentagonal bipyramid with the tridentate and hydrazido ligands defining the equatorial plane and the imido and chloride ligands occupying axial positions. The five ligands in the equatorial positions bend away slightly from the ideal plane containing them and the W atom; the W atom sits ~0.23 Å above the least-squares plane defined by the five nitrogen atoms. Both WC$_2$N$_2$ rings are puckered. The fact that the N(3)-W-N(5) angle (146.0 (3)°) is considerably less than 180° allows the hydrazido ligand to bind to W in η^2-fashion in the pseudoequatorial plane. The W-N(1) and W-N(2) distances (2.07 (1) and 2.061 (8) Å) and N(1)-W-N(2) angle (39.8 (4)°) are within experimental error the same as those found in isoelectronic Cp*WMe$_4$(η^2-NHNH$_2$),[6] whose structure is roughly analogous (three methyl groups and the hydrazido ligand in a pentagonal arrangement). The N(1)-N(2) distance (1.41 (1) Å) should be compared with the N-N distances in the two independent molecules of WCp*Me$_4$(η^2-NHNH$_2$) (1.39 (3) and 1.35 (3) Å),[6] [WCp*Me$_3$(η^2-NHNH$_2$)]$^+$ (1.39 (1) Å),[6] and [Co{MeC(CH$_2$PPh$_2$)$_3$}(η^2-NHNH$_2$)]$^+$ (1.384 (14) Å).[7] It is interesting to note that H(2A), which was located, points away from the imido ligand and that the O(3)···H(2A) distance is only 2.2 (1) Å, which could be construed as a hydrogen bond. (The NH proton in Cp*WMe$_4$(η^2-NHNH$_2$) also points away from the Cp* ligand.) In this circumstance no orbital is available to receive the lone electron pair on N(2), and if the imido ligand in **2** behaves as a 2π, 1σ ligand, the metal electron count in any case is 18.



(3)

2

One would expect that the hydrazido ligand in **2** could be protonated easily. Addition of 1 equiv of triflic acid to **2** yields yellow [W(NAr)[N(NTs)$_2$](η^2-NH$_2$NH$_2$)Cl][OTf] (**3**). Compound **3** is virtually insoluble in hydrocarbon solvents and diethyl ether, and only sparingly soluble in dichloromethane and THF. The structure of **3** is proposed to be analogous to that of **2**. Note added in proof: The structure of **3** has now been solved and shown to be essentially the same as that of **2** with W-N bond lengths of 2.11 and 2.12 Å and an N-N bond length of 1.42 Å. The proton NMR spectrum of **3** in CD$_2$Cl$_2$ shows only one broad resonance at 8.60 ppm for the protons in the NH$_2$NH$_2$ ligand, consistent with rapid proton exchange or hydrazine exchange in η^2-N$_2$H$_4$ under these conditions. Low solubility of **3** has prevented elucidation of the exchange process at low temperature. Monometallic complexes that contain unsubstituted η^2-hydrazine are extremely rare.[7] There is a remote possibility that the proton has added somewhere other than the electron pair on N(2).

Reduction of **2** and **3** by zinc amalgam and subsequent addition of concentrated HCl to the reaction mixture generates 1.19 and 1.67 equiv of ammonia, respectively.[8] Analogous reactions in the presence of 2,6-lutidine hydrochloride yield only 0.46 and 0.61 equiv of ammonia, respectively. We believe that protonation of the hydrazido(1−) and hydrazine ligands in **2** and **3** competes with reduction, although experimental problems so far have prevented confirmation that hydrazine is formed in such circumstances.

We conclude that the W(NAr)[N(NTs)$_2$] core shows some characteristics of the WCp*Me$_3$ core[1,2] in forming complexes that contain N$_2$H$_y$ ligands which can be reduced in the presence of protons to give ammonia. Future studies will focus on variations of this ligand set and expansion of the chemistry of complexes that contain it and related ligand systems that are relevant to the reduction of dinitrogen to ammonia. Note added in proof: An example of a NHNH$_2$(1−) complex of molybdenum in a sulfur coordination sphere has just been published (Sellmann, D.; Kern, W.; Pöhlmann, G.; Knoch, F.; Moll, M. *Inorg. Chim. Acta* **1991**, *185*, 155). A NHNMe$_2$ derivative was structurally characterized.

