Contribution from the Department of Chemistry,
University of Kansas, Lawrence, Kansas 66045

Insertion and Substitution Reactions of Dihalocarbene Precursors with Bis(h^5-cyclopentadienyl)tungsten Dihydride

KON SWEE CHEN, JACOB KLEINBERG, and JOHN A. LANDGREBE*

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The reactivity of bis(h^5-cyclopentadienyl)tungsten dihydride toward dihalocarbene precursors was investigated. The thermal decomposition of sodium trichloroacetate in glyme in the presence of bis(h^5-cyclopentadienyl)tungsten dihydride produced the insertion product, bis(h^5-cyclopentadienyl)tungsten dichloromethide hydride. However, the thermal decomposition of sodium chlorodifluoroacetate in a chlorobenzene–diglyme mixture in the presence of the same hydride substrate gave the substitution product, bis(h^5-cyclopentadienyl)tungsten bis(chlorodifluoroacetate).

Of particular interest, yet virtually unstudied, are reactions between divalent carbon species (carbenes) and bonds to transition metals. In those instances in which apparent carbene insertions into palladium–chlorine and iridium–chlorine bonds were reported,[1] the reactions between the metal compound and a diazo compound undoubtedly did not involve intervention of a divalent carbon species.[2,3] There are a few known examples of actual insertion by carbenes into metal-hydrogen,[4] metal-halogen,[5] and metal-carbon[6] bonds, but in no instance is a transition metal involved. Also, it should be pointed out that none of the previously reported carbene complexes of tungsten[7a,b] or any other metal[7c–e] has been synthesized through the intermediacy of a carbene species. The insertion of $:CCl_2$ into a tin-tin bond[8] has been reported.

We wish to report the reactions of WCp_2H_2 (Cp is cyclopentadienyl) with sodium trichloroacetate and chlorodifluoroacetate under conditions where the latter normally give dichlorocarbene and difluorocarbene, respectively. A preliminary communication on the reaction of the hydride with the trichloroacetate has been reported.[9]

Experimental Section

Materials and Techniques. Tungsten hexachloride was prepared according to the method of Porterfield and Tyree.[10] The hexachloropropene was obtained from Columbia Organics and used without further purification. Sodium borohydride was obtained from Ventron Corp. and used without further purification. Reagent grade dicyclopentadiene, from Aldrich Chemical Co., was distilled through a 3-foot Vigreux column to obtain cyclopentadiene. Sodium trichloroacetate was obtained from K & K and was dried over P_4O_{10} for 40 hr in a drying pistol at 100° (0.01 mm). Sodium chlorodifluoroacetate was obtained from Peninsular ChemResearch Corp. and was treated in the same manner as sodium trichloroacetate before use. All solvents were made oxygen-free and dry by distillation from $LiAlH_4$ or CaH_2 either under vacuum or under oxygen-free, dry nitrogen. They were thoroughly degassed prior to use. Reactions and manipulations involving all compounds were carried out either under oxygen-free nitrogen or argon in dry bags or in specially constructed glassware made for manipulation in an inert atmosphere.[11]

Infrared spectra were taken on a Perkin-Elmer Model 421 spectrometer and are reported in reciprocal centimeters with the following abbreviations: vw = very weak; w = weak; m = medium; ms = medium strong; s = strong; vs = very strong; b = broad; sh = sharp; sld = shoulder; db = doublet. Nuclear magnetic resonance spectra were obtained on a Varian HA-100 spectrometer and are reported in τ units (tetramethylsilane internal standard). Melting points were obtained in capillary tubes which had been sealed under argon. Microanalyses for carbon, hydrogen, chlorine, and fluorine were done by Ms. Kathy Widiger on a F & M Model 185 C, H, and N analyzer, as well as by Huffman, Galbraith, and Chemalytics Laboratories. Tungsten was determined as the 8-hydroxyquinolate.[12]

Mass spectra were obtained with a Varian Model CH-5 spectrometer at 70 eV. Samples were introduced directly into gold cups under a blanket of argon and placed into the evacuated reaction chambers immediately. Mass spectral data for each compound are listed in order of oven temperature, m/e value, relative abundance in parentheses, and probable assignment. Only important or relatively abundant peaks above m/e 34 are shown. Cp stands for C_5H_5, and for the chlorine-containing compounds only peaks corresponding to ^{184}W and ^{35}Cl are listed. The assignments of peaks are based on calculated isotopic distributions[13] as compared to those observed.

