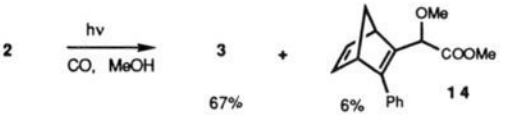
Hegedus has noted differences between nucleophilic trapping of free and chromium-complexed ketenes,[8a] but the effects of chromium complexation on the known electrocyclization reaction[18,19] of dienylketenes[20] is not known. Future experiments are directed toward addressing this interesting question.



(6)

In conclusion, we have demonstrated a new photochemical benzannulation reaction of chromium carbene complexes that promises to have broad application to the synthesis of *o*-alkoxy aromatic alcohols and *o*-quinones. Current experiments are exploring a range of substituent effects including the use of aminocarbene and (alkylthio)carbene complexes as benzannulation substrates.

Acknowledgment. We thank the UCLA Academic Senate, Committee on Research, for their financial support.

Supplementary Material Available: Sample experimental procedure and spectral and analytical data for compounds **3–14** (3 pages). Ordering information is given on any current masthead page.

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(18) Quinkert, G.; Kleiner, E.; Freitag, B.-J.; Glenneberg, J.; Billhardt, U.-M.; Cech, F.; Schmieder, K. R.; Schudok, C.; Steinmetzer, H.-C.; Bats, J. W.; Zimmermann, G.; Dürner, G.; Rehm, D.; Paulus, E. F. *Helv. Chim. Acta* **1986**, *69*, 469.

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Synthesis and Reactivity of the Organometallic Oxoanions $[Cp^*MoO_3]^-$ and $[Cp^*WO_3]^-$ and Their Use To Form New Heterobimetallic μ-Oxo Complexes

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The chemistry of organometallic oxo complexes is currently an area of high interest due to the relevance of these compounds to metal-catalyzed oxidation processes and the realization that the M═O bond is not as inert as earlier assumed.[1] In particular, Herrmann's extensive study of Cp^*ReO_3 (**1**, $Cp^* = \eta\text{-}C_5Me_5$) and related Re–oxo compounds have greatly extended our knowledge of the ways in which oxo ligands can react with organic substrates.[2]

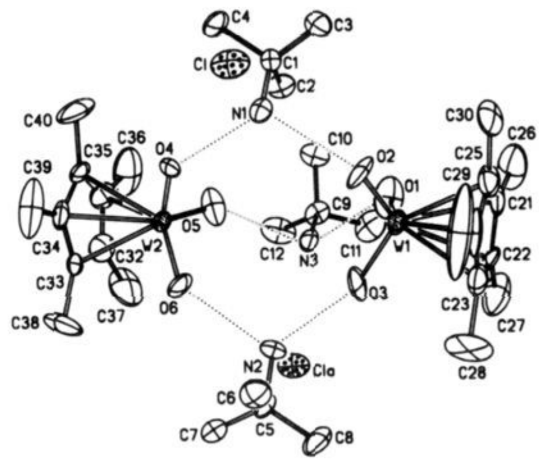
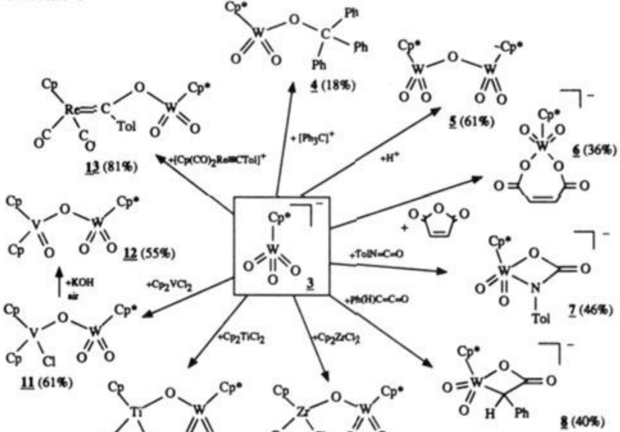


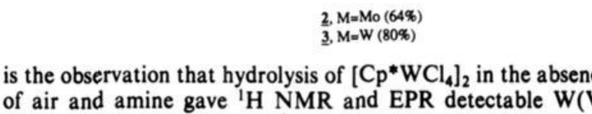
Figure 1. An ORTEP diagram of $[Bu^tNH_3]_3[Cp^*WO_3]_2Cl$. W–O(av), 1.75 (1) Å; O–W–O(av), 105.2 (7)°. Heavy-atom H-bonded contacts (Å): N(1)–O(2), 2.71 (2); N(1)–O(4), 2.70 (2); N(2)–O(3), 2.68 (2); N(2)–O(6), 2.70 (2); N(3)–O(1), 2.80 (2); N(3)–O(5), 2.75 (2); N(1)–Cl, 3.21 (1); N(2)–Cl(a), 3.21 (1); N(3)–Cl(a), 3.29 (1).