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Supplementary Material Available: Text giving experimental details, NMR spectral data, analytical data, and a description of the X-ray structure determination, a labeled ORTEP drawing, and tables listing crystal data, final positional parameters, final thermal parameters, bond distances and angles, and least-squares planes (19 pages); a listing of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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(5) Crystal data for WClS$_2$O$_4$N$_7$C$_{35}$H$_{44}$ at −72 (1) °C: monoclinic, space group $P2_1/n$, a = 13.892 (2) Å, b = 16.111 (3) Å, c = 16.537 (3) Å, β = 95.60 (2)°, Z = 4, ρ = 1.641 g cm^{-3}, μ = 34.31 cm^{-1}. A total of 5236 reflections were collected in the range of 2.8° < 2θ < 45° ($h,k,\pm l$). Of these, 5082 were unique and 3534 with $I > 3.00\sigma(I)$ were used in the structure solution. $R(F)$ = 0.043 and $R_w(F)$ = 0.045. One acetonitrile molecule was found in each asymmetric unit of the cell. There is no contact between the tungsten molecule and acetonitrile in the asymmetric unit.

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(8) (a) Complexes **2** and **3** ((3-4) × 10^{-2} mmol) and 6 equiv of zinc amalgam (and 12 equiv of lutidine hydrochloride) were placed in a 50-mL Schlenk flask, and then cold THF (10 mL) was added. The reaction flask was sealed with a rubber septum, and the mixture was stirred at room temperature for two days. Concentrated HCl (0.1 mL) was added to the reaction mixture by syringe. The solvent was then removed in vacuo, and the residue was extracted with distilled water. The colorless extract was tested quantitatively for ammonia by using the indophenol method.[8b] (b) Chaney, A. L.; Marbach, E. P. *Clin. Chem.* **1962**, *8*, 130.

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Low-Temperature Spectroelectrochemical Study of (Bu$_4$N)Re$_2$Cl$_9$ and (Bu$_4$N)$_2$Re$_2$Cl$_8$: Discovery of Re$_2$Cl$_9$$^{3-}$

In the 27 years since the recognition[1] of the first quadruple metal-metal bond in Re$_2$Cl$_8$$^{2-}$, dirhenium halide complexes have continued to challenge both experimentalists and theoreticians. We now report that the spectroelectrochemical study of (Bu$_4$N)$_2$Re$_2$Cl$_8$ and (Bu$_4$N)Re$_2$Cl$_9$ at low temperature has resulted in the identification of the new species Re$_2$Cl$_8$^{0}, Re$_2$Cl$_9$^{0}, Re$_2$Cl$_9$$^{3-}$, and transient Re$_2Cl_9$$^{4-}$. Furthermore, the octa- and nonahalide forms are shown to interconvert in a systematic fashion, controlled by oxidation level.

Redox processes alter the occupancy of the metal-based orbital manifold responsible for Re-Re multiple bonding in the octahalide. Elegant electrochemical investigations[2] of variously substituted

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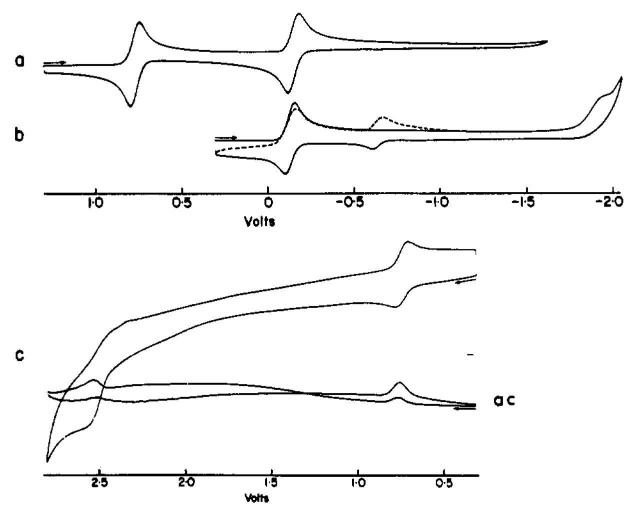

