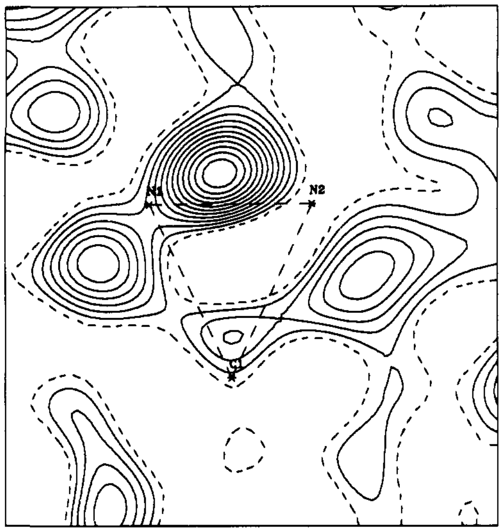

Figure 2. X–X_{HO} map on a plane through the diazirine group. Contours are at 0.04 e/Å^3. Zero and negative contour lines are broken.

Colorless crystals[8] of (I) can be grown from a pentane solution. The crystals diffract to sin $(\theta)/\lambda$ = 1.0 Å^{-1}. They are reasonably stable in the X-ray beam at –65 °C (a deterioration of 7.2% over a data collection of 10414 reflections), though they slowly crumble at lower temperatures. At –65 °C, the diazirine ring is well defined, with an N=N bond length of 1.229 (3) Å, C—N distances of 1.459 (2) and 1.460 (2) Å, and an N—C—N bond angle of 49.8 (1)°. These compare with the dimensions of 1.228 (3), 1.482 (3) Å (mean), and 48.9° derived[9] from the rotational spectrum of H_2CN_2 and are not significantly different from all the known values for this system with the exception of F_2CN_2, where the dimensions are 1.293 (9), 1.426 (4) Å, and 53.9 (4)°, respectively (see Table I).

The deformation electron densities have been calculated for the molecule. Figure 1 shows the electron density for the diazirine ring, and Figure 2 shows the deformation density calculated by routine X–X_{HO} techniques. Figure 2 clearly shows the expected[10] "bent" bonds for the three-membered ring and also shows the effect of the double bond between the nitrogen atoms. The bonding density along the C-N bonds can be seen to be drawn toward the nitrogen atoms, and at the nitrogen atoms the lone-pair electrons can also be seen. It has been observed[14] before that the lone-pair electron density at a nitrogen atom is noticeably less than that observed in the nitrogen π bonds. These effects can best be seen if an exact transparent copy of Figure 2 is placed over Figure 1. The observed density in the diazirine ring does not contain a perfect 2-fold axis nor would this be expected. The torsional angle O_1–C_2–C_1–Cl is –82.4°, which brings the diazirine C_1–N_1 bond to the "inside" of the molecule, oriented toward the phenoxy oxygen atom, while C_1–N_2 is on the "outside" of the molecule. Thus C_1–N_1, but not C_1–N_2, comes close to one set of lone-pair electrons on the oxygen O_1. This will cause more compression of the bonding density toward the C–N bond axis for C_1–N_1 and allow the density associated with C_1–N_2 to spread further away from its bond axis (see Figure 2). Interestingly, the two C–N bond densities integrate planimetrically within 1% to the same total density. The lone-pair electron densities are also different on N_1 and N_2. In this context, it may be significant that the axis of the lone pair on N_2 points toward the plane of the phenyl ring (close to C_6) of a related molecule. An interaction between the lone pair on N_2 and the aromatic system would reduce the lone-pair density at N_2 (see Figure 2). The deformation density of the aromatic portion of the ring (details deposited) resembles that reported[15] for *p*-nitropyridine *N*-oxide, except that it shows a slight tendency toward a quinoidal form. Work is continuing with data refinements which include multipole parameters.[14,15]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to T.S.C. and M.T.H.L., to the Commonwealth Office for a graduate scholarship to P.B., and to the Killam Trust for a graduate scholarship to B.B.

Supplementary Material Available: Tables of fractional coordinates and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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[8] IR 1588 cm^{-1}; ^{1}H NMR δ 4.05 (s, CH_2, 2 H), 6.3–8.00 (arom, 4 H); mp 35 °C, prepared by Graham[11] oxidation of the corresponding amidine hydrochloride. Unlike other diazirines, I does not exhibit fine structure in the 310–360-nm UV region. Crystal Data: triclinic $P\bar{1}$; a = 6.034 (1) Å, b = 8.492 (3), c = 9.805 (2), α = 107.51 (2), β = 96.58 (2), γ = 91.21 (1); V = 471.6 (2) Å^3; Z = 2, T = 208 ± 1 K, μ = 3.905 cm^{-1}; CAD4 diffractometer, λ(Mo $K_{\alpha 1}$) 0.709 26 Å, sin $(\theta_{max})/\lambda$ = 1.0 Å^{-1}, 10414 measured reflections, 2410 unique observed ($I > 3\sigma(I)$), R = 0.0297, R_w = 0.030. Structure refined by CRYSTALS with Dunitz and Seiler weights.[12,13] X–X_{HO} maps[14,15] calculated for deformation density; multipole[14,15] refinement now in progress.

