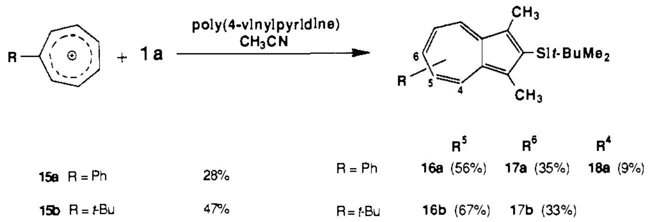
Scheme II



the acid scavenger of choice, although this reagent did not prove suitable for use in relatively slow annulations involving highly substituted allenes or allenes which are not very soluble in acetonitrile. For example, treatment of allenylsilane **1b** with 2 equiv of $TpBF_4$ and excess poly(4-vinylpyridine) furnished the desired azulene in only 46% yield (68% based on recovered allene) after 67 h at 25 °C.[5] In cases such as this superior results are obtained by employing *methyltrimethoxysilane* as the acid scavenger (entries 2–6).

As indicated in Table I, the new azulene synthesis proceeds best with 1,3-dialkyl(*tert*-butyldimethylsilyl)allenes. Annulations employing (*tert*-butyldimethylsilyl)allenes are more efficient than those involving trimethylsilyl derivatives, since in the latter reactions desilylation of the intermediate vinyl cations occurs to generate propargyl-substituted cycloheptatrienes as significant byproducts. As expected, allenylsilanes lacking C-1 alkyl groups (Scheme I, R^1 = H) do not participate in the reaction since in these cases the desired annulation would require the unfavorable rearrangement of a secondary to primary vinyl cation. Finally, reactions employing allenylsilanes lacking C-3 substituents (e.g., entry 7) proceed in diminished yield due to the partial destruction of annulation product initiated by the electrophilic attack of tropylium cation at C-3 of the azulene.[6]

Preliminary experiments indicate that this [3 + 2] annulation can also be applied to substituted tropylium derivatives provided that the substituent does not bear protons on its α-carbon atom.[7] Thus as shown in Scheme II, allenylsilane **1a** was found to combine with phenyl- (**15a**)[8] and *tert*-butyltropylium tetrafluoroborate (**15b**)[9] to afford a mixture of isomeric azulenes in which the C-5 substituted product is the predominant regioisomer.

To our knowledge the annulation products produced in this study are the first 2-silylazulenes to be reported. If desired, the 2-trialkylsilyl group can easily be removed by protodesilylation. For example, exposure of **8** to 48% aqueous HBF_4 in CH_3CN at 25 °C for 30 min furnished blue crystals of 1,3-dimethylazulene[10] in quantitative yield. We anticipate that this annulation strategy will find wide application for the preparation of diverse substituted azulenes.

Acknowledgment. We thank the National Science Foundation for generous financial support.

Supplementary Material Available: Full characterization for all annulation products (7 pages). Ordering information is given on any current masthead page.

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(5) In the case of relatively slow annulations, decomposition of $TpBF_4$ becomes a serious problem. In a control experiment, $TpBF_4$ was exposed to poly(4-vinylpyridine) in the absence of allenylsilane under standard annulation conditions. After 24 h, only 10% of the $TpBF_4$ remained unchanged.

(6) Electrophilic substitution reactions of azulenes with tropylium cations are well known: Hafner, K.; Stephan, A.; Bernhard, C. *Liebigs Ann. Chem.* **1961**, *650*, 42. Anderson, A. G., Jr.; Replogle, L. L. *J. Org. Chem.* **1963**, *28*, 262. Nozoe, T.; Toda, T.; Asao, T.; Yamanouchi, A. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2935.

(7) Under the conditions of our annulation tropylium ions bearing alkyl groups with α-hydrogens undergo deprotonation to afford heptafulvene derivatives which rapidly polymerize. For related reactions, see: Nozoe, T.; Takahashi, K.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3277.