Bis(h^5-cyclopentadienyl)tungsten dihydride was prepared by essentially the same method as that described in the literature.[14] After the reaction between WCl_6, NaC_5H_5, and $NaBH_4$ and the removal of solvent, the dark-colored material was sublimed at 120° (0.01 mm) to give yellow needles of Cp_2WH_2. The yield was about 25%. In order to obtain a larger yield of the dihydride (75% based on starting tungsten hexachloride), the residue following sublimation of the pure Cp_2WH_2 was treated with deaerated 2 M HCl (reaction very exothermic) and filtered, and then the solution was treated with deaerated 2 M NaOH until Cp_2WH_2 precipitated. The solid was filtered, dried, and sublimed at 120° (0.01 mm). The product obtained was resublimed to ensure purity. The ir, nmr, and mass spectra, melting point,[15] and elemental analysis confirmed the authenticity of the product. *Anal.* Calcd for $C_{10}H_{12}W$: C, 38.00; H, 3.83; W, 58.17. Found: C, 37.94; H, 3.83; W, 57.83. Nmr spectrum (glyme): τ 5.57 (10 H, s, $2C_5H_5$), 22.38 (2 H, s, W-H). Ir spectrum

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(KBr pellets; checked with Nujol mull) 3114 (w, b), 3102 (w, b), 3078 (m, sh), 1918 (s, b, W–H), 1417 (sld, b), 1414 (ms, sh), 1360 (ms, sh), 1249 (w, sh), 1094 (ms, sh), 1063 (vw, b), 1051 (vw, b), 999 (s, sh), 982 (s, sh), 902 (ms, sh), 874 (w, b), 818 (s, sh), 772 (s, sh), 727 (vw, b), 597 (w, sh). Mass spectrum (114°): 316 (0.1) $C_{10}H_{12}W\cdot^{+}$, 314 (100) $C_{10}H_{10}W\cdot^{+}$, 287 (27.0) $C_8H_7W\cdot^{+}$, 274 (1.0) $C_7H_6W\cdot^{+}$, 261 (11.2) $C_6H_5W^{+}$, 248 (1.6) $C_5H_4W\cdot^{+}$, 235 (4.2) $C_4H_3W^{+}$, 223 (2.1) $C_3H_3W^{+}$, 209 (1.1) C_2HW^{+}, 197 (0.1) CHW^{+}, 184 (0.2) $^{184}W\cdot^{+}$, 157 (17.6) $C_{10}H_{10}W^{2+}$, 143.5 (3.0) $C_8H_7W\cdot^{2+}$, 130.5 (1.2) $C_6H_5W\cdot^{2+}$, 77 (0.1) $C_6H_5^{+}$, 65 (0.2) $C_5H_5^{+}$, 39 (0.3) $C_3H_3^{+}$.

Bis(h^5-cyclopentadienyl)tungsten Dichloromethide Hydride. To 50 ml of 1,2-dimethoxyethane (glyme, freshly distilled from $LiAlH_4$ and degassed with argon) in a 100-ml, round-bottomed flask with a side arm was added 1.00 g (3.16 mmol) of Cp_2WH_2 and the mixture was stirred under argon. A 1.75-g (9.48 mmol) sample of sodium trichloroacetate was added to the yellow solution, which was then stirred to dissolve the solids. The mixture was thoroughly flushed with argon and maintained at reflux for 5 hr under a blanket of argon. The initially yellow solution slowly turned dark while a light brown precipitate (shown to be mostly sodium chloride together with a small amount of Cp_2WCl_2[16]) formed as the sodium trichloroacetate was decarboxylated.[17] The small amount of Cp_2WCl_2 formed was identified by ir and mass spectra and melting point. Following the reaction, the mixture was filtered, concentrated to approximately 15–20% of the original volume, and set aside. The green-black needles which appeared slowly turned to a brown oil on contact with air. The crystalline material did not melt sharply but darkened beginning at *ca.* 150° and decomposed at *ca.* 300°. The yield of the product based on the assigned structure $Cp_2WH(CHCl_2)$ (see Results and Discussion) was at least 20%. *Anal.* Calcd for $C_{11}H_{12}Cl_2W$: C, 33.12; H, 3.03; Cl, 17.96; W, 45.86. Found: C, 33.39; H, 2.88; W, 45.69. Found (second sample): C, 31.06; H, 2.93; Cl, 17.77; W, 46.08.