Figure 1. Voltammetric study of $(Bu_4N)Re_2Cl_9$: (a, b) CH_2Cl_2, 208 K, 100 mV/s; (c) CH_2Cl_2/CH_3CN (1:1), 223 K, 100 mV/s, including cyclic ac scan.

Scheme I

$$\begin{tikzcd}
d^2d^3 & d^3d^3 & d^3d^4 & d^4d^4 & d^4d^5 \\
Re_2Cl_9^{0} \arrow[r, rightleftharpoons, "2.53V"] & Re_2Cl_9^{1-} \arrow[r, rightleftharpoons, "0.75V"] & Re_2Cl_9^{2-} \arrow[r, rightleftharpoons, "-0.17V"] & Re_2Cl_9^{3-} \arrow[r, "-1.81V"] \arrow[d, "-Cl^-"] & \{Re_2Cl_9^{4-}\} \arrow[d, "-Cl^-"] \\
 & Re_2Cl_8^{0} \arrow[u, "+Cl^-"] \arrow[r, rightleftharpoons, "1.88V"] & Re_2Cl_8^{1-} \arrow[u, "+Cl^-"] \arrow[r, rightleftharpoons, "1.44V"] & Re_2Cl_8^{2-} \arrow[r, rightleftharpoons, "-0.64V"] & Re_2Cl_8^{3-}
\end{tikzcd}$$

$Re_2X_{8-y}L_y^{n-}$ species (X = halogen, L = neutral donor) have probed the nature of this bond as a function of oxidation state, and complexes have been characterized with Re–Re formal bond orders ranging from 4 ($\sigma^2\pi^4\delta^2$) to electron-rich 3 ($\sigma^2\pi^4\delta^2\delta^{*2}$).[2,3]

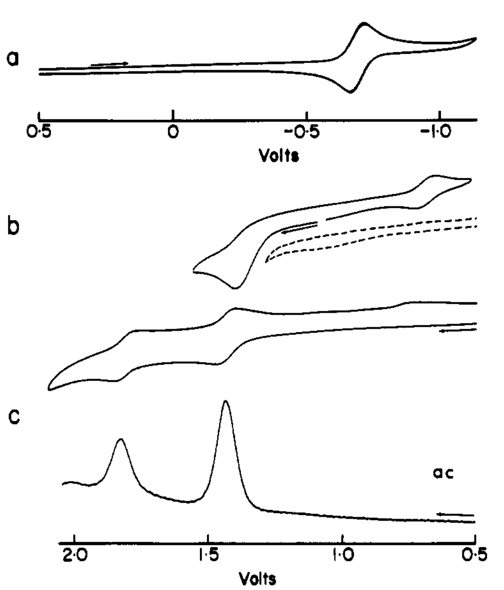

Figure 2. Voltammetric study of $(Bu_4N)_2Re_2Cl_8$: (a) CH_2Cl_2, 260 K, 50 mV/s; (b) CH_2Cl_2, 260 K, 200 mV/s; (c) CH_2Cl_2/CH_3CN (1:1), 220 K, 200 mV/s, including ac scan.