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$(\eta^5\text{-}C_5Me_5)_2W{=}O$: An Exceptionally Reactive Organometallic Oxo Derivative. Reduction with Dihydrogen and Reaction with Dioxygen Resulting in Insertion of Oxygen into a Tungsten–Carbon Bond

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The chemistry of organometallic compounds containing oxo and peroxo ligands is an area of increasing interest with potential relevance to selective catalytic oxidation of hydrocarbons. Very few peroxo-alkyl derivatives have been isolated,[1] and their reactivity patterns are still largely unexplored. Recently there has been an increased emphasis placed on the synthesis of transition-metal compounds containing oxo groups in combination with alkyl or hydride ligands.[2] The most extensively studied organotransition-metal-oxo system comprises $Cp^*Re({=}O)_3$ (Cp^* = $(\eta^5\text{-}C_5Me_5)$) and its derivatives, and here the Re=O bonds are found to undergo reduction with carbon monoxide and cycloaddition of diphenylketene and phenylisocyanate, in addition to more conventional metathetical reactions with halide, hydride, and alkyl derivatives of main group elements such as Li, Al, Si, or Zn.[3]

We report herein the synthesis of $Cp^*_2W{=}O$, an exceptionally reactive organometallic oxo derivative, which may be both reduced by H_2 to $Cp^*_2WH_2$, and cleanly oxidized with O_2 to the W(VI) derivative $(\eta^5\text{-}C_5Me_5)W({=}O)_2(OC_5Me_5)$. The latter compound arises from an unusual reaction which effects insertion of an oxygen atom from dioxygen into a W-$(\eta^5\text{-}C_5Me_5)$ bond.

The oxo derivative, $Cp^*_2W{=}O$,[4] is obtained by reaction of $Cp^*_2WCl_2$[5] with $KOH_{(aq)}$, similar to the preparation of $Cp_2W{=}O$[6] (eq 1). $Cp^*_2W{=}O$ is a member of a relatively rare, but growing,

$$Cp^*_2WCl_2 + 2KOH_{(aq)} \xrightarrow{THF} Cp^*_2W{=}O + 2KCl + H_2O \quad (1)$$

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(1) (a) Faller, J. W.; Yinong, Ma *Organometallics* **1988**, *7*, 559–561. (b) van Asselt, A.; Trimmer, M. S.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 8254–8255. (c) Legzdins, P.; Phillips, E. C.; Rettig, S. J.; Sanchez, L.; Trotter, J.; Yee, V. C. *Organometallics* **1988**, *7*, 1877–1878.

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(4) $Cp^*_2W{=}O$: Elemental Anal. Found (Calcd) C, 51.2 (51.1); H, 6.4 (6.4). ^1H NMR (400 MHz, C_6D_6) δ 1.87 (s, $\eta^5\text{-}C_5(CH_3)_5$); ^{13}C NMR (100 MHz, C_6D_6) δ 13.6 (q, $^1J_{C-H}$ = 127, $\eta^5\text{-}C_5(CH_3)_5$), δ 107.6 (s, $\eta^5\text{-}C_5(CH_3)_5$); ^{17}O NMR (12.5 MHz, C_6D_6, relative to external H_2O^{17}) δ 770 (s, W=O). $(\eta^1\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_5)W({=}O)_2$: Elemental Anal. Found (Calcd) C, 48.8 (49.4); H, 5.9 (6.2). ^1H NMR (400 MHz, C_7D_8, 25 °C) δ 1.80 (s, $\eta^5\text{-}C_5(CH_3)_5$); ^1H NMR (400 MHz, C_7D_8, –90 °C) δ 1.52 (s, $\eta^5\text{-}C_5(CH_3)_5$), 1.92 (s, 2($CH_3$) of $\eta^1\text{-}C_5(CH_3)_5$), 2.00 (s, 2($CH_3$) of $\eta^1\text{-}C_5(CH_3)_5$), 2.56 (s, 1($CH_3$) of $\eta^1\text{-}C_5(CH_3)_5$); ^{13}C NMR (100 MHz, C_7D_8, –90 °C) δ 10.1 (q, $\eta^5\text{-}C_5(CH_3)_5$), 117.4 (s, $\eta^5\text{-}C_5(CH_3)_5$), 11.2 (q, 2C of $\eta^1\text{-}C_5(CH_3)_5$), 12.5 (q, 2C of $\eta^1\text{-}C_5(CH_3)_5$), 30.5 (q, 1C of $\eta^1\text{-}C_5(CH_3)_5$), 83.3 (s, 1C of $\eta^1\text{-}C_5(CH_3)_5$), 134.0 (s, 2C of $\eta^1\text{-}C_5(CH_3)_5$), 2C of $\eta^1\text{-}C_5(CH_3)_5$ obscured by solvent; ^{17}O NMR (12.5 MHz, C_6D_6, relative to external $H_2{}^{17}O$) δ 738 (s, 2W=O). $Cp^*W({=}O)_2(OC_5Me_5)$: Elemental Anal. Found (Calcd) C, 47.5 (47.8); H, 5.8 (6.0). ^1H NMR (400 MHz, C_6D_6) δ 1.85 (s, $\eta^5\text{-}C_5(CH_3)_5$), 1.40 (s, 1($CH_3$) of $\eta^1\text{-}C_5(CH_3)_5$), 1.62 (q, partially resolved, $^5J_{C-H}$ = 1,2(CH_3) of $\eta^1\text{-}C_5(CH_3)_5$), 1.78 (q, partially resolved, $^5J_{C-H}$ = 1,2(CH_3) of $\eta^1\text{-}C_5(CH_3)_5$); ^{13}C NMR (100 MHz, C_6D_6) δ 11.0 (q, $^1J_{C-H}$ = 127, $\eta^5\text{-}C_5(CH_3)_5$), 118.5 (s, $\eta^5\text{-}C_5(CH_3)_5$), 23.9 (q, $^1J_{C-H}$ = 127, 1(CH_3) of $\eta^1\text{-}C_5(CH_3)_5$), 10.2 (q, $^1J_{C-H}$ = 125, 2(CH_3) of $\eta^1\text{-}C_5(CH_3)_5$), 11.4 (q, $^1J_{C-H}$ = 125, 2(CH_3) of $\eta^1\text{-}C_5(CH_3)_5$), 93.4 (s, 1C of $\eta^1\text{-}C_5(CH_3)_5$), 134.7 (s, 2C of $\eta^1\text{-}C_5(CH_3)_5$), 137.3 (s, 2C of $\eta^1\text{-}C_5(CH_3)_5$); ^{17}O NMR (12.5 MHz, C_6D_6, relative to external $H_2{}^{17}O$) δ 684 (s, 2W=O), δ W-O-C_5Me_5 (unknown since the required labeled derivative has not yet been synthesized).

