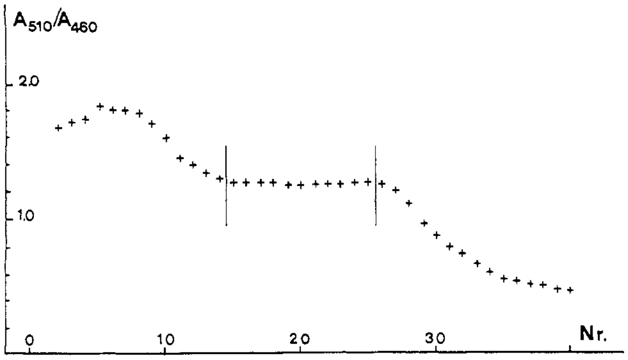

Figure 1. Ratio of the absorbances at 510 nm (A_{510}) and at 460 nm (A_{460}) as a function of the fraction number. The counting of the fraction was started with the elution of the first band.

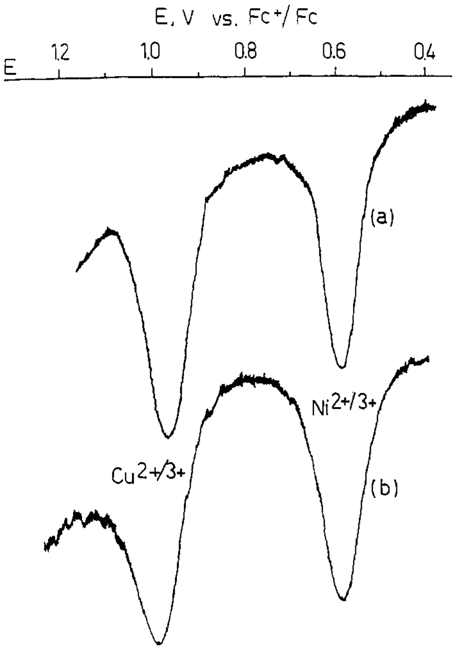

Figure 2. Differential-pulse polarograms for acetonitrile solutions (0.1 M Et_4NBF_4): (a) mixture of 10^{-4} M Ni(cyclam)$(ClO_4)_2$ and 10^{-4} M Cu(cyclam)$(ClO_4)_2$; (b) 10^{-4} M NiCu(biscyclam)$(ClO_4)_4$. Conditions: pulse voltage, 10 mV; potential scan rate, 1 mV s^{-1}; platinum working electrode.

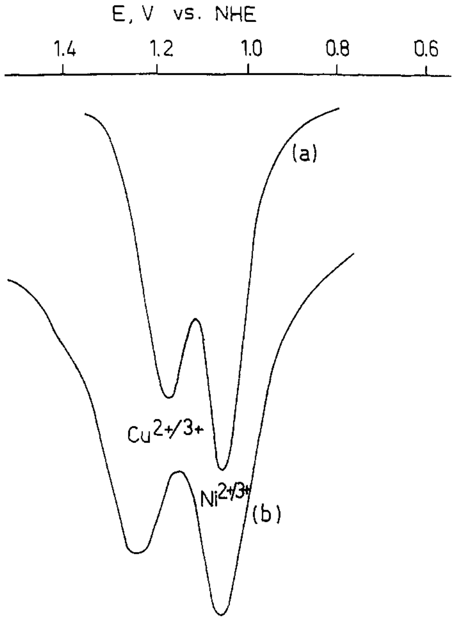

Figure 3. Differential-pulse polarograms for 70% $HClO_4$ solutions: (a) mixture of 5×10^{-4} M Ni(cyclam)$(ClO_4)_2$ and 5×10^{-4} M Cu(cyclam)$(ClO_4)_2$; (b) 5×10^{-4} M NiCu(biscyclam)$(ClO_4)_4$. Conditions: pulse voltage, 10 mV; potential scan rate, 1 mV s^{-1}; platinum working electrode. A silver wire calibrated vs. the Fe^{3+}/Fe^{2+} couple was used as a quasi-reference electrode. Potentials were referred to the NHE by using the formula of Ciavatta.[16]