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Activation of Alkynes by Rhenium Polyhydrides in the Presence of Electrophiles: Facile Formation of Hydrido–Alkylidyne Complexes

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Received September 3, 1991

While rhenium forms a myriad of mononuclear hydride complexes that can contain up to nine hydrido ligands per metal center,[1] the *protonolysis* of such species in the presence of unsaturated organic substrates has not hitherto led to any extensive organometallic chemistry, although a variety of well-defined coordination compounds can be formed through protonation,[2] a process that may be followed by loss of dihydrogen and the coordination of various ligand molecules.[3] This behavior contrasts with the relative ease of activating compounds such as $ReH_7(PR_3)_2$ and $ReH_5(PR_3)_3$ toward reaction with saturated and unsaturated organic molecules under thermal[4,5] and photochemical conditions,[5,6] as well as in the presence of a hydrogen acceptor such

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[1] For example, see: (a) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1 and references contained therein. (b) Conner, K. A.; Walton, R. A. In *Comprehensive Coordination Chemistry*; Pergamon: Oxford, England, 1987; Chapter 43, pp 125–213.

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[3] The remarkable stability of some of these species is illustrated by the failure of the $[ReH_4(PMe_2Ph)_4]^+$ cation to react with the unsaturated organic molecules C_2H_4, PhC≡CPh, CO, and CH_3CN.[2b]

[4] (a) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Organomet. Chem.* **1982**, *224*, 363. (b) Baudry, D.; Cormier, J.-M.; Ephritikhine, M.; Felkin, H. *J. Organomet. Chem.* **1984**, *277*, 99. (c) Zeiher, E. H. K.; DeWit, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 7006. (d) DeWit, D. G.; Folting, K.; Streib, W. E.; Caulton, K. G. *Organometallics* **1985**, *4*, 1149.

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as 3,3-dimethylbutene.[7] We now describe a novel activation of internal and terminal alkynes by a polyhydride complex in the presence of the electrophiles H^+ and Ph_3C^+ which results in the facile high-yield synthesis of a new class of stable hydrido–alkylidyne complexes.

The addition of aqueous HPF_6 (0.01 mL) to a pre-formed mixture of $ReH_4(mq)(PPh_3)_2$ (mq is the monoanion of 2-mercaptoquinoline)[8] (0.07 g, 0.08 mmol) and $HC{\equiv}CPh$ (0.09 mL, 0.80 mmol) in 5 mL of dichloromethane immediately generates a clear pale orange colored solution. The mixture was stirred for a few minutes at room temperature, and an excess of diethyl ether (50 mL) was added slowly to precipitate the tan colored crystalline alkylidyne complex $[ReH_2({\equiv}CCH_2Ph)(mq)(PPh_3)_2]PF_6{\cdot}2H_2O$ in high yield (0.070 g, 78%).[9] Similar products are formed with other 1-alkynes ($HC{\equiv}C$-*p*-tol and $HC{\equiv}CC_3H_7$) and, surprisingly, with internal alkynes such as $CH_3C{\equiv}CPh$, $CH_3C{\equiv}CC_2H_5$, and $C_2H_5C{\equiv}CC_2H_5$, the isolated yields in every case exceeding 70% (reaction 1). No identifiable products were

$$ReH_4(mq)(PPh_3)_2 + RC{\equiv}CR' + [E]PF_6 \xrightarrow{CH_2Cl_2} [ReH_2({\equiv}CCH_2R'')(mq)(PPh_3)_2]PF_6 + EH \quad (1)$$

$$E = H^+, Ph_3C^+$$

$$R = C_2H_5 \text{ when } R' = C_2H_5 \text{ and } R'' = n\text{-}C_4H_9$$

$$R = H \text{ when } R' = R'' = n\text{-}C_3H_7, \text{ Ph, or } p\text{-tol}$$

$$R = CH_3 \text{ when } R' = C_2H_5 \text{ or Ph and } R'' = n\text{-}C_3H_7 \text{ or } CH_2Ph$$