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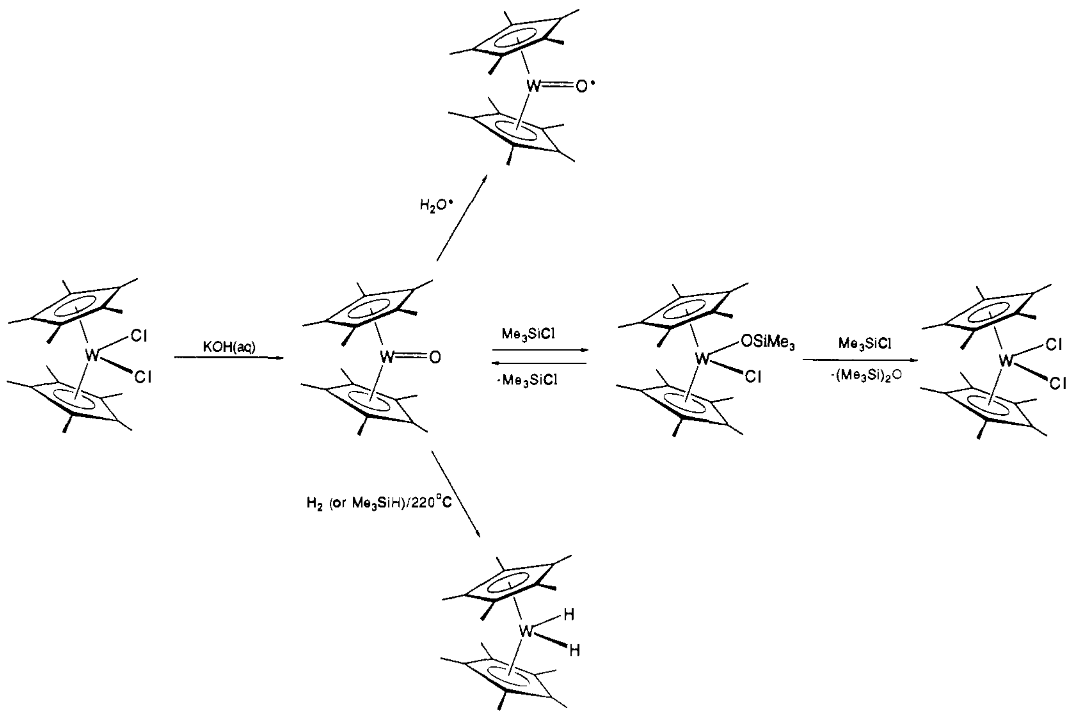
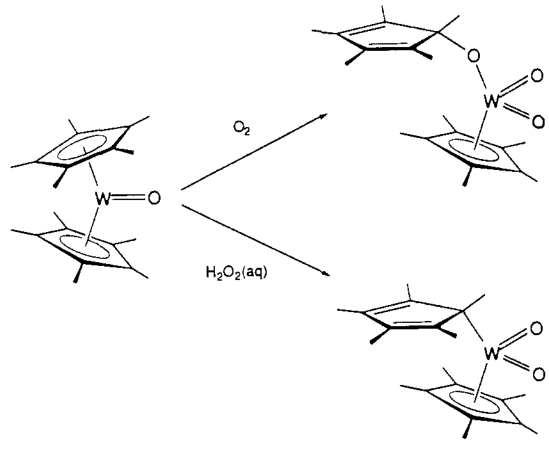
Scheme I