electron oxidation of the Cu(II) center, occurs at a potential 30 mV more positive than that observed for the monomeric reference system, Cu(cyclam)$^{2+}$ (curve a). Figure 3 reports the DPP in concentrated (11.6 M) $HClO_4$ solution for both the equimolar Ni(cyclam)$^{2+}$/Cu(cyclam)$^{2+}$ mixture and the NiCu(biscyclam)$^{4+}$ complex. In this medium the second peak (Cu(II)/Cu(III)) is much closer to the first one (Ni(II)/Ni(III)), as compared to MeCN. This reflects the well-known effect of the "inert electrolyte" (11.6 M ClO_4^-), which stabilizes Cu(III) and destabilizes Ni(III) in tetraaza macrocyclic complexes.[16] Also in this case, the potential separation for the biscyclam complex is 60 mV greater than that observed for the solution containing the monomeric cyclam complexes. This generally reflects the increased difficulty in oxidizing Cu(II) to Cu(III) in the presence of a tripositive cation Ni(III) at a distance of about 8 Å (as estimated by molecular models), compared to a situation in which the metal centers are far apart. The fact that the difference between the Ni(II)/Ni(III) and Cu(II)/Cu(III) peaks for the biscyclam complex is greater in 70% $HClO_4$ than in MeCN (60 and 30 mV, respectively) could be interpreted in terms of solvent-moderated interaction between the metal centers. In the $HClO_4$ solution the massive amount of electrolyte strongly competes for the solvent molecules, so that the bimetallic species is poorly solvated, and the repulsive electrostatic effect exerted by Ni(III) on the proximate redox center is particularly large.

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Registry No. **1**, 84507-37-9; **2**, 102632-51-9; Cu_2(biscyclam)$^{4+}$, 102649-29-6; Ni_2(biscyclam)$^{4+}$, 102649-30-9; CuNi(biscyclam)$^{4+}$, 102649-31-0.

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Generation and Reactions of Chiral, Pyramidal, Transition-Metal Lewis Acids of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+X^-$

Sir:

Transition-metal complexes of weakly coordinating ligands such as BF_4^- and PF_6^- are currently the focus of much synthetic, structural, and mechanistic interest.[1-5] Such complexes are often

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(2) (a) LaCroce, S. L.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312. (b) Markham, J.; Menard, K.; Cutler, A. *Inorg. Chem.* **1985**, *24*, 1581.

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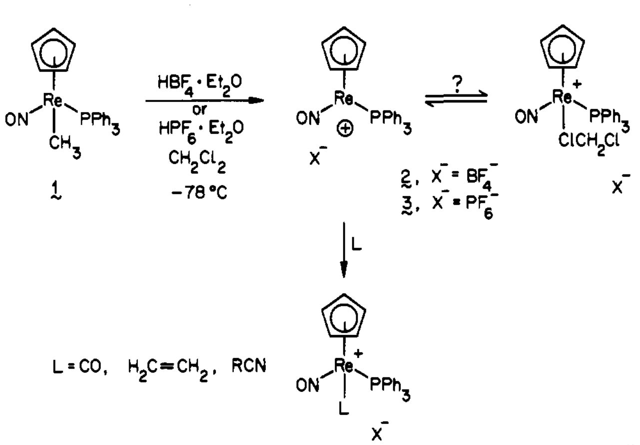
in facile equilibrium with coordinatively unsaturated metal cations that are capable of reacting with and activating small molecules. In an important series of papers, Beck[1] and Cutler[2] have described the synthesis and chemistry of weakly bound BF_4^- and PF_6^- complexes of the $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)]^+$ moiety. Graham has reported a BF_4^- complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$,[3] and Wojcicki and Legzdins have prepared BF_4^- and PF_6^- complexes of the dinitrosyl cations $[(\eta^5\text{-}C_5H_5)M(NO)_2]^+$ (M = Cr, W).[4] In this communication, we report the synthesis of BF_4^- and PF_6^- complexes of the pyramidal coordinatively unsaturated cation $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ and reactions that illustrate their utility as precursors to a variety of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ species. We further demonstrate that these complexes can be generated in enantiomerically pure form, thereby providing the first observable transition-metal Lewis acids that are optically active and have metal-centered chirality.

