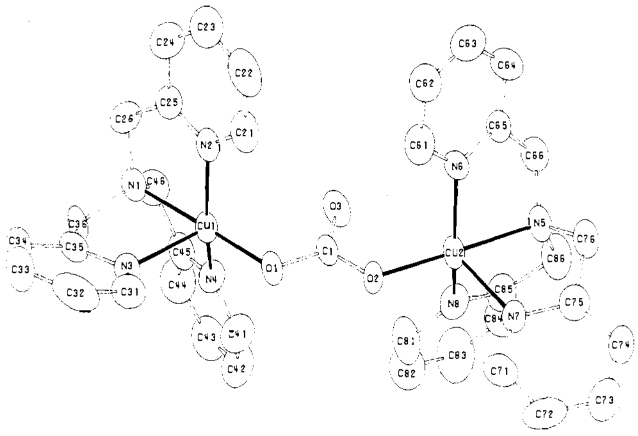

Figure 1. ORTEP diagram of $[(LCu^{II})_2(CO_3^{2-})]^{2+}$, showing the atom labeling scheme. Selected bond lengths (Å) and angles (deg) are as follows: Cu1···Cu2, 5.375 (1); Cu1–O1, 1.920 (7); Cu1–N1, 2.075 (9); Cu1–N2, 2.002 (8); Cu1–N3, 2.218 (10); Cu1–N4, 1.996 (9); C1–O1, 1.299 (12); C1–O2, 1.306 (13); C1–O3, 1.238 (14); Cu1···O3, 2.836, Cu2···O3, 2.819; O1–Cu1–N1, 178.8 (3); O1–Cu1–N2, 97.7 (3); O1–Cu1–N3, 97.5 (3); O1–Cu1–N4, 98.8 (3); N1–Cu1–N2, 83.0 (4); N1–Cu1–N3, 81.5 (4); N1–Cu1–N4, 81.0 (4); N2–Cu1–N3, 96.2 (3); N2–Cu1–N4, 150.6 (4); N3–Cu1–N4, 105.6 (3); Cu1–O1–C1, 113.6 (8); Cu2–O2–C1, 113.5 (7); O1–C1–O2, 114.8 (12); O1–C1–O3, 123.0 (11); O2–C1–O3, 122.2 (10).

yield from **1** and 81% yield[2] from **2** (iodometric titration). Under similar conditions, however, addition of 3–4 equiv of H^+ to **3** resulted in no UV-vis spectral change,[14] and addition of excess acid provides a chemical yield of only 12% hydrogen peroxide. Furthermore, phenols act as proton donors toward **1** and **2**, with liberation of H_2O_2 and production of phenoxo–copper(II) complexes; by contrast, they react with **3** by hydrogen atom abstraction, giving oxidatively coupled products typical of those found from the production of phenol radicals.[15]

$$\mathbf{1} \text{ or } \mathbf{2} + H^+ \rightarrow H_2O_2 + \text{Cu(II) products}$$

$$\mathbf{3} + H^+ \rightarrow \text{no reaction}$$

Acylation reactions of **1**–**3** at −80 °C follow the trend observed for protonation. Reactions of ArC(O)Cl with **1** are rapid, and, when followed by removal of Cl^-, they give μ-1,1-acylperoxo–dicopper(II) complexes, $[Cu_2(XYL\text{-}O\text{-})(OOC(O)Ar)]^{2+}$.[16] These react quantitatively with PPh_3 to give $O{=}PPh_3$ and $[Cu_2(XYL\text{-}O\text{-})(OC(O)Ar)]^{2+}$ [17] In the case of **2**, benzoyl chloride reacts slowly, and protonation is required to then cause oxygenation of added PPh_3.[18] Surprisingly, there is *no* reaction of acyl chlorides with **3**.

Differences in the observed reactivity of substrates with **1** and **2** compared to that for **3** also are seen in reactions with PhMgBr (source of Ph^-). Here, a preference for reaction with **1** or **2** to produce PhOH is observed (e.g., oxygen atom transfer), where the other product is biphenyl, derived from radical coupling ($PhOH/Ph_2$ is 75:25 and 84:16 for **1** and **2**, respectively). By contrast, reactions of **3** with PhMgBr give a $PhOH/Ph_2$ ratio of 43:57, showing a preference for one-electron oxidation of the added reagent, similar to that seen in the reactions with phenols.