Nmr spectrum for $Cp_2WH(CHCl_2)$ (glyme): τ 4.36 (10 H, s, $2C_5H_5$), 23.33 (1 H, s, W–H), 2.14 (1 H, s, $CHCl_2$). As suggested by a referee, a spectrum was obtained on a mixture of the product (7.586×10^{-5} mol) and an internal standard, *p*-di-*tert*-butylbenzene (4.056×10^{-5} mol), in 2 ml of glyme. Values calculated and found for the various absorptions based on a value of 18.00 for the *tert*-butyl hydrogen atoms of the standard are displayed below. The adjusted figures compensate for the fact that the integration of the four aromatic hydrogen atoms of the internal standard is low by 8.4%. With or without the adjustment the values verify the 1:10:1 ratio of the three nmr absorptions in the product.

	$CHCl_2$	$2C_5H_5$	WH	*t*-Bu-C_6H_4-*t*-Bu
Calcd	1.87	18.70	1.87	4.00
Found	1.84	17.33	1.76	3.69
Adjusted	1.99	18.79	1.91	4.00

Ir spectrum for $Cp_2WH(CHCl_2)$ (KBr pellet; checked with Nujol mull): 3112 (m, b), 2950 (w, b, –CH), 1940 (s, b, W–H), 1415 (m, sh), 1360 (w, sh), 1260 (ms, sh, W–C), 1095 (ms, sh), 1053 (vw, b), 999 (m, sh), 986 (m, sh), 940 (vw, b), 897 (w, b), 816 (ms, sh), 774 (m, sh), 725 (vw, b), 600 (w, sh).

Mass spectrum for $Cp_2WH(CHCl_2)$ (188°): 398 (3.1) $C_{11}H_{12}WCl_2\cdot^{+}$, 384 (76.4) $C_{10}H_{10}WCl_2\cdot^{+}$, 349 (74.4) $C_{10}H_{10}WCl^{+}$, 319 (100) $C_5H_5WCl_2^{+}$, 314 (10.2) $C_{10}H_{10}W\cdot^{+}$, 293 (59.0) $C_3H_3WCl_2^{+}$, 288 (5.7) $C_8H_8W\cdot^{+}$, 284 (26.7) $C_5H_5WCl\cdot^{+}$, 270 (14.1) $C_4H_3WCl\cdot^{+}$, 258 (35.8) $C_3H_3WCl\cdot^{+}$, 248 (2.2) $C_5H_4W\cdot^{+}$, 244 (5.8) $C_2HWCl\cdot^{+}$, 232 (5.0) $CHWCl\cdot^{+}$, 223 (2.6) $C_3H_3W^{+}$, 219 (6.6) WCl^{+}, 192 (7.5) $C_{10}H_{10}WCl_2^{2+}$, 184 (1.1) $^{184}W^{+}$, 174.5 (8.6) $C_{10}H_{10}WCl\cdot^{2+}$, 159.5 (10.7) $C_5H_5WCl_2\cdot^{2+}$, 146.5 (5.4) $C_3H_3WCl_2^{2+}$, 129 (3.2) $C_3H_3WCl^{2+}$, 65 (5.4) $C_5H_5^{+}$, 39 (14.3) $C_3H_3^{+}$, 37 (8.0) $^{37}Cl^{+}$, 36 (1.9) $HCl\cdot^{+}$, 35 (23.8) $^{35}Cl^{+}$.