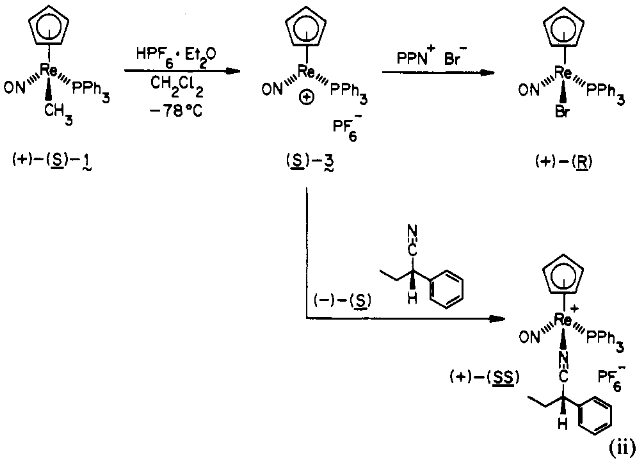
Reaction of the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**)[6] with $HBF_4{\cdot}Et_2O$ (1.01 equiv, CH_2Cl_2 or CD_2Cl_2, −78 °C) gave, as analyzed in situ at −86 °C, a complex (**2**) with the following spectral characteristics: ^{1}H NMR δ 5.60 (s); ^{31}P NMR 12.4 ppm (s); ^{19}F NMR −152.45 ppm (s); IR $\nu_{N{\equiv}O}$ = 1684 cm^{-1}.[7] The ^{1}H NMR spectrum also showed CH_4 (δ 0.14, s) and uncomplexed Et_2O to be present. A similar reaction of **1** with $HPF_6{\cdot}Et_2O$ gave a complex (**3**) that had $\eta^5\text{-}C_5H_5$ ^{1}H NMR and PPh_3 ^{31}P NMR resonances identical with those of **2**. The ^{19}F NMR resonance of **2** was nearly coincident with that of free BF_4^- in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (−90 °C, −152.64 ppm (s)),[6] and the ^{19}F and ^{31}P NMR spectra of **3** showed resonances (−86 °C, −73.5 ppm (d, J_{PF} = 710 Hz); −145.0 ppm (septet, J_{PF} = 712 Hz)) that were identical with those of free PF_6^- in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$.[8] Hence, there is at present no direct evidence for BF_4^- or PF_6^- binding to rhenium in **2** and **3**.

Additional information on the compositions of **2** and **3** was provided by reactions with donor ligands. Reaction of **2** with CO (CH_2Cl_2, 225 psi; −78 °C; then warming) gave the carbonyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ in 85% yield after workup. Similar reactions with ethylene (180 psi) and CH_3CN gave the corresponding complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+BF_4^-$ (81%)[8] and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3CN)]^+BF_4^-$ (73%),[8] respectively. Reaction of **3** (CH_2Cl_2, −78 °C, then warming) with CO (225 psi) and (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ (1.1 equiv) gave $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$ (61%)[6] and (*SS*,*RS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^-$ (86%, 1:1 mixture of diastereomers),[8,9] respectively. Hence, we formulate complexes **2** and **3** as $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+BF_4^-$ and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+PF_6^-$, or weakly bound CH_2Cl_2 adducts thereof (eq i).[7b]



(i)

The syntheses of **2** and **3** were repeated with optically active methyl complex (+)-(*S*)-**1**[9,10] (≥98% ee). Subsequent addition of PPN^+Br^- (1.0 equiv, −78 °C; $PPN^+ = [Ph_3P{\cdots}N{\cdots}PPh_3]^+$) gave the optically active bromide complex (+)-(*R*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Br)$[9,11] (>99% ee) in 55% and 65% yields after workup (eq ii). Similar reaction of optically active **3** with (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ (1.1 equiv, >95% ee, −78 °C) gave (+)-(*SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^-$ ((94 ± 2):(6 ± 2) diasteromer ratio in crude reaction mixture) in 81% yield and 95% ee. These reactions, which proceed with overall retention of configuration at rhenium, require **2** and **3** to be chiral and configurationally stable. Accordingly, MO calculations show that d^6 $(\eta^5\text{-}C_5H_5)MLL'$ complexes should have pyramidal ground states.[12] Brunner has established manganese analogues of **2** and **3** as reaction intermediates from rate data and shown that they have sizable inversion barriers and combine with donor ligands with retention.[13] Hence, the reactions of **2** and **3** with donor ligands are proposed to proceed with retention at rhenium. In turn, reactions of (+)-(*S*)-**1** with $HBF_4{\cdot}Et_2O$ and $HPF_6{\cdot}Et_2O$ must proceed with retention to give (*S*)-**2** and (*S*)-**3**.



