Table II. Summary of Rebinding Studies of Templated Copper-Complexing Copolymers

entry	polymer	original template	rebinding substrate	substrate bound,[a,b] mmol/g of polymer	rel substrate selectivity in competitive binding[b,c]
1	P-1		**2a**	0.42	
2	P-1		**3a**	0.43	
3	P-1		**2a** + **3a**		$\alpha_{3a/2a} = 1.02$
4	P-2	**2a**	**2a**	0.33	
5	P-2	**2a**	**3a**	0.22	
6	P-2	**2a**	**2b**	0.016	
7	P-2	**2a**	**2a** + **3a**		$\alpha_{2a/3a} = 1.17$
8	P-2 (Cu free)	**2a**	**2a** + **3a**		$\alpha_{2a/3a} = 1.04$
9	P-3	**3a**	**3a**	0.24	
10	P-3	**3a**	**2a**	0.17	
11	P-3	**3a**	**3b**	0.014	
12	P-3	**3a**	**2a** + **3a**		$\alpha_{3a/2a} = 1.15$
13	P-3 (Cu free)	**3a**	**2a** + **3a**		$\alpha_{3a/2a} = 1.04$

[a] Saturation binding studies: >5-fold molar excess of substrate over theoretical binding sites. [b] Amounts bound determined from analysis of unbound substrates after equilibration, using 500-MHz ^{1}H NMR and an internal reference of known concentration (single substrate binding) or relative peak intensities (for competitive binding). [c] Competitive binding: equimolar mixtures of substrates used. α_{ij} is the ratio of i to j in the bound state.

zacyclononane (0.025 M) followed by aqueous EDTA (0.1 M, pH 7.0) removed more than 95% of the bound copper. The copper ions can be reloaded quantitatively by treating the polymers with aqueous $CuCl_2$. The polymerization process and subsequent workup are illustrated in Scheme I, and results are summarized in Table I.

Substrate recognition and selective binding abilities of the templated polymers were determined by both saturation rebinding and competitive rebinding experiments with substrates **2** and **3** (Table II). While the templated polymers exhibit selectivity for their templates over the close structural analogue (entries 7 and 12 in Table II), polymer P-1 prepared without template exhibits essentially no selectivity (entry 3). The separation factors of 1.15–1.17 for the templated polymers are significant in view of the fact that substrates **2a** and **3a** are indistinguishable by reverse-phase HPLC and ligand-exchange chromatography on Cu^{II}IDA. One can expect significantly higher selectivities for less similar substrates.

It is not clear whether orientation of the binding sites (multiple-site binding) or shape selectivity governs the binding selectivities of imprinted polymers.[7] To obtain insights into the origin of the observed substrate selectivity of these metal-coordinating templated polymers, rebinding experiments were performed on both copper-loaded and copper-free polymers using substrates **2a**, **2b**, **3a**, and **3b**. As can be seen from Table II, the inability of copper-free polymers to bind their templates (entries 8 and 13) and the low binding of substrates **2b** and **3b** having no imidazole ϵ-nitrogen (entries 6 and 11) rule out the possibility that simple shape selectivity is the primary source of binding selectivity. Furthermore, when templated polymer P-2 was used, the maximum capacities ($Q_{\max}$)[8] for substrates **2a**, **2c** (a pseudotemplate having a single imidazole residue), and *N*-benzylimidazole were found to be 0.33, 0.30, and 0.55 mmol/g of polymer, respectively. That nearly twice as many sites are available to *N*-benzylimidazole as to **2a** and that the capacities for **2a** and **2c** are similar are consistent with the view that two copper ions are closely spaced in the binding cavities. The order of apparent Langmuir binding constants (K_L)[8] for the substrates is **2a** (3800 M^{-1}) > *N*-benzylimidazole (2800 M^{-1}) > **2c** (1700 M^{-1}). The higher binding constant for **2a** compared to those for the substrates containing only one imidazole nitrogen may partly reflect interactions by the favorably disposed metal ions in the templated polymers toward the bifunctional template substrates, although one would expect a larger differential in the binding affinities for two-point versus one-point binding. Direct spectroscopic determination of the template binding configuration will be required to determine the extent to which two-point binding contributes to selectivity.

Acknowledgment. F.H.A. gratefully acknowledges support from the National Science Foundation (PYI program) and a fellowship from the David and Lucile Packard Foundation.

Supplementary Material Available: Experimental details for the synthesis of bisimidazoles **2a** and **3a** (1 page). Ordering information is given on any current masthead page.

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(7) (a) Wulff, G.; Shauhoff, S. *J. Org. Chem.* **1991**, *56*, 395. (b) Shea, K. J.; Sasaki, D. Y. *J. Am. Chem. Soc.* **1989**, *111*, 3442.