Mass spectrum for Cp_2WCl_2 (150°): 384 (14.9) $C_{10}H_{10}WCl_2\cdot^{+}$, 349 (59.9) $C_{10}H_{10}WCl^{+}$, 314 (100) $C_{10}H_{10}W\cdot^{+}$, 287 (48.8) $C_8H_7W^{+}$, 274 (15.6) $C_7H_6W\cdot^{+}$, 261 (34.3) $C_6H_5W^{+}$, 248 (6.4) $C_5H_4W\cdot^{+}$, 235 (7.0) $C_4H_3W^{+}$, 222 (6.6) $C_3H_2W^{+}$, 184 (0.8) $^{184}W^{+}$, 174.5 (6.4) $C_{10}H_{10}WCl^{2+}$, 157 (21.1) $C_{10}H_{10}W^{2+}$, 143.5 (6.6) $C_8H_7W\cdot^{2+}$, 65 (3.1) $C_5H_5^{+}$, 39 (0.3) $C_3H_3^{+}$, 37 (1.7) $^{37}Cl^{+}$, 35 (5.1) $^{35}Cl^{+}$.

Bis(h^5-cyclopentadienyl)tungsten Bis(chlorodifluoroacetate). A 0.5-g (1.58 mmol) sample of Cp_2WH_2 was placed into a 100-ml, round-bottomed flask with a side arm and the flask was flushed several times with argon. Then, 50 ml of freshly distilled chlorobenzene (distilled from $LiAlH_4$ *in vacuo*) was added to dissolve the Cp_2WH_2. To the yellow solution, 1.3 g (7.00 mmol) of sodium chlorodifluoroacetate was added and the whole mixture was brought to reflux under a blanket of argon. Bis(2-methoxyethyl) ether (1 ml, diglyme, distilled from $LiAlH_4$ *in vacuo*) was then added *via* a syringe to aid decarboxylation. The solution immediately began to turn dark and bubbles appeared as decarboxylation occurred. The mixture was maintained at reflux for 5 hr and then allowed to cool. The reddish-brown solution was filtered under argon and the light gray solid on the frit was found to be mostly unreacted acetate with very small amounts of sodium chloride and Cp_2WCl_2. The filtrate was evacuated to dryness, redissolved in acetone, and passed through an alumina column. The eluate was reddish brown, and following evacuation of the acetone, reddish-brown platelets were obtained, mp 163–164°, with decomposition to an oil. The $Cp_2W(O_2C_2ClF_2)_2$ decomposed to a dark solid when heated to about 100° in the presence of air or oxygen. *Anal.* Calcd for $C_{14}H_{10}O_4F_4Cl_2W$: C, 29.35; H, 1.76; F, 13.26; Cl, 12.37; W, 32.09. Found: C, 29.58; H, 1.75; F, 13.46; Cl, 12.37; W, 32.28.

^1H nmr spectrum (benzene): τ 5.10 (s); ^1H nmr (acetone) τ 4.06 (s). ^{19}F nmr spectrum (acetone): singlet 106.4 Hz upfield from $NaO_2C_2ClF_2$.

Ir spectrum (KBr pellet; checked with Nujol mull): 3138 (ms, sh), 1705 (vs, b, –C=O), 1479 (vw, sh), 1428 (m, sh), 1410 (w, sh), 1355 (vs, sh), 1280 (m, sh), 1150 (vs, sh), 1065 (vw, sh), 1010 (w, b, sld), 990 (w, b, sld), 962 (ms, sh), 896 (w, b), 883 (w, b, db), 832 (ms, sh), 812 (ms, sh), 725 (ms, sh), 634 (m, sh), 588 (vw, sh).

Mass spectrum (123°): 572 (51.7) $C_{14}H_{10}O_4Cl_2F_4W^{+}$, 537 (9.4) $C_{14}H_{10}O_3Cl_2F_3W^{+}$, 478 (3.4) $C_{12}H_{10}O_3ClF_3W^{+}$, 459 (5.4) $C_{12}H_{10}O_3ClF_2W^{+}$, 443 (42.2) $C_{12}H_{10}O_2ClF_2W^{+}$, 408 (4.2) $C_{12}H_{10}O_2F_2W^{+}$, 365 (3.8) $C_{10}H_{10}O_2FW^{+}$, 349 (100) $C_{10}H_{10}OFW^{+}$, 333 (34.0) $C_{10}H_{10}FW^{+}$, 319 (22.3) $C_9H_8FW^{+}$, 300 (47.0) $C_9H_8W^{+}$, 287 (24.2) $C_8H_7W^{+}$, 274 (8.3) $C_7H_6W^{+}$, 261 (3.6) $C_6H_5W^{+}$, 248 (1.7) $C_5H_4W^{+}$, 184 (1.1) $^{184}W^{+}$, 174.5 (10.5) $C_{10}H_{10}OFW^{2+}$, 166.5 (3.8) $C_{10}H_{10}FW^{2+}$, 65 (8.6) $C_5H_5^{+}$, 39 (0.5) $C_3H_3^{+}$, 37 (6.7) $^{37}Cl^{+}$, 35 (21.4) $^{35}Cl^{+}$.