Scheme I



Compound **1** is unusually reactive because of the nucleophilic character of its oxo ligands, a consequence of the need for each oxo ligand to donate only 2e⁻ to the Re center to achieve a satisfactory 18e⁻ count, in contrast to the many oxo complexes in which this ligand is a formal 4e⁻ donor. Herein we describe the preparation and properties of the isoelectronic group VI complexes $[Cp^*MoO_3]^-$ (**2**) and $[Cp^*WO_3]^-$ (**3**). The anionic character of these complexes lends them enhanced nucleophilicity and makes them especially useful for the formation of heterobimetallic μ-oxo complexes.

Complexes **2** and **3** were prepared as their $Bu^tNH_3^+$ salts by the reaction of $[Cp^*MCl_4]_2$[3] with excess Bu^tNH_2 and H_2O in the presence of air, eq 1. Relevant to the mechanism of this reaction



$$1/2\,[Cp^*MCl_4]_2 + 5\,Bu^tNH_2 + 3\,H_2O \xrightarrow[\text{-[H]}]{CH_2Cl_2/\text{air}} [Cp^*M(=O)_3]^- \; Bu^tNH_3^+ + 4\,[Bu^tNH_3]Cl \quad (1)$$

2, M=Mo (64%)
3, M=W (80%)

is the observation that hydrolysis of $[Cp^*WCl_4]_2$ in the absence of air and amine gave ^1H NMR and EPR detectable W(V) hydroxy chloro intermediates,[4] which upon air exposure led to the known complex Cp^*WO_2Cl[5] in near quantitative yield. Subse-

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(1) See, for example: (1) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (c) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, NY, 1988. (d) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic: New York, NY, 1981.

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(3) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.

(4) $[CpWCl_2(OH)_2]$: ^1H NMR (CD_2Cl_2) δ 14.88 (br, Cp*), 30.82 (br, OH); MS (EI), m/z = 407 ($M^+ - H_2O$). $[Cp^*WCl(OH)_3]$: ^1H NMR (CD_2Cl_2) δ 12.75 (br, Cp*), 35.76 (br, OH).

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quent treatment of this latter species with excess aqueous Bu^tNH_2 gave **3** in high yield. Compounds **2** and **3** were isolated by concentration of the CH_2Cl_2 solution, drying with $MgSO_4$, filtering off of the $MgSO_4$ and the precipitated $[Bu^tNH_3]Cl$, and then crystallization of the $[Bu^tNH_3]^+$ salts of **2** and **3** by addition of hexane and Et_2O to the filtrate. Spectroscopic data[6,7] indicate that this method consistently gives a product contaminated with 1-2 equiv of $[Bu^tNH_3]Cl$, and a crystal structure (Figure 1) showed the formation of the mixed salt $[Bu^tNH_3]_3[Cp^*WO_3]_2Cl$. The $[Cp^*WO_3]^-$ anion is clearly evident, although with extensive hydrogen bonding to the cation.[8] We have also found that $[Bu^tNH_3][Cp^*WO_3]$ can be obtained free of $[Bu^tNH_3]Cl$ by treatment of $[Cp^*WO_2]_2(\mu\text{-}O)$ (**5**, see below) with Bu^tNH_2/H_2O and that the $[(Ph_3P)_2N]^+$ and $[Bu_4N]^+$ salts can be obtained by metathesis reactions.