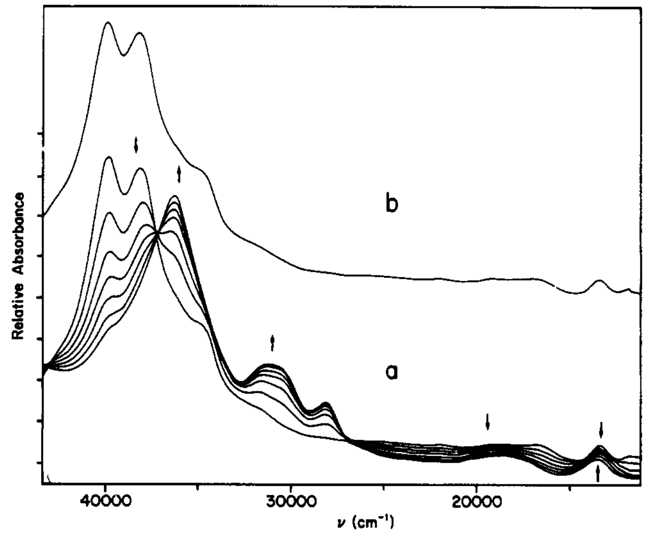

Figure 3. (a) Spectroelectrochemical monitoring of the reversible reoxidation of $Re_2Cl_9^{3-}$ to $Re_2Cl_9^{2-}$, in CH_2Cl_2 and 0.5 M $[Bu_4N]Cl$ at 188 K. (b) UV/vis spectrum of $Re_2Cl_9^{3-}$ at 188 K.

In contrast, for the homoleptic complexes $Re_2X_8^{n-}$ (X = F, Cl, Br, I) only the quadruply bonded dianion has been isolated. At ambient temperature electron-rich $Re_2Cl_8^{3-}$ forms only transiently in an irreversible electrochemical reduction,[4] while the electron-poor $Re_2Cl_8^-$ species of the same bond order is a short-lived product of both photochemical and electrochemical oxidation of $Re_2Cl_8^{2-}$.[5] In recent electrochemical studies in chloroaluminate molten salt solutions, Hussey and co-workers[6] observed that $Re_2Cl_9^{2-}$ decomposes to $Re_2Cl_8^{2-}$ upon reduction while $Re_2Cl_8^{2-}$ can be reduced reversibly to $Re_2Cl_8^{3-}$. Anodic processes of $Re_2Cl_9^-$ or $Re_2Cl_8^{2-}$ are inaccessible in the melts. The advantage of low-temperature electrochemical studies in such systems has been demonstrated by our work on the later nonahalides $M_2X_9^{3-}$ (M = Ru, Os, Ir; X = Cl, Br),[7] where several previously unknown oxidation states were characterized in chilled CH_2Cl_2. The present results are summarized in Scheme I.

Four stepwise one-electron processes are observed in the voltammetry[8] of $(Bu_4N)Re_2Cl_9$. In CH_2Cl_2 solution at 208 K, reversible reductions to $Re_2Cl_9^{2-}$ and $Re_2Cl_9^{3-}$ (Figure 1a) are followed by a further well-defined but nonreversible (ec) reduction at −1.81 V, forming $Re_2Cl_8^{3-}$ as a daughter product (vide infra). Cyclic scans confirm the growth of a reversible wave at −0.64 V assigned to $Re_2Cl_8^{2-}/Re_2Cl_8^{3-}$ (Figure 1b). There is voltammetric evidence for transient existence of $Re_2Cl_9^{4-}$ as in Scheme I. Similarly, the $Re_2Cl_9^{2-}/Re_2Cl_9^{3-}$ couple is linked to the chemical reaction $Re_2Cl_9^{3-} \rightarrow Re_2Cl_8^{2-} + Cl^-$ at higher temperatures and becomes completely nonreversible well below 273 K. In a CH_2Cl_2/CH_3CN solution at 223 K, a quasi-reversible oxidation to $Re_2Cl_9^{0}$ at the extreme potential of 2.53 V is observable by both ac and dc cyclic voltammetry (Figure 1c).

Two one-electron oxidations and one reduction are observed in the voltammetric study of $(Bu_4N)_2Re_2Cl_8$, in accord with

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(8) All solvents were freshly distilled and degassed: 0.5 M $[Bu_4N][PF_6]$ was used as supporting electrolyte; all measurements were carried out with a Princeton Applied Research 170 potentiostat under a dry-N_2 atmosphere, versus a Ag/AgCl reference electrode for which the ferrocene/ferrocenium redox couple was measured at 0.55 V.