Results and Discussion

Bis(h^5-cyclopentadienyl)tungsten dihydride was chosen for this study because of (a) its thermal stability (found to be stable to about 130° in ethers) and (b) its reasonable reactivity toward Lewis acids and other electron-deficient species.[15,18] The dihalocarbenes were generated by the thermal decarboxylation of the appropriately substituted sodium acetates in either glyme or diglyme.

The decomposition of sodium trichloroacetate in the presence of Cp_2WH_2 gave rise to an insertion product as indicated in the equation

$$Cp_2WH_2 + NaO_2C_2Cl_3 \xrightarrow[84°,\ 5\ hr]{glyme} Cp_2WH(CHCl_2) + NaCl + CO_2$$

The product, a greenish-black solid, was shown by mass spectrometry (Experimental Section) to have a molecular weight of 398. The relative intensities of the isotopic peaks in the molecular ion cluster were characteristic of the presence of WCl_2 in the molecule and distinctly different from the intensities anticipated for WCl or WCl_3.[13] Elemental analyses for tungsten, chlorine, and hydrogen are in excellent agreement with $C_{11}H_{12}Cl_2W$. Although the analyses for carbon were erratic, the other analytical data taken together with mass spectral and nmr data (to be discussed) unequivocally verify the number of carbon atoms in the molecular formula as 11.

By analogy with the characteristic nmr absorptions of closely related known structures, such as the starting compound, Cp_2WH_2, ten cyclopentadienyl hydrogens and a single metal-bound hydrogen[19] are readily assigned. These

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[19] Due to low solubility of $Cp_2WHCHCl_2$ in glyme, experimental conditions required to obtain the nmr spectrum did not permit the resolution required to observe the weak coupling between cyclopentadienyl and metal-bound hydrogen. The line width for the τ 4.36 peak was 1.7 Hz.

assignments require that the remaining hydrogen at τ 2.14 be associated with a dichloromethyl group attached to tungsten.

The only reported chemical shift value for a dichloromethyl group attached to a metal is the value of τ 4.00 associated with phenyl(dichloromethyl)mercury.[20] In comparing the latter compound with $Cp_2WH(CHCl_2)$ at least two differences in these structures would dictate that the dichloromethyl hydrogen of $Cp_2WH(CHCl_2)$ should appear at substantially lower field in the nmr spectrum than that for $PhHgCHCl_2$. First, Ginsberg[21] has noted that the shielding effect of transition metals increases on going from left to right in the periodic table. For example, the cyclopentadienyl hydrogens of dicyclopentadienylmetal hydrides of tantalum, tungsten, and rhenium (benzene solvent) are found at τ 5.24, 5.76, and 6.36, respectively. The position of tungsten to the left of mercury in the periodic table would dictate that a dichloromethyl group attached to tungsten should be subjected to a lower shielding effect than one attached to mercury. Second, since cyclopentadienyl groups are better π acceptors than phenyl groups, the two cyclopentadienyl groups of $Cp_2WH(CHCl_2)$ should produce a substantially greater downfield shift for the dichloromethyl group of $Cp_2WH(CHCl_2)$ than that produced in $PhHgCHCl_2$ by the single phenyl group.

Additional evidence in support of the structure comes from the ir spectrum (KBr pellet) which shows among others a band at 2950 cm^{-1}, which can be assigned to the C-H stretching of the $CHCl_2$ group, and a band at 1940 cm^{-1} assigned to a W-H stretch. The band at 1260 cm^{-1}, which has no counterpart in the starting compound, may correspond to a W-C stretching vibration.[22] Because there were several bands present in the region normally associated with the C-Cl stretch, an unequivocal assignment could not be made for the CCl_2 group.