(ii)

Complex **3** decomposed to a multitude of products over the course of 15 min at −20 °C. The phosphine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)_2]^+PF_6^-$[6,8] was subsequently detected by ^{1}H (δ 5.28, 31% yield) and ^{31}P (15.8 ppm) NMR. Complex **2** was cleanly converted to a new complex (**4**) over the course of a few hours at −20 °C. Complex **4** was isolated in 64% yield[14] and reacted with CH_3CN (reflux, 5 h) as shown in eq iii to give

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[4] (a) Regina, F. J.; Wojcicki, A. *Inorg. Chem.* **1980**, *19*, 3803. (b) Legzdins, P.; Martin, D. T. *Organometallics* **1983**, *2*, 1785.

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[7] (a) The ^{19}F NMR spectrum of **2** contained three other weak resonances, and the IR spectrum of **2** (−90 °C) contained a second $\nu_{N{\equiv}O}$ band at 1714 cm^{-1} that disappeared upon annealing the sample (−60 °C, then −86 °C). (b) The −85 °C $^{13}C\{^1H\}$ NMR spectrum of (*S*)-**2** showed the expected $\eta^5\text{-}C_5H_5$ resonance (92.21 ppm) and a reproducible broad resonance that may be coordinated CD_2Cl_2 (≃78 ppm); in CH_2Cl_2 (no lock) this resonance sharpened (78.31 ppm).

[8] Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.

[9] *R*/*S* absolute configurations are assigned as described previously,[8,10,11] with the ligand priorities Br > $\eta^5\text{-}C_5H_5$ > Cl > PPh_3 > NO > RCN.

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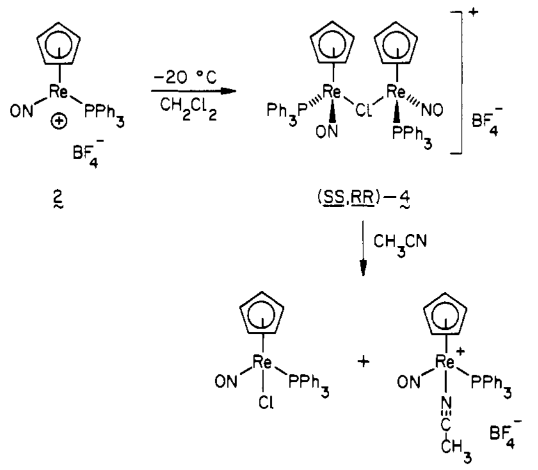
[14] Data on (*SS*,*RR*)-**4**: isolated as orange-red needles of **4**$\cdot 0.45CH_2Cl_2$ from CH_2Cl_2/ether; mp 244–248 °C dec. Anal. Calcd for $C_{46}H_{40}BF_4NORe{\cdot}0.45CH_2Cl_2$: C, 44.70; H, 3.25; Cl, 5.41. Found: C, 44.41; H, 3.29; Cl, 5.18. IR (cm^{-1}, KBr): $\nu_{N{\equiv}O}$ 1662 s; ν_{B-F} 1068 m, 1046 m, 1034 m. ^{1}H NMR (δ, CD_2Cl_2): 7.60–7.43 (m, 2 C_6H_5), 7.18–7.10 (m, C_6H_5); 5.34 (s, 0.45 CH_2Cl_2), 5.40 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2): PPh_3 at 133.62 (d, J_{CP} = 9.9 Hz), 132.97 (d, J_{CP} = 56.0 Hz, ipso), 131.46 (d, J_{CP} = 2.1 Hz, para), 129.10 (d, J_{CP} = 11.3 Hz); 93.05 (s, C_5H_5). $^{31}P\{^1H\}$ NMR (ppm, CH_2Cl_2, −80 °C): 15.1 (s).



(iii)

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3CN)]^+BF_4^-$ (96%) and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ (98%). From these data, **4** was assigned as the bridging chloride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\mu\text{-}Cl)(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^+BF_4^-$. Complex **4** was further assigned as a *dl* (*SS*,*RR*) as opposed to a meso diastereomer on the basis of the following observations: (1) decomposition of (*S*)-**2** yielded *optically active* (+)-(*SS*)-**4**, $[\alpha]^{22}_{589} = 549^\circ$ ($c = 0.71$ mg/mL); (2) the optically active chloride complex (+)-(*S*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ reacted *rapidly* (−60 °C, 2–3 h) with (*S*)-**2** to give (+)-(*SS*)-**4** (74%), $[\alpha]^{22}_{589} = 528^\circ$; (3) efforts to prepare (*SR*,*RS*)-**4** (meso) from (−)-(*R*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ and (*S*)-**2**, which reacted only slowly at 0 °C, were unsuccessful.