Scheme I summarizes the reactions observed for $[Cp^*WO_3]^-$. Preliminary experiments indicate that $[Cp^*MoO_3]^-$ behaves similarly. All of the products illustrated have been isolated as microcrystalline solids and have been spectroscopically characterized.[9-17] Alkylation of **3** with $[Ph_3C]BF_4$ gave the new triphenylmethoxide complex **4**[18] and protonation led to the formation of the known μ-oxo complex **5**,[19] presumably via condensation of initially formed $Cp^*WO_2(OH)$. Complex **3** ring-opened maleic anhydride to give **6**, and it reacted with the heterocumulenes TolN=C=O and PhHC=C=O by [2 + 2] cycloaddition across one of the W=O bonds to give complexes **7** and **8**.[20] For comparison, Herrmann showed that complex **1** underwent a similar [2 + 2] cycloaddition with PhN=C=O, but the ketene $Ph_2C{=}C{=}O$ reacted with **1** by [3 + 2] cycloaddition across the ReO_2 unit to give a five-membered metallacycle.[21]

An important consequence of the nucleophilic character of **3** is the ability of its oxo ligands to displace halides from other metals to form heterobimetallic μ-oxo complexes. This is illustrated in Scheme I by the formation of complexes **9-11**. Also illustrated are the addition of $[Cp^*WO_3]^-$ to the electrophilic carbyne carbon of $[Cp(CO)_2Re{\equiv}CTol]^+$ to form the bimetallic carbene complex **13** and the oxidation of **11** to form **12**. These new heterobimetallic species were isolated in excellent yields and have been spectroscopically characterized.[13-17] The formation of **9-13** presages the utility of **2** and **3** for the formation of an extensive series of bimetallic complexes possessing bridging oxo and various oxygenated organic ligands, and studies in those directions are continuing.

Acknowledgment. This research was supported by the National Science Foundation through Grant CHE8802025.

Supplementary Material Available: Tables of atomic positional parameters, selected bond angles and distances, and crystallographic data for $[Bu^tNH_3]_3[Cp^*WO_3]_2Cl$ (5 pages). Ordering information is given on any current masthead page.

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(6) **2**: IR (KBr) ν_{MoO} = 860 (vs), 825 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.88 (Cp*, 15 H), 1.34 (Bu^t, 25 H); MS (FAB^-), m/z = 281 (M^-).

(7) **3**: IR (KBr) ν_{WO} = 898 (vs), 822 (vs) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.01 (Cp*, 15 H), 1.34 (Bu^t, 13 H); MS (FAB^-), m/z = 367 (M^-). Anal. Calcd for $[Bu^tNH_3]_3[Cp^*WO_3]_2Cl$: C, 38.74; H, 6.71. Found: C, 39.08; H, 6.96.

(8) Crystal data for $[Bu^tNH_3]_3[Cp^*WO_3]_2Cl$: $C_{22}H_{51}ClN_3O_3W$, monoclinic, $P2_1/n$, a = 13.822 (4) Å, b = 17.894 (4) Å, c = 17.277 (4) Å, β = 95.06 (2)°, V = 4256.5 (9) $Å^3$, Z = 4, $R(F)$ = 6.26% on 6352 independent data (3667 observed at $4\sigma F_o$), T = 295 K.

(9) **4**: IR (KBr) ν_{WO} = 923 (m), 915 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.06 (Cp*), 7.21-7.31 (Ph); ^{13}C NMR (CD_2Cl_2) δ 147.4 (CPh_3), 119.9 ($C_5(CH_3)_5$), 130.0-127.6 (Ph), 10.8 ($C_5(CH_3)_5$); MS (EI), m/z = 610 (M^+).

(10) **6**: IR (KBr) ν_{CO} = 1718 (m), ν_{WO} = 874 (m), 865 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.01 (Cp*), 6.14 (CH=CH); ^{13}C NMR ($CDCl_3$) δ 134.7 (CH=CH), 168.2 (CO), 120.1 ($C_5(CH_3)_5$), 10.3 ($C_5(CH_3)_5$); MS (FAB^-), m/z = 464 (M^-).

(11) **7**: IR (KBr) ν_{CO} = 1696 (m), ν_{WO} = 937 (s), 892 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.14 (Cp*), 2.23 ($TolCH_3$), 7.05-7.20 (aryl); ^{13}C NMR ($CDCl_3$) δ 155.4 (CO), 20.7 ($TolCH_3$), 132.4, 131.9, 120.7, 119.6 (aryl), 120.3 ($C_5(CH_3)_5$), 10.4 ($C_5(CH_3)_5$).