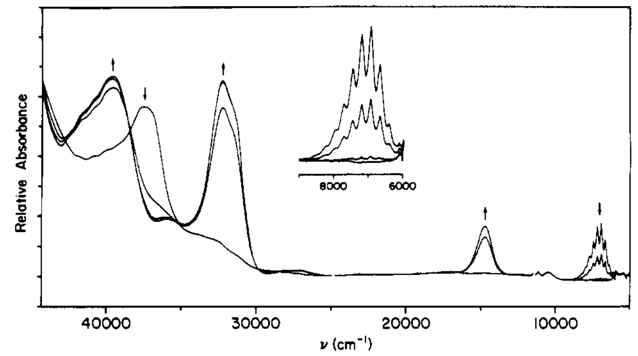

Figure 4. Spectroelectrochemical monitoring of the reversible oxidation of $Re_2Cl_8^{3-}$ to $Re_2Cl_8^{2-}$, in CH_2Cl_2/CH_3CN (1:1) and 0.5 M $[Bu_4N]$-$[BF_4]$ at 233 K. Inset: $\delta^2\delta^* \rightarrow \delta\delta^{*2}$ near-infrared band of $Re_2Cl_8^{3-}$.

Scheme I. In CH_2Cl_2 at 260 K, $Re_2Cl_8^{2-}$ exhibits a reversible reduction to $Re_2Cl_8^{3-}$ (Figure 2a) and an irreversible oxidation near 1.5 V. However, below 220 K, successive reversible oxidations to $Re_2Cl_8^-$ and $Re_2Cl_8^0$ occur in 1:1 CH_2Cl_2/CH_3CN solution, a compromise between improved solubility and elevated freezing point (Figure 2c). At 260 K, where $Re_2Cl_8^-$ is short-lived, $Re_2Cl_9^-$ forms as a daughter product ($Re_2Cl_9^{2-}$ is oxidized at the prevailing potential) and is identified by the emerging $Re_2Cl_9^-/Re_2Cl_9^{2-}$ couple at 0.75 V (Figure 2b).

The interconversions of $Re_2Cl_9^{z-}$ and $Re_2Cl_8^{(z-1)-}$, initially detected voltammetrically, were studied spectroelectrochemically by optically transparent thin-layer electrode (OTTLE) techniques described elsewhere.[9] Reduction of the nonahalide at −0.30 V (in CH_2Cl_2, 213 K) shows the collapse of the $Re_2Cl_9^{2-}$ spectrum and the growth of peaks at 39 900, 38 200, and 34 800 cm^{-1} attributed to $Re_2Cl_9^{3-}$. However, this spectrum rapidly gives way to the readily recognized $Re_2Cl_8^{2-}$, even though the reduction is reversible in the voltammetric time scale. Equally, in the time course of the OTTLE experiment, oxidation of $Re_2Cl_8^{2-}$ at 1.55 V at 233 K shows only the emergence of the $Re_2Cl_9^-$ spectrum (ece process, vide supra). In contrast, the reductions of $Re_2Cl_9^{2-}$ at 188 K and of $Re_2Cl_8^{2-}$ at 233 K show sharp isosbestic points consistent with efficient reversible generation of $Re_2Cl_9^{3-}$ and $Re_2Cl_8^{3-}$, respectively (Figures 3 and 4), according to Scheme I.

In summary, the chemical processes associated with the decomposition of electrogenerated dirhenium halide complexes are significantly retarded at low temperature, permitting recognition of four novel species in this study. There is now the prospect of rational synthetic manipulation of the dirhenium systems under suitable conditions. For example, $Re_2Cl_9^{3-}$ and $Re_2Cl_8^{3-}$ may both be accessible by chemical reduction of their corresponding dianions.