(8) Arnold, F. H.; Schofield, S. A.; Blanch, H. W. *J. Chromatogr.* **1986**, *355*, 1.

Cyclization Reactions of Chromium Dienylcarbene Complexes. Entry to Ortho-Substituted Aromatic Alcohols via a Designed Photoreaction

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The benzannulation reaction based on alkyne cycloaddition to chromium carbene complexes, reported by Dötz in 1975,[1] has become the most studied reaction[2] of Fisher carbene complexes and the most useful for synthesis of natural products.[3] It is uniquely suited for the synthesis of *p*-alkoxyphenols and, by oxidation thereof, 1,4-quinones. However, the large number of natural products, in particular antitumor agents, that possess *o*-alkoxyphenol or *o*-quinone[4] type structures argues for the development of chromium carbene based strategies that will provide access to substitution patterns other than para.

Consideration of a simplified mechanism[5,6] for the Dötz benzannulation reaction (Scheme I) suggests that an alternative pathway to ortho-substituted products is feasible. They key intermediate is the dienylcarbene complex I, resulting from metathesis of an alkyne, which inserts carbon monoxide to form a dienylketene complex II, which can then undergo an electrocyclization reaction. If this is a reasonable mechanistic pathway,[7] then *starting with a dienylcarbene complex, without added alkyne, should lead to ortho-substituted phenolic products* (Scheme II). Added support for this proposal comes from the recent work of

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(1) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644.

(2) For reviews, see: (a) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol. 5. (b) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (c) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Hingham, MA, 1989. (d) Wulff, W. D.; Tang, P.-C.; Chan, K.-S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (e) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (f) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(3) For examples, see: (a) Boger, D. L.; Jacobson, I. C. *J. Org. Chem.* **1990**, *55*, 1919. (b) Yamashita, A.; Toy, A.; Ghazal, N. B.; Muchmore, C. R. *J. Org. Chem.* **1989**, *54*, 4481. (c) Yamashita, A. *J. Am. Chem. Soc.* **1985**, *107*, 5823. (d) Dötz, K. H.; Popall, M. *Tetrahedron* **1985**, *41*, 5797. (e) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W.; Zask, A. *Tetrahedron* **1985**, *41*, 5803.

(4) For a recent review, see: Tisler, M. *Adv. Heterocycl. Chem.* **1989**, *45*, 37.

(5) McCallum, J. S.; Kunng, F.-A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346 and references therein.

(6) There are other proposed mechanisms. See: (a) Hofmann, P.; Hämmerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908. (b) Casey, C. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2.

(7) Similar arguments lead to the same conclusions using the other[6] mechanisms.

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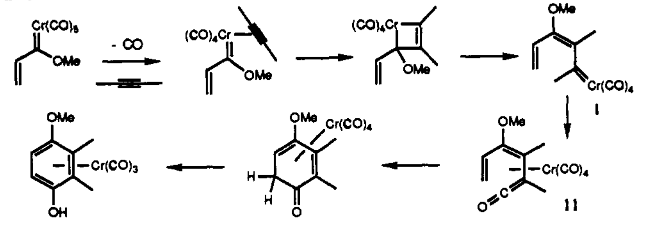
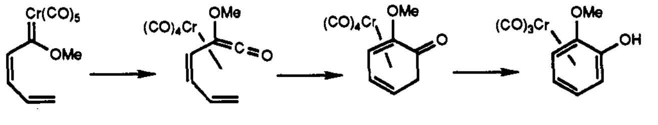
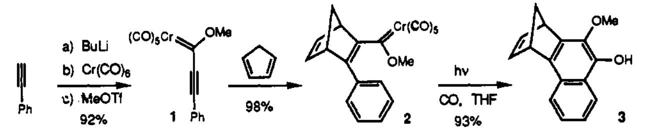
Scheme I