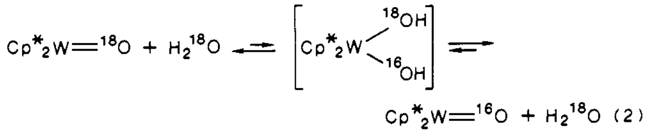


class of neutral transition-metal-oxo compounds in which the metal center is closed shell (18 electron) without oxygen-to-metal lone-pair donation. We propose to denote these as "class b" M=O derivatives in order to distinguish them from the more common "class a" ($M{=}O \leftrightarrow M^+{\equiv}O^-$) derivatives, for which lone-pair donation from oxygen to the metal center imparts triple bond character. Thus, the W=O bond order for $Cp^*_2W{=}O$ is aptly described as two, with little triple bond character contributing. The comparatively weak, and hence, reactive W=O bond is evident from both its spectroscopic features and its chemical reactivity. For example, $Cp^*_2W{=}O$ is characterized by a strong $\nu(W{=}O)$ in its infrared spectrum at 860 cm^{-1} (820 cm^{-1} for $Cp^*_2W{=}^{18}O$) (cf. $\nu(M{\equiv}O) \approx$ 930–1000 cm^{-1} for class a).[7-10] Oxygen exchange between $Cp^*_2W{=}O$ and water, as followed by isotopic exchange with $H_2{}^{18}O$ or $H_2{}^{17}O$ (IR or ^{17}O NMR), is rapid, even at room temperature. In THF solution at 25 °C, for example, the second-order rate constant for oxygen exchange is approximately $2(1) \times 10^{-4}\ s^{-1}{\cdot}M^{-1}$, larger than representative values reported for anionic and cationic complexes in aqueous solutions.[11] The dihydroxy derivative, $Cp^*_2W(OH)_2$, formed by an overall

Scheme II



1,2-addition of the HO–H bond across the W=O double bond, is a likely intermediate (eq 2). Similarly, $Cp^*_2W{=}O$ reacts



$$Cp^*_2W{=}^{18}O + H_2{}^{18}O \rightleftharpoons \left[Cp^*_2W \begin{matrix} {}^{18}OH \\ {}^{16}OH \end{matrix} \right] \rightleftharpoons Cp^*_2W{=}^{16}O + H_2{}^{18}O \quad (2)$$

reversibly with Me_3SiCl to give $Cp^*_2W(OSiMe_3)Cl$ via a 1,2-addition of the Si–Cl bond across the W=O double bond. The $Cp^*_2W(OSiMe_3)Cl$ so formed reacts further with Me_3SiCl to give $Cp^*_2WCl_2$ and $(Me_3Si)_2O$ (Scheme I).