The preliminary results thus indicate that in **1** and **2**, the dioxygen (peroxo) ligand can act as a base (e.g., protonates readily) or nucleophile (e.g., with respect to reactions with CO_2 or SO_2). By contrast, in $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**), the bound dioxygen ligand cannot be protonated or acylated, and it is unreactive toward CO_2 and is relatively more reactive with substrates capable of facile one-electron-transfer reactions. A species closely related to **3** has been shown by us to be capable of the hydroxylation of an arene,[19] and the behavior described for $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) is consistent with an electrophilic nature for this type of $\{Cu_2\text{–}O_2\}^{2+}$ unit, more typical of early transition-metal–peroxo complexes.[4,20] The differences in reactivity may be attributed to the presence of fewer ligand donors per copper in **3** compared to that found in **1** or **2**. On the basis of solution X-ray absorption studies,[3b] we have also suggested that an unusual η^2,η^2-O_2 structural moiety be considered for **3**. Further investigations will be necessary to unambiguously determine the nature of the bound O_2 ligand in **3** or its analogues and unravel the novel chemical reactivity.

Acknowledgment. We thank the National Institutes of Health through Grants GM 28962 and GM 34909 for support of this research. We also thank Professor Ken Suslick for useful discussions.

Supplementary Material Available: Listing of atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors (7 pages). Ordering information is given on any current masthead page.

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[13] (a) Karlin, K. D.; Cruse, R. W.; Gultneh, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 596–600. (b) Karlin, K. D.; Ghosh, P.; Cruse, R. W.; Farooq, A.; Gultneh, Y.; Jacobson, R. R.; Blackburn, N. J.; Strange, R. W.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 6769–6780.

[14] (a) Haka, M. S., Ph.D. Dissertation, State University of New York at Albany, 1987. (b) Farooq, A., Ph.D. Dissertation, State University of New York at Albany, 1987.

[15] Tyeklar, Z.; Karlin, K. D., et al. To be published.

[16] The X-ray structure for the derivative Ar = m-ClC_6H_4 has been determined: Ghosh, P.; Tyeklar, Z.; Karlin, K. D.; Jacobson, R. R.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 6889–6891.

[17] At −80 °C, triphenylphosphine displaces O_2 when reacted with **1** or **2** giving PPh_3-coordinated Cu(I) products.[1a,2] A similar reaction does not occur with **3**.

[18] We speculate that the slow reaction is due to steric hindrance of the coordinated peroxo ligand, producing a sterically hindered $\{LCu^{II}\text{-}OOC(O)\text{-}Ar\}^+$ moiety plus $\{LCu^{II}\text{-}Cl\}^+$; protonation, however, liberates RC(O)OOH causing oxygenation of PPh_3.

[19] The ligand has a m-xylyl, rather than $-(CH_2)_4-$ connecting moiety, and a similar $\{Cu_2\text{–}O_2\}^{2+}$ moiety has been shown to form prior to hydroxylation of the arene containing ligand. See: (a) Karlin, K. D.; Gultneh, Y.; Hayes, J. C.; Cruse, R. W.; McKown, J.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 2121–2128. (b) Tyeklar, Z.; Ghosh, P.; Karlin, K. D.; Farooq, A.; Cohen, B. I.; Cruse, R. W.; Gultneh, Y.; Haka, M. S.; Jacobson, R. R.; Zubieta, J. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series, 1988; Vol. 372, Chapter 5, pp 85–104.

[20] It is also interesting to note that the distinctive UV-vis spectral characteristics of **3** and its relatives show a striking similarity to that observed for oxyhemocyanin (O_2-carrier) and oxytyrosine (monooxygenase),[21] much more so than do complexes **1** or **2**.

[21] (a) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding (Berlin)* **1983**, *53*, 1–57. Solomon, E. I. In *Metal Ions in Biology*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1981; Vol. 3, pp 41–108.

A New Synthesis of Substituted Azulenes

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More than 100 years have passed since the first azulene was isolated by Piesse from the distillation of chamomile oil. Today the azulenes constitute the most well-known class of polycyclic nonbenzenoid aromatic compounds, and with their unusual electronic structure and remarkable colors they continue to be a source of fascination for organic chemists.[1] Recently, the novel electronic properties and biological activity of certain natural and synthetic azulene derivatives have led to commercially important applications of these compounds in fields such as medicine and