Finally, the cracking pattern exhibited in the mass spectrum of the compound (Experimental Section) is entirely consistent with the assigned structure. Fragmentation appears to follow the paths indicated in Scheme I.

Scheme I

$$\begin{tikzcd}
(C_5H_5)_2WH(CHCl_2)\cdot^+ \arrow[r, "-CH_3"] & (C_5H_5)_2WCl_2\cdot^+ \arrow[r, "-Cl\cdot"] \arrow[d, "-C_5H_5\cdot"] & (C_5H_5)_2WCl^+ \arrow[d, "-Cl\cdot"] \\
C_5H_5WCl\cdot^+ \arrow[d, "-C_2H_2"] & (C_5H_5)WCl_2^+ \arrow[l, "-Cl\cdot"', shift right] \arrow[l, leftarrow, shift left] \arrow[d, "-C_2H_2"] & (C_5H_5)_2W\cdot^+ \arrow[d, "-C_2H_2"] \\
C_3H_3WCl\cdot^+ & C_3H_3WCl_2^+ \arrow[l, "-Cl\cdot"', shift right] \arrow[l, leftarrow, shift left] & (C_5H_5)(C_3H_3)W\cdot^+ \arrow[d, "-C_3H_3"] \\
 & & (C_5H_5)W\cdot^+
\end{tikzcd}$$

In addition to the formation of $Cp_2WH(CHCl_2)$, a small amount of Cp_2WCl_2 coprecipitated with the NaCl. The structure of the dichloride product was confirmed by suitable comparison of physical and spectral properties with those reported for the compound in the literature.[16] The mass spectral cracking pattern for this compound was distinctly different from that exhibited for $Cp_2WH(CHCl_2)$ in that chlorine atoms were lost first from the parent ion and such loss was followed by breakdown of the cyclopentadiene rings.

In contrast to the results with dichlorocarbene, the treatment of Cp_2WH_2 in chlorobenzene-diglyme with sodium chlorodifluoroacetate, under conditions which should have generated difluorocarbene, gave the substitution product, $Cp_2W(O_2C_2ClF_2)_2$.[23] This compound exhibits properties similar to those of $Cp_2W(O_2C_2F_3)_2$ prepared by Harriss and coworkers.[24] Our compound dissolves quite readily in most organic solvents and melts sharply with decomposition at 163-164°. Although there is still a basic site on the tungsten atom, the compound does not appear to form a salt with dilute strong acid. The $Cp_2W(O_2C_2ClF_2)_2$ is converted to starting hydride by treatment with sodium borohydride in tetrahydrofuran at reflux.

Mass spectrometry (Experimental Section) indicated a molecular ion at *m/e* 572 with relative isotopic abundances corresponding to the presence of WCl_2. Elemental analyses are in excellent agreement with values calculated for $C_{14}H_{10}O_4F_4Cl_2W$. Nmr data show only a single type of hydrogen in the cyclopentadienyl region of the spectrum. However, the ^{19}F nmr spectrum showed a singlet that was shifted 106.4 Hz upfield from that of sodium chlorodifluoroacetate in acetone. The explanation of this upfield shift is unclear but it could be due to the shielding of the tungsten. Because both the fluorine and proton resonance signals are singlets, it is clear that the acetate groups have been substituted for the original hydridic hydrogen atoms.

The infrared spectrum shows peaks for the cyclopentadienyl groups along with a very strong peak at 1705 cm^{-1} attributed to the -C=O of the acetate groups. No peaks were observed in the W-H region.

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Registry No. WCp_2H_2, 1271-33-6; $NaO_2C_2Cl_3$, 650-51-1; $Cp_2WH(CHCl_2)$, 12715-65-0; $NaO_2C_2ClF_2$, 1895-39-2; $Cp_2W(O_2C_2ClF_2)_2$, 39394-73-5.

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(22) E. O. Fischer and A. Massbol, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964), have assigned a W-C vibration for the compound $CpW(CO)_3CH_3$ at 1179 cm^{-1}.

(23) Although a 10% yield of sodium chloride was found indicating that some difluorocarbene was generated, no insertion product was observed.

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