The relative facility of this 1,2-addition of polar X–Y groups with the M=O bonds is also apparent in the reaction of the related isoelectronic, d^0, derivative $Cp^*_2Ta({=}O)H$[12] with water. $Cp^*_2Ta({=}O)H$, like $Cp^*_2W{=}O$, is a class b oxo derivative, ($\nu(Ta{=}O)$ = 850 cm^{-1}), and undergoes rapid oxygen exchange with water. By analogy with the rapid interconversion $Cp^*_2Ta({=}CH_2)H \rightleftharpoons [Cp^*_2Ta{-}CH_3]$,[12,13] the alternative sequence for

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[7] Illustrative comparisons of ν(M–O) stretching frequencies: class a CH_3ReO_3; 999 and 960 cm^{-1} (ref 8); class b Cp^*ReO_3, 909 and 878 cm^{-1} (ref 9). Published data on ^{17}O chemical shifts are thus far limited so that no firm conclusions can be presently drawn regarding the ^{17}O chemical shifts for the different classes (a and b) of oxo ligands. For reference, ^{17}O chemical shifts for some other oxo (terminal and bridging) derivatives are given in ref 10.

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[11] We are not aware of similar measurements of the rates for oxygen exchange in other *neutral* oxo compounds; however, the ^{18}O exchange kinetics for ionic complexes in *aqueous* solution have been reviewed. Typical second-order rate constants ($\approx$25 °C, corrected for $[H_2O]$) include $[ReO_4]^-$, $10^{-8}\ s^{-1}{\cdot}M^{-1}$; *trans*-$[Re(en)_2O_2]^+$, 10^{-6}, $s^{-1}{\cdot}M^{-1}$; $[WO_4]^{2-}$ $10^{-2}\ s^{-1}{\cdot}M^{-1}$. It should be noted that for all these examples the rate laws are complex, and the rates are very pH dependent. Gamsjager, H.; Murmann, R. K. *Advances in Inorganic and Bioinorganic Mechanisms*, Sykes, A. G., Ed.; Academic Press: London, 1983; Vol. 2, pp 317–380.

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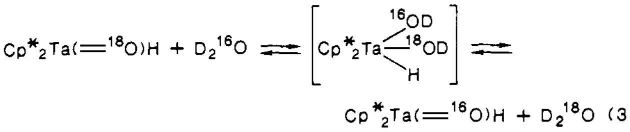
oxygen exchange with H_2O must be considered: α-H migration from $Cp^*_2Ta(O^*)H$ to yield $[Cp^*_2Ta^{III}\text{-}O^*H]$, oxidative addition of HO-H, reductive elimination of H_2O^*, and α-H elimination to give the isotopomer $Cp^*_2Ta({=}O)H$. The latter possibility is eliminated, however, by the observation that treatment of $Cp^*_2Ta({=}^{18}O)H$ with excess $D_2{}^{16}O$ results in rapid exchange of oxygen isotopes but no *H/D exchange* (eq 3).[14]


(3)

Significantly, the W=O bond of $Cp^*_2W{=}O$ reacts even with nonpolar σ bonds such as H–H and H-$SiMe_3$, albeit under more forcing conditions, to afford $Cp^*_2WH_2$[15] (Scheme I).[16]

In light of the d^2, W^{IV}, nature of $Cp^*_2W{=}O$, we have also investigated reactions which could result in oxidation of the tungsten center. Thus, reaction of $Cp^*_2W{=}O$ with either $H_2O_{2(aq)}$ or Me_3CO_2H results in oxygen atom transfer[17] to give the dioxo (W^{VI}) derivative, $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W({=}O)_2$[4] [$\nu(WO_2)_{sym} = 895\ cm^{-1}$, $\nu(WO_2)_{asym} = 935\ cm^{-1}$], which has been structurally characterized by X-ray diffraction methods.[18]

The clean reaction with O_2 (1 atm, 25 °C), shown in Scheme II, further illustrates the exceptional chemical reactivity of $Cp^*_2W{=}O$. The structure of the isolated product $(\eta^5\text{-}C_5Me_5)W({=}O)_2(OC_5Me_5)$[4] has been determined by X-ray diffraction methods.[19] As is apparent, one of the Cp* ligands has been transferred to oxygen. IR and ^{17}O NMR studies indicate that the W-*O*-C_5Me_5 oxygen originates exclusively from O_2. These results do not allow a distinction between the two most probable pathways for the formation of $(\eta^5\text{-}C_5Me_5)W({=}O)_2(OC_5Me_5)$: (i) formation of $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W({=}O)(\eta^2\text{-}O_2)$, followed by migration of the $(\eta^1\text{-}C_5Me_5)$ ligand to $(\eta^2\text{-}O_2)$, or (ii) direct attack by O_2 at the W–Cp* bond leading to a bridging peroxo species. In either case, the subsequent rearrangement of the proposed intermediate $[(\eta^5\text{-}C_5Me_5)W({=}O)(OOC_5Me_5)]$ to $(\eta^5\text{-}C_5Me_5)W({=}O)_2(OC_5Me_5)$ is similar to the rearrangement of $(\eta^5\text{-}C_5Me_5)_2Hf(R)(OOCMe_3)$ to $(\eta^5\text{-}C_5Me_5)_2Hf(OR)(OCMe_3)$,[20] acid-catalyzed rearrangement of $Cp^*_2Ta(\eta^2\text{-}O{-}O)CH_3$[1b] to $Cp^*_2Ta({=}O)OCH_3$, and the conversion of Ti and Zr alkyls to alkoxides upon exposure to O_2.[21]