$$R = C_2H_5 \text{ when } R' = C_2H_5 \text{ and } R'' = n\text{-}C_4H_9$$

isolated from the reactions between $ReH_4(mq)(PPh_3)_2$ and alkynes in the absence of HPF_6. Since 1-pentyne ($HC{\equiv}CC_3H_7$) and 2-pentyne ($CH_3C{\equiv}CC_2H_5$) yield the same product, viz., $[ReH_2({\equiv}C\text{-}n\text{-}C_4H_9)(mq)(PPh_3)_2]PF_6$, rapid alkyne isomerization must occur in the case of the internal alkynes. The same reaction course occurs when $Ph_3C^+PF_6^-$ is used in place of HPF_6, so it is apparent that H^+ and Ph_3C^+ activate the rhenium center through loss of H^-. The requirement that a terminal ${\equiv}CH$ carbon be present, or at least accessible through isomerization, is shown by the failure of $PhC{\equiv}CPh$ to react in a similar fashion under these same conditions.

The complex $[ReH_2({\equiv}C\text{-}n\text{-}C_4H_9)(mq)(PPh_3)_2]PF_6$, whose properties are representative of this class of compounds, shows weak ν(Re–H) modes in its IR spectrum between 2000 and 1900 cm^{-1}. Its ^1H NMR spectrum (in CD_2Cl_2) displays the Re*H* resonance as a binomial triplet at δ +2.39 (J_{P-H} = 22 Hz) and alkylidyne resonances between δ +2.1 and +0.8 (multiplets, CH_2, 6 H) and at δ +0.59 (triplet, CH_3, 3 H). The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at δ +26.5, while the ^{31}P NMR spectrum is a poorly resolved triplet at this same chemical shift.

These yellow dihydride complexes can be reversibly deprotonated by triethylamine (reaction 2) to give the corresponding neutral, purple colored, monohydride complexes. The monohydrides display a triplet for the Re*H* resonance in their ^1H NMR spectra, (e.g., for R = *n*-C_4H_9, δ −1.85 with J_{P-H} = 19 Hz).[10]

$$[ReH_2({\equiv}CCH_2R'')(mq)(PPh_3)_2]PF_6 \underset{HPF_6}{\overset{NEt_3}{\rightleftharpoons}} ReH({\equiv}CCH_2R'')(mq)(PPh_3)_2 \quad (2)$$

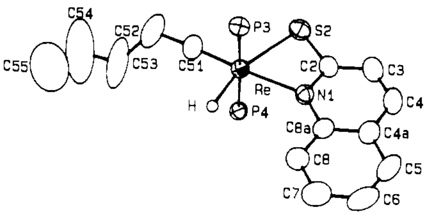

Figure 1. ORTEP representation of the structure of the $ReH({\equiv}C\text{-}n\text{-}C_4H_9)(mq)(PPh_3)_2$ molecule with the phenyl rings of the PPh_3 ligands and hydrogen atoms of the organic ligands omitted. The thermal ellipsoids are drawn at the 50% probability level. Some important bond distances (angstroms) and bond angles (degrees) are as follows: Re–S(2) 2.542 (1), Re–P(3) 2.387 (1), Re–P(4) 2.392 (1), Re–N(1) 2.262 (4), Re–C(51) 1.755 (5), Re–H 1.68 (6), C(51)–C(52) 1.469 (8), C(52)–C(53) 1.55 (2); P(3)–Re–P(4) 176.41 (4), P(3)–Re–S(2) 91.79 (4), P(3)–Re–N(1) 90.1 (1), P(3)–Re–C(51) 89.5 (2), P(3)–Re–H 87 (2), S(2)–Re–N(1) 63.8 (1), S(2)–Re–C(51) 112.6 (2), S(2)–Re–H 160 (2).

Confirmation of the identity of these complexes comes from an X-ray crystal structure determination of the complex $ReH({\equiv}C\text{-}n\text{-}C_4H_9)(mq)(PPh_3)_2$ (**1**).[12,13] This structure (Figure 1) can be described in terms of a distorted octahedral geometry. The phosphorus atoms of the phosphine ligands are trans to one another with a P–Re–P angle of 176.41 (4)°. The single hydride ligand has a Re–H distance (1.68 (6) Å) which is typical for mononuclear rhenium hydride systems as determined by X-ray diffraction.[14] The alkylidyne ligand shows bond lengths and angles characteristic of ligands with metal–carbon triple bonds. The rhenium–carbon distance of 1.755 (5) Å is at the short end of the range for rhenium–alkylidyne complexes.[15] The C_α–C_β distance is typical for a C–C single bond, and the Re–C–C angle is close to being linear (176.9 (5)°).[16]