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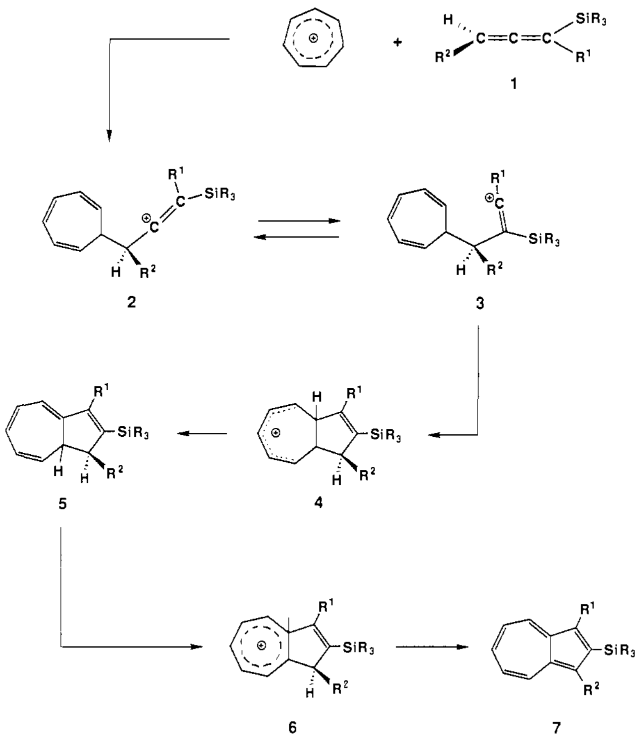
[1] For recent reviews of the chemistry of azulenes, see: (a) Zeller, K.-P. in *Methoden der Organischen Chemie*; Kropf, H., Ed.; Georg Thieme Verlag: Stuttgart, 1985; Vol. V/2c, p 127. (b) Lloyd, D. *Non-benzenoid Conjugated Carbocyclic Compounds*; Elsevier: Amsterdam, 1984; pp 352–377. (c) Mochalin, V. B.; Porshnev, Yu. N. *Russ. Chem. Rev.* **1977**, *46*, 530.

0002-7863/89/1511-0389$01.50/0

Scheme I

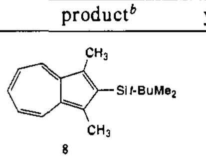
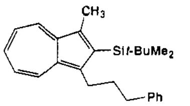
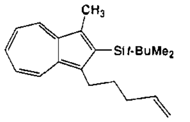
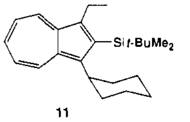
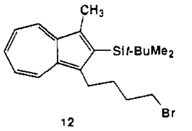
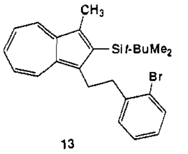
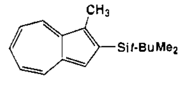


electrophotography. However, progress in these areas has been hindered by the availability of relatively few general methods for the synthesis of azulenes, particularly substituted systems.[1,2] Herein we report a new [3 + 2] annulation route to azulenes which complements the existing methodology and should provide more efficient access to a variety of substituted derivatives.

As outlined in Scheme I, our new azulene synthesis involves the addition of tropylium cations to allenylsilanes and is based on the general [3 + 2] annulation strategy which we have previously employed for the preparation of several classes of five-membered carbocycles and heterocycles.[3] Addition of tropylium ion to C-3 of the allenylsilane generates the vinyl cation **2**, which rapidly rearranges to the isomeric vinyl cation **3**. Cyclization of **3** next furnishes a cycloheptadienyl cation **4**, which undergoes elimination of H$^+$ to generate the dihydroazulene **5**. Dehydrogenation of this intermediate can conveniently be accomplished simply by employing 2 equiv of tropylium salt for the reaction: hydride abstraction by this carbocation provides the more stable (delocalized) tropylium derivative **6**, which finally aromatizes by elimination of the C-3 proton to afford the desired azulene **7**.[4]

Initial experiments quickly established the feasibility of our strategy. Thus, exposure of several allenylsilanes to 2 equiv of tropylium tetrafluoroborate (TpBF$_4$) in acetonitrile at 25 °C resulted in the rapid development of beautiful blue solutions and the subsequent isolation (25–30% yield) of mixtures of the desired silylazulenes (**7**) accompanied by the corresponding protodesilylated compounds. Also obtained in these experiments were significant quantities of acetylenic products generated by the protodesilylation of the allenylsilane starting materials.

Table I. Synthesis of Substituted Azulenes

entry	allenylsilane	method[a]	product[b]	yield[c] (%)
1	**1a**[d] (R^1 = R^2 = CH$_3$)	A	 8	52–59
2	**1b**[e] (R^1 = CH$_3$, R^2 = (CH$_2$)$_3$Ph)	B	 9	57
3	**1c**[e] (R^1 = CH$_3$, R^2 = (CH$_2$)$_3$CH=CH$_2$)	B	 10	43[g]
4	**1d**[f] (R^1 = cyclohexyl, R^2 = CH$_2$CH$_3$)	B	 11	44 (58)
5	**1e**[e] (R^1 = CH$_3$, R^2 = (CH$_2$)$_4$Br)	B	 12	55
6	**1f**[e] (R^1 = CH$_3$, R^2 = (CH$_2$)$_2$(*o*-bromo- phenyl))	B	 13	63
7	**1g**[d] (R^1 = CH$_3$, R^2 = H)	C	 14	22