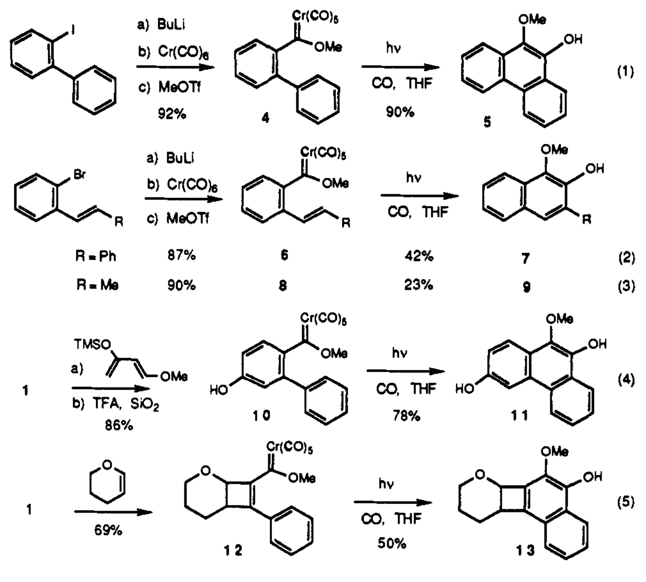


Scheme II



Scheme III





Hegedus,[8] who has demonstrated that *direct* carbon monoxide insertion in simple chromium carbene complexes, to generate ketene complexes, can be effected by simple photolysis. We report herein the successful realization of these concepts.

As an initial test substrate, we examined the reactivity of chromium carbene complex **2**, readily available from phenylacetylene in two steps (Scheme III). Photolysis of **2** employing a 450-W Hanovia lamp with a Pyrex filter in THF solvent provided a 65% yield of **3**,[9] in an excellent realization of our reaction design. Performing the reaction under carbon monoxide sparging increased the yield of **3** to 93%. The product was easily identified by the hydroxyl proton at 6.00 ppm in the ^{1}H NMR spectrum, 12 distinct ^{13}C NMR signals between 121 and 145 ppm, and an OH stretch at 3535 cm^{-1}.

Test substrates **4**, **6**, **8**, **10**, and **12**, which all formally contain a dienylcarbene moiety, were prepared to test this new chromium carbene based benzannulation. Compound **10** was obtained in high yield from a Diels–Alder reaction[10] of acetylenic carbene complex **1**, as was **2**. The dihydropyran adduct **12** was prepared by exploiting the known propensity of acetylenic carbene complexes to participate in [2 + 2] cycloaddition reactions with enol ethers.[11] A survey of the reactivity of the test substrates reveals the ability to readily construct functionalized aromatic systems from these carbene complexes (eqs 1–5). In particular, the reaction is independent of the nature of the unsaturation that comprises the dienyl component of the carbene complex. Substrates possessing aryl groups as the α,β-unsaturation (eqs 2 and 3) or the γ,δ-unsaturation (Scheme III and eq 5), or both (eqs 1 and 4), were all effective for the photoactivated CO insertion and electrocyclization. The low yield in the propenyl-substituted substrate **8** (eq 3) reflects the instability of the carbene complex rather than difficulty in the annulation reaction. In fact, the analogous (2-vinylphenyl)carbene complex immediately polymerized upon attempted isolation. One expected requirement of the cyclization, alluded to in Schemes I and II, is that the γ,δ-unsaturation and the carbene moiety must be cis disposed. Attempted reaction of (3-phenyl-1-methoxy-2-propenylidene)(pentacarbonyl)chromium resulted in no detectable benzannulation products. Therefore, our initial efforts were directed toward substrates with the α,β-unsaturation constrained in a ring.

It should be noted that these reactions employed photoactivation instead of thermal conditions, which are typically used for the alkyne plus carbene benzannulation reaction. We initially chose photochemical conditions, since Hegedus has demonstrated[8] that photolysis of alkoxy- and aminocarbene complexes leads to direct CO insertion forming ketene complexes,[12] which is exactly what we required. Thermal reactions of substrate **2** did occasionally produce the annulated product **3**, but in the best case (heptane reflux) only a 29% yield of **3** was obtained from a complex mixture, while other substrates provided little or no benzannulation. This suggests that photolysis may promote electrons from the HOMO Cr–CO π-back-bonding orbital to the LUMO Cr–CR(OR) π^* orbital thus facilitating CO insertion.[13] In contrast, thermal conditions may promote competing side reactions such as CO loss. Also of note is the beneficial use of CO in the reaction. While the presence of CO inhibits the Dötz benzannulation reaction,[14] Hegedus has noted that CO facilitates photochemical reactions of chromium carbene complexes.[15] Presumably, CO traps tetracarbonyl carbene complexes formed by thermal or photoinduced[16,17] CO loss. Such tetracarbonyl complexes would not be expected to undergo CO insertion, due to enhanced π-back-bonding, and would lead to side products. An added benefit of performing the reaction in the presence of CO is that $Cr(CO)_6$ is recovered in 40–70% yield at the end of the reaction.

In order to test the competition between electrocyclization and trapping of the intermediate ketene, a photoreaction of **2** was performed in methanol solvent (eq 6). A 67% yield of the benzannulation product **3** was obtained and only 6% of the α-methoxy ester **14**. This supports the concept of an intermediate ketene, but also indicates the facility of electrocyclization of the dienylketene. An intriguing aspect, though, is the effect of complexation of the dienylketene by a chromium carbonyl fragment.