(12) **8**: IR (KBr) ν_{CO} = 1720 (m), ν_{WO} = 937 (s), 891 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (Cp*), 3.61 (CH), 7.30 (Ph); ^{13}C NMR ($CDCl_3$) δ 45.1 (CHPh), 175.5 (CO), 135.1-126.6 (Ph), 120.3 ($C_5(CH_3)_5$), 10.4 ($C_5(CH_3)_5$); MS (FAB^-), m/z = 485 (M^-).

(13) **9**: IR (KBr) ν_{WO} = 924 (s), 881 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.14 (Cp*), 6.37 (Cp); ^{17}O NMR (CD_2Cl_2) δ 350.5 (WOZr), 639.8 ($W(=O)_2$); MS (FAB), m/z = 623 (M^+). Anal. Calcd for $C_{20}H_{25}O_3ClWZr$: C, 38.50; H, 4.04. Found: C, 38.28; H, 4.19.

(14) **10**: IR (KBr) ν_{WO} = 923 (s), 875 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (Cp*), 6.42 (Cp); ^{17}O NMR (CD_2Cl_2) δ 449.5 (WOTi), 632.6 ($W(=O)_2$); MS (FAB), m/z = 580 (M^+). Anal. Calcd for $C_{20}H_{25}O_3ClTiW$: C, 41.37; H, 4.34. Found: C, 41.16; H, 4.51.

(15) **11**: IR (KBr) ν_{WO} = 904 (m), 849 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.12 (Cp*), 4.69 (br, Cp). Anal. Calcd for $C_{20}H_{25}O_3ClVW$: C, 41.16; H, 4.32. Found: C, 41.66; H, 4.65.

(16) **12**: IR (KBr) ν_{WO} = 928 (s), 885 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.16 (Cp*), 6.62 (Cp).

(17) **13**: IR (KBr) ν_{CO} = 1946 (vs), 1865 (vs) cm^{-1}, ν_{WO} = 937 (m), 892 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.12 (Cp*), 2.30 ($TolCH_3$), 5.34 (Cp), 7.12-7.58 (aryl); ^{13}C NMR (CD_2Cl_2) δ 10.1 ($C_5(CH_3)_5$), 21.2 ($TolCH_3$), 88.7 (C_5H_5), 120.0 ($C_5(CH_3)_5$), 125.3, 128.2, 135.5, 153.2 ($TolC_6H_4$), 203.1 (CO), 280.4 (Re=C).

(18) The compound (tmtaa)Ti=O (tmtaa = 7,6-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato) has also been shown to undergo oxygen alkylation with $[Ph_3C]^+$: Housmekerides, C.; Geoffroy, G. L., unpublished results.

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(20) The $[(PPh_3)_2N]^+$ salt of **3** was used for the preparation of **8**.

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Intracellular Analysis with an Immobilized-Enzyme Glucose Electrode Having a 2-μm Diameter and Subsecond Response Times

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The search for small, rapid, and selective glucose sensors has resulted in a large repertoire of different electrode strategies.[1] Platinized microelectrodes have recently been used with immobilized glucose oxidase to detect glucose with response times of only a few seconds.[2] Pantano et al.[3] recently reported an enzyme-modified microelectrode constructed by linking horseradish peroxidase via a biotin/avidin/biotin tether to carbon fiber electrodes with an 8-μm diameter defining the electroactive surface area and a slightly larger total structural diameter. These electrodes have response times on the order of 300 ms. In this communication, we present a simple procedure to construct enzyme-modified electrodes with total tip diameters as small as 2-μm using platinized carbon ring electrodes.

Carbon ring electrodes were constructed as described previously by Kim et al.[4] The general procedure for immobilizing glucose oxidase on the electrode was similar to that described by Ikariyama et al.[5] Carbon ring electrodes were platinized by reduction of 10 mM hexachloroplatinate in the presence of lead acetate for 3 min. The resulting porous platinum-coated electrodes were then oxidized in phosphate buffer (0.5 M, pH 7.0) at 1.1 V vs a sodium saturated calomel reference electrode (SSCE) for 15 min, oxidized in glucose oxidase (100 mg/mL) for 15 min, and immersed in bovine serum albumin (5% by weight) and finally a gluteraldehyde

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