[a] Method A: reaction was carried out with 2 equiv of TpBF$_4$ and poly(4-vinylpyridine) (158 mg/mmol of TpBF$_4$) in CH$_3$CN at 25 °C for 24 h. Method B: annulations were accomplished employing 4 equiv of TpBF$_4$ and 7 equiv of MeSi(OMe)$_3$ in CH$_3$CN at 25 °C for 48 h. Method C: reaction was carried out with 3 equiv of TpBF$_4$ and poly(4-vinylpyridine) (123 mg/mmol of TpBF$_4$) in 1:1 CH$_3$CN–heptane at 65 °C for 2 h. [b] IR, UV, ^{1}H NMR, ^{13}C NMR, and mass spectral data were fully consistent with the assigned structures. Elemental analyses and/or high-resolution mass spectra were obtained for all annulation products. [c] Isolated yields of products purified by column chromatography on silica gel. Yields in parentheses are corrected for recovered allenylsilane. [d] Reference 3b. [e] These allenes were prepared by sequential treatment of 1-methyl-1-(*tert*-butyldimethylsilyl)-allene[d] in THF with 1.1–1.2 equiv of *n*-BuLi (−78 °C, 0.5–1 h) followed by alkylation (−78 to 25 °C). For **1b**: 1.04 equiv of Ph(CH$_2$)$_3$Br, 79%; **1c**: 1.05 equiv of H$_2$C=CH(CH$_2$)$_3$Br, 95%; **1e**: 3.2 equiv of Br(CH$_2$)$_4$Br, 99%; **1f**: 1.0 equiv of 1-bromo-2-(2-bromophenyl)ethane, 14% (not optimized). [f] Prepared in 84% yield by sequential treatment of 1-cyclohexyl-1-(*tert*-butyldimethylsilyl)allene (ref 3c) with 1.37 equiv of *n*-BuLi (−78 °C, 45 min) and 4.6 equiv of EtI (−78 to 25 °C). [g] A small amount (6%) of the desilylated azulene was also isolated.

Further improvement in the efficiency of the annulation required the identification of an acid scavenger which would be capable of intercepting the HBF$_4$ produced in the two elimination steps (Scheme I) but which would not react at a significant rate with tropylium cation. Among a wide range of reagents surveyed, two compounds were found to be unusually effective at inhibiting the undesirable desilylation reactions. Table I summarizes our results. For annulations involving simple allenylsilanes (e.g., entries 1 and 7), commercially available poly(4-vinylpyridine) was found to be

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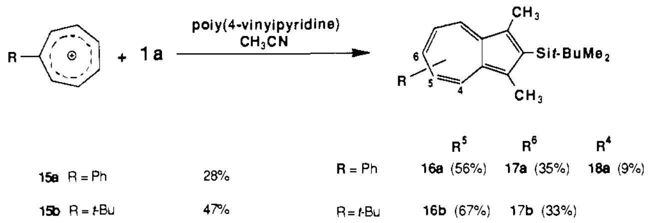
(2) The most useful methods for the synthesis of azulenes include: (a) Ziegler-Hafner synthesis; for a review, see: Jutz, J. C. *Top. Curr. Chem.* **1978**, *73*, 125. (b) Annulation methods based on 2*H*-cyclohepta[*b*]furan-2-ones: Nozoe, T.; Takase, K.; Nakazawa, T.; Fukuda, S. *Tetrahedron* **1971**, *27*, 3357. Yang, P.-W.; Yasunami, M.; Takase, K. *Tetrahedron Lett.* **1971**, 4275. (c) Scott azulene synthesis: Scott, L. T.; Minton, M. A.; Kirms, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 6311. (d) Methods based on [6 + 4] cycloadditions: Mukherjee, D.; Dunn, L. C.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 251 and references cited therein.

(3) (a) Cyclopentene synthesis: Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935. (b) Dihydrofurans and pyrrolines: Danheiser, R. L.; Kwasigroch, C. A.; Tsai, Y.-M. *J. Am. Chem. Soc.* **1985**, *107*, 7233. (c) Isoxazoles: Danheiser, R. L.; Becker, D. A. *Heterocycles* **1987**, *25*, 277.

(4) For [3 + 2] annulation routes to hydroazulene derivatives involving allenylmetal reagents, see ref 3a; Watkins, J. C.; Rosenblum, M. *Tetrahedron Lett.* **1985**, *26*, 3531 and references cited therein.

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.

(8) Okamato, K.; Komatsu, K.; Murai, O.; Sakaguchi, O.; Matsui, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1785.

(9) Heyd, W. E.; Cupas, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 6086.

(10) Braun, S.; Kinkeldei, J. *Tetrahedron* **1977**, *33*, 1827.

$(\eta^5\text{-}C_5Me_5)_2W{=}O$: 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 $W\text{-}(\eta^5\text{-}C_5Me_5)$ 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,

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

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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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