In summary, the "class b" metal-oxo nature for $Cp^*_2W{=}O$ actuates a series of interesting reactions leading to reduction of the W=O bond order via 1,2-additions of both polar and nonpolar σ bonds as well as oxidations of the metal center by H_2O_2, HO_2CMe_3, or even O_2. The product, $(\eta^5\text{-}C_5Me_5)W({=}O)_2(OC_5Me_5)$, arises from insertion of an oxygen atom from O_2 into a W-$(\eta^5\text{-}C_5Me_5)$ bond. This facile oxo transfer chemistry, both to and from tungsten, augurs well for organotungsten derivatives in effecting catalytic oxidation reactions.

Acknowledgment. We thank Professors Jack Faller, Peter Legzdins, and Bob Bergman for providing information prior to publication and David Wheeler for measuring ^{17}O NMR spectra. This work was supported by the National Science Foundation (Grant No. CHE-8600875) and by Shell Companies Foundation, which are gratefully acknowledged. G.P. acknowledges support through a NATO Postdoctoral Fellowship administered through the Science and Engineering Research Council (U.K.).

Supplementary Material Available: Experimental details describing the synthesis of $Cp^*_2W{=}O$, $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W({=}O)_2$, and $(\eta^5\text{-}C_5Me_5)W({=}O)_2(OC_5Me_5)$ (1 page). Ordering information is given on any current masthead page.

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[14] Similarly, the reaction of $Cp^*_2Ta({=}NPh)H$ with D_2O yields $Cp^*_2Ta({=}O)H$ and $PhND_2$.

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[16] In the reaction with H_2, the yield of $Cp^*_2WH_2$ is approximately 50%; C_5Me_5H is also formed, presumably as a product of the secondary reaction of water with $Cp^*_2WH_2$ and/or $Cp^*_2W{=}O$. In the reaction with $HSiMe_3$, $Cp^*_2WH_2$ is obtained in >90% yield together with $(Me_3Si)_2O$; however, some H/D exchange with benzene-d_6 accompanies the reaction under the reaction conditions (220 °C, 12 h).

[17] Surprisingly, N_2O does not cleanly transfer an oxygen atom to generate $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W({=}O)_2$, unlike that observed in other systems, e.g.: (a) Vaughan, G. A.; Rupert, P. B.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1987**, *109*, 5538-5539. (b) van Asselt, A.; Parkin, G.; Whinnery, L. L.; Trimmer, M. S.; Bercaw, J. E. Unpublished results.

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Fluoride-Induced Trifluoromethylation of Carbonyl Compounds with Trifluoromethyltrimethylsilane (TMS-CF_3). A Trifluoromethide Equivalent[1]

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Although the literature abounds with examples of introducing perfluoroalkyl groups into carbonyl compounds through organometallic reagents of zinc,[2] calcium,[3] manganese,[4] magnesium,[5] silver,[4] and lithium,[6] the procedures are seldom applicable to trifluoromethylation. The trifluoromethide anion (CF_3^-) or its metalloorganic equivalents generally show great tendency for fluoride elimination. On the other hand, trifluoromethylation of aromatics is achieved rather readily with a variety of methods most notable using trifluoromethylcopper (CF_3Cu),[7] sodium trifluoroacetate,[8] trifluoromethyl triflate,[9] bis(trifluoromethyl)mercury ($(CF_3)_2Hg$),[10] and other related reagents.[11]

We wish to report now a very efficient nucleophilic trifluoromethylation reaction for carbonyl compounds using easily prepared trifluoromethyltrimethylsilane (TMS-CF_3).[12] Over the years

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