While details of the mechanism remain to be elucidated, including the mechanism of the alkyne isomerization, we note that the ^1H NMR spectrum of a freshly prepared CD_2Cl_2 solution of $ReH_4(mq)(PPh_3)_2$ and $HC{\equiv}CPh$, to which HPF_6 has been added, displays after 5 min only the resonances for the product $[ReH_2({\equiv}CCH_2Ph)(mq)(PPh_3)_2]PF_6$ and a resonance at δ +4.6 due to free H_2. As yet we have no evidence for the formation of vinylidene or σ-alkenyl intermediates. However, the generation of a vinylidene intermediate, $[ReH_3({=}C{=}CHR'')(mq)(PPh_3)_2]^+$, followed by rapid proton transfer from the metal to the vinylidene ligand to give $[ReH_2({\equiv}CCH_2R'')(mq)(PPh_3)_2]^+$ is plausible, given the precedent for the conversion of vinylidenes to carbynes upon treatment with acid.[17,18] Moreover, such a pathway has been proposed previously[18] from kinetic studies of the protonation of *trans*-$ReCl({=}C{=}CHPh)(dppe)_2$ to give *trans*-$[ReCl({\equiv}CCH_2Ph)(dppe)_2]^+$. To our knowledge there is no substantiated

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(7) For example, see: (a) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243. (b) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1982**, 606. (c) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1235. (d) Baudry, D.; Ephritikhine, M.; Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 788. (e) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1283. (f) Baudry, D.; Boydell, P.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1986**, 525.

(8) This rhenium(V) polyhydride is prepared by the reaction of $ReH_7(PPh_3)_2$ with 2-mercaptoquinoline (mqH). See: Leeaphon, M. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1991.

(9) Anal. Calcd for $C_{53}H_{49}F_6NO_2P_3SRe$: C, 54.98; H, 4.28. Found: C, 54.28; H, 3.96.

(10) Integration of the Re*H* resonances for the cationic dihydrides and neutral monohydrides is fully in accord with the protonation/deprotonation occurring at the metal center.

(11) Luo, X.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 2788.

(12) Attempts to grow suitable X-ray quality crystals of the dihydrides have so far been unsuccessful. Over time these solutions afford significant quantities of the monohydride even in the absence of added base.

(13) Crystal data for **1** (+20 °C): space group $P\bar{1}$; a = 11.181 (1) Å, b = 12.299 (1) Å, c = 16.641 (1) Å, α = 103.59 (6)°, β = 104.17 (1)°, γ = 99.50 (8)°; V = 2095 (5) Å^3, Z = 2, d_{calcd} = 1.491 g/cm^3; Enraf-Nonius diffractometer, Mo Kα radiation; 5464 unique reflections with 4° < 2θ < 45° collected, 4622 reflections with $I > 3\sigma(I)$ used in the refinement; all non-hydrogen atoms refined anisotropically; empirical absorption correction applied (μ = 30.95 cm^{-1}); R = 0.024, R_w = 0.029, GOF = 0.781.

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(16) We have recently completed the single-crystal X-ray structure determination of $ReH({\equiv}CCH_2Ph)(mq)(PPh_3)_2$. It closely resembles in all important respects the structure of **1**.

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mechanism in the literature for the metal hydride catalyzed isomerism of internal to terminal alkynes.

The hydrido–alkylidyne species, $[ReH_2(\equiv CCH_2R)(mq)(PPh_3)_2]^+$, provide an interesting alternative class of rhenium(VII) alkylidynes to the important Schrock complexes, in which imido, alkoxide, and/or alkylidene ancillary ligands are also present.[19,20] The mechanism of the formation of the hydrido–alkylidyne complexes is under investigation, as are studies exploring the synthetic scope of these reactions and the reactivity of the resulting complexes.

Acknowledgment. Support from the National Science Foundation, through Grant Nos. CHE88-07444 and CHE91-07578 to R.A.W. and Grant No. CHE86-15556 for the purchase of the microVAX II computer and diffractometer, is gratefully acknowledged.

Supplementary Material Available: Listings of atomic positional parameters for the structure of $ReH(\equiv C\text{-}n\text{-}C_4H_9)(mq)(PPh_3)_2$ (Table S1) (3 pages). Ordering information is given on any current masthead page.

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Oxo–Alkyls of Cr^V and Cr^{VI}

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Transition-metal complexes featuring both alkyl and oxo ligands command a growing share of attention of organometallic chemists.[1] The chemistry of such oxo–alkyls is relevant to stoichiometric and catalytic oxidations of organic molecules mediated by transition metals.[2] While high-valent chromium reagents have a long history of use as oxidants in organic synthesis,[3] no chromium alkyls containing oxo ligands (Cr=O) have been reported.[4] Our exploration of the reactivity of paramagnetic organochromium compounds[5] has now yielded several of these molecules. Herein we describe the synthesis, structural characterization, and preliminary reactivity studies of oxo–alkyls of chromium in its highest oxidation states (V and VI).