In summary, we have demonstrated the ready availability of a chiral, optically pure, transition-metal Lewis acid. In future reports, we will describe the mechanism of formation of these species, their configurational stability, and important applications in organic synthesis.[15]

Acknowledgment. We thank the Department of Energy for support of this research. NMR spectrometers utilized were provided by NSF and DOD instrumentation grants.

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(15) Fernández, J. M.; Emerson, K.; Larsen, R. H.; Gladysz, J. A., manuscript in preparation.

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Trivalent Nickel: Sulfur Coordination ($NiN_2O_2S_2$) vs. Oxygen Coordination (NiN_2O_4)

Sir:

The high (>2) oxidation levels of nickel and their redox reactions are of current interest.[1,2] The low-spin ($S = {}^1/_2$) trivalent state is now known to be present[3] in several bacterial hydrogenases, at least two of which having been shown[4] to have sulfur ligation to nickel. In this context we wish to report for the first time the results of some experiments designed to answer this important question: Does sulfur coordination make nickel(III) more easily accessible than oxygen coordination in similarly constituted species? Lower reduction potential of the nickel(III)–nickel(II) couple and better thermal stability of the nickel(III) species are taken as criteria of accessibility.

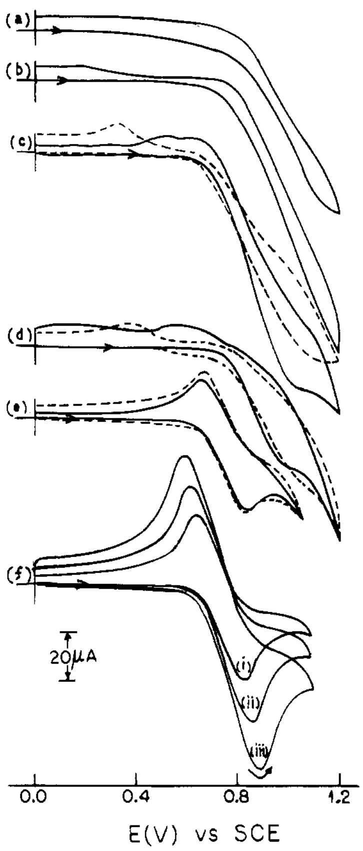

Figure 1. Cyclic voltammograms in dichloromethane (0.1 M TEAP) at a platinum electrode (unless otherwise stated, the scan rate is 50 mV/s and the temperature is 298 K for solid lines and 263 K for broken lines): (a) Zn(II) analogue of **5**, (b) Zn(II) analogue of **6**, (c) **5**, (d) **7**, (e) **6**, (f) **8**, with a scan rate of (i) 50, (ii) 100, or (iii) 200 mV/s.

Triazene 1-oxide ligands[5-7] **1–4** were used in this work. The basis of this choice is twofold: (i) there is systematic replacement of ether oxygen (**1**, **3**) by thioether sulfur (**2**, **4**) such that NiN_2O_4 and $NiN_2O_2S_2$ coordination spheres could be constructed; (ii) should tridentate ligation (**1**, **2**) fail to sustain metal oxidation, hexadentate ligation (**3**, **4**) might still be successful. Ligands **1** and **2** afford[6] pseudooctahedral paramagnetic ($S = 1$) bis complexes of nickel(II) (**5**, **6**) and similarly **4** furnishes[8] **8**. Species **3** and **7** are new,[9,10] and both have the same magnetic moment (3.08 μ_B) in the solid state at 298 K. The gross stereochemical similarity of the complexes in dichloromethane (this solvent is used

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(9) The ligand (**3**) was synthesized by condensing *N*-methylhydroxylamine with the diazotized diamine,[10] and the nickel(II) chelate was prepared in the usual manner[6] from nickel(II) acetate and **3**. Anal. Calcd for $NiC_{16}H_{20}N_6O_4$: C, 46.07; H, 4.31; N, 20.15. Found: C, 46.17; H, 4.31; N, 19.87.

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