The electrochemistry of the $Re_2Cl_9^{z-}$ species parallels the recently reported[7b] behavior of the diosmium nonahalides, with the rhenium couples shifted negatively by ~0.35 V compared to the corresponding (isovalent) steps for $Os_2X_9^{z-}$. A contrary effect is seen for $Re_2X_8^{z-}$ and $Os_2X_8^{z-}$; namely, the rhenium couples are each shifted by ~+0.20 V relative to those of osmium.[10] Clearly, in the octahalides the splitting of the binuclear metal-based orbital manifold overrides the normal periodicity trends established[11] for hexahalometallates.

Upon chemical oxidation[12] with Cl_2, or one-electron electrochemical oxidation in the presence of chloride,[5] face-to-face $Re_2Cl_8^{2-}$ converts to the face-sharing bioctahedral $Re_2Cl_9^-$. Our results show that such a rearrangement can also be electrochemically induced with simultaneous abstraction of chloride from further $Re_2Cl_8^{2-}$. Similar behavior is observed voltammetrically in tetrahydrofuran, implying that CH_2Cl_2 is not the source of Cl^-. We do observe halide-depleted byproducts in the corresponding oxidation of $Re_2Br_8^{2-}$, and these results will be described separately. Self-abstraction of chloride ions has been reported in the electrochemical oxidation of $Re_2Cl_4L_4$ to $Re_2Cl_5L_3$ and $Re_2Cl_6L_2$ (L = PR_3).[2a]

It is remarkable that both Re_2Cl_9 and Re_2Cl_8 stoichiometries can persist over as many as four oxidation levels, Re_2^{8+} to Re_2^{5+}, even though one form is strongly preferred at each stage. The nonachloride is favored in the higher oxidation states, Re_2^{8+} and Re_2^{7+}, while the octachloride is favored for Re_2^{6+} and Re_2^{5+}. Of particular interest is the Re^{III}_2 case, where both $Re_2Cl_8^{2-}$ and $Re_2Cl_9^{3-}$ are now well characterized in solution. Electrochemically induced structural changes have been reported[7b] between the diosmium deca- and nonahalide complexes but have yet to be identified between diosmium octa- and nonahalides.

The near-infrared electronic spectrum for electrogenerated $Re_2Cl_8^{3-}$ exhibits exceptionally well-developed vibrational fine structure in solution (Figure 4). Assignment of the 6950-cm^{-1} band as a $\delta^2\delta^* \rightarrow \delta\delta^{*2}$ transition is unequivocal.[2d,3a,f] The Frank-Condon progression shows a $(Re-Re)^{5+}$ vibrational frequency of approximately 270 cm^{-1}, notably similar to the Raman absorption[13] (272-275 cm^{-1}) of $Re_2Cl_8^{2-}$. This leads to an estimated extension of ca. 0.07 Å in the Re-Re multiple bond upon electronic excitation (which involves formal reduction of the bond order by one). The δ/δ^* band of $Re_2Cl_8^{3-}$ in chloroaluminate salt solution has also been observed,[6a] although the details are not yet published. The spectrum of isoelectronic $Tc_2Cl_8^{3-}$ contains a strictly analogous band.[14] Most recently, we have characterized hitherto unknown $Re_2Br_8^{3-}$, where the corresponding band is centered at 7200 cm^{-1}.

Our data establish the stoichiometries of all species of Scheme I. Questions still remain with regard to their structures, particularly those of the $Re_2Cl_9^0$ to $Re_2Cl_9^{4-}$ sequence. Thus, the electrochemical reversibility of the Re_2^{8+}/Re_2^{7+} and Re_2^{7+}/Re_2^{6+} couples for the nonachloride (Figure 1a) is consistent with retention of the D_{3h} geometry[15] of $Re_2Cl_9^-$ but also with rapid, reversible structural rearrangements. Further studies to elucidate the electrochemically induced structural transformations of dirhenium complexes are in progress.

Acknowledgment. We thank Dr. Lucjan Dubicki for his assistance in the analysis of the optical spectra and the Institute for Advanced Studies, ANU, for financial support of this work.

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Effect of Tridentate Phosphine Ligand Structure on the Basicities of Tungsten Tricarbonyl Complexes

Multidentate phosphine ligands have been used extensively[1,2] in transition-metal coordination chemistry in part because of the

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