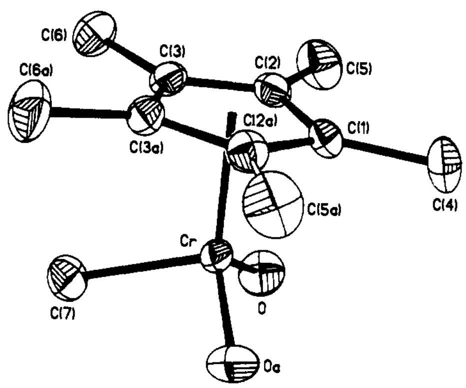


Figure 1. Molecular structure of $Cp^*Cr^{VI}(O)_2CH_3$ (**2**). Selected bond distances: Cr–O, 1.605 (3) Å; Cr–C(7), 2.054 (5) Å. Interatomic angles: C(7)–Cr–O, 97.5 (1)°; O–Cr–O_a, 109.4 (2)°.

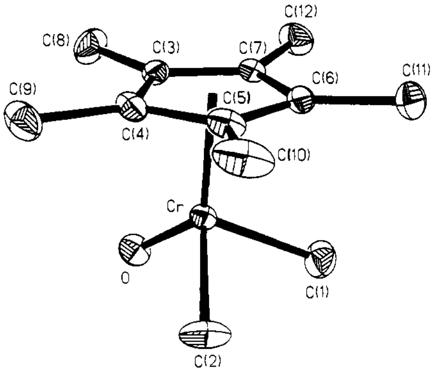
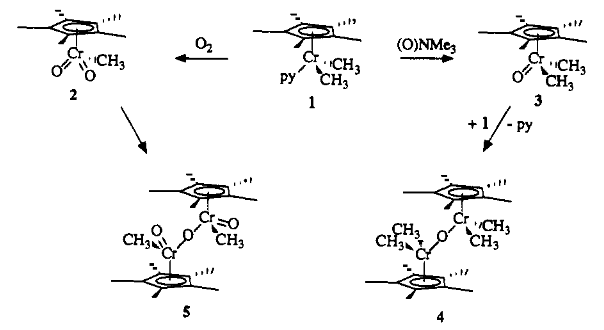


Figure 2. Molecular structure of $Cp^*Cr^V(O)(CH_3)_2$ (**3**). Selected bond distances (values in parentheses refer to the second molecule in the asymmetric unit): Cr–C(1), 2.044 (6) Å (2.041 (6) Å); Cr–C(2), 2.042 (5) Å (2.045 (5) Å); Cr–O, 1.579 (3) Å (1.581 (3) Å). Interatomic angles: C(1)–Cr–C(2), 90.8 (2)° (89.2 (2)°); C(1)–Cr–O, 100.4 (2)° (101.9 (2)°); C(2)–Cr–O, 101.3 (2)° (101.0 (2)°).

Scheme I



Admission of an excess (>1.5 equiv) of dry dioxygen to cooled (−78 °C) ether solutions of $Cp^*Cr^{III}(py)(CH_3)_2$ (**1**) (Cp^* = η^5-pentamethylcyclopentadienyl, py = pyridine), followed by slow warming to room temperature, induced a sequence of color changes (from brown through green to red). Evaporation of the solvent, extraction of the solid residue with pentane, and recrystallization from the same solvent yielded dark red crystals of $Cp^*Cr^{VI}(O)_2CH_3$ (**2**) in 40% yield (Scheme I).[6] Sharp NMR resonances in the expected range attested to the diamagnetic nature of **2**,

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[6] **2**: ^1H NMR (C_6D_6) δ 1.53 (s, 15 H), 1.35 (s, 3 H); ^{13}C NMR (C_6D_6) δ 120.1, 25.6, 10.5; IR (KBr) 3015 (m), 2978 (sh), 2953 (sh), 2920 (s), 2857 (m), 1443 (m), 1375 (s) 1358 (m), 1121 (m), 951 (m, sh), 914 (s), 804 (m) cm^{-1}; UV-vis (THF) 472 nm (ϵ 1630), 350 (4310), 233 (14280); MS (70 eV) 234 (M^+, 28), 202 (52), 134 (77) 119 (100); HRMS calcd for $C_{11}H_{18}CrO_2$ 234.0712, found 234.0715; mp 93 °C.

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