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[8] (a) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122. (b) Hegedus, L. S.; Schwindt, M. A.; De Lombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*, 2264. (c) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364.

[9] All new compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, and infrared spectroscopy, and elemental composition was established by combustion analysis and/or high-resolution mass spectroscopy.

[10] For Diels–Alder reactions of chromium carbene complexes, see: Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642 and references therein.

[11] Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 8727.

[12] For a review on metal ketene complexes, see: Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1.

[13] (a) Block, T. F.; Fenske, R. F. *J. Organomet. Chem.* **1977**, *139*, 235. (b) Sheridan, J. B.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1514.

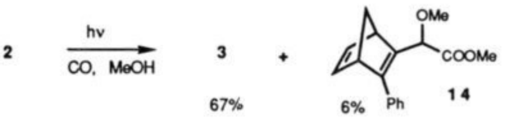
[14] (a) Dötz, K. H.; Dietz, R. *Chem. Ber.* **1977**, *110*, 1555. (b) Fischer, H.; Mühlemeier, J.; Märkl, R.; Dötz, K. H. *Chem. Ber.* **1982**, *115*, 1355.

[15] See refs 8b,c and the following: Hegedus, L. S.; Imwinkelreid, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* **1990**, *112*, 1109.

[16] It has been reported that photoinduced CO loss is the primary photoreaction of carbene complexes, even with the use of Pyrex filters: Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

[17] Reduced yields for the reactions reported herein were obtained when Vycor filters or no filters were used in the quartz photoreactor, thus indicating the predominance of CO loss, instead of insertion, at short-wavelength irradiation.

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.

(19) For recent applications of electrocyclizations of dienylketenes, see: Danheiser, R. L.; Brisbois, R. G.; Kowalczyk, J. J.; Miller, R. F. *J. Am. Chem. Soc.* **1990**, *112*, 3093 and references therein.

(20) For reviews, see: (a) Tidwell, T. T. *Acc. Chem. Res.* **1990**, *23*, 273. (b) Brady, W. T. *Tetrahedron* **1981**, *37*, 2949. (c) *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: New York, 1980; Parts 1 and 2.

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]

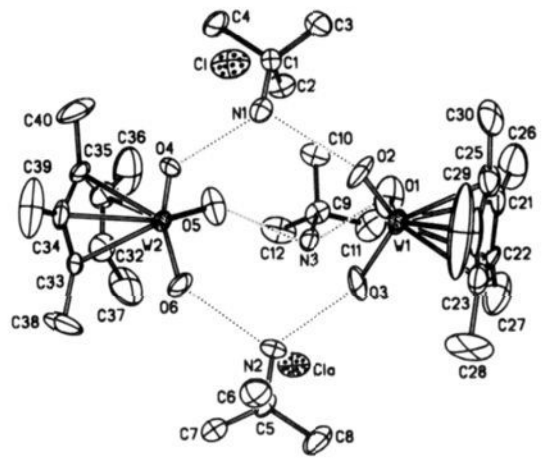
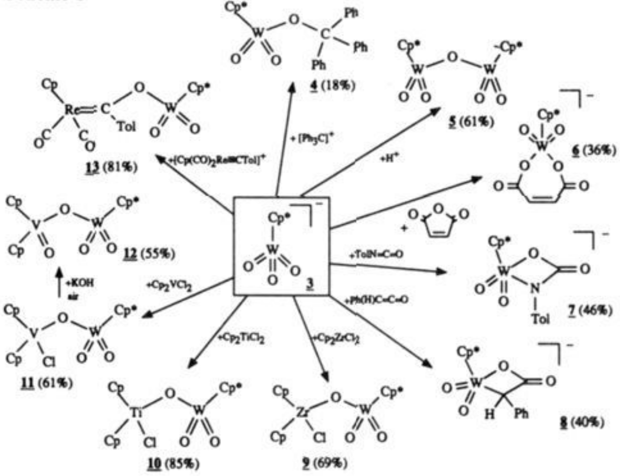


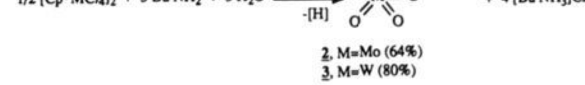
Figure 1. An ORTEP diagram of $[Bu^tNH_3]_3[Cp^*WO_3]_2Cl$. W–O(av), 1.75 (1) Å; O–W–O(av), 105.2 (7)°. Heavy-atom H-bonded contacts (Å): N(1)–O(2), 2.71 (2); N(1)–O(4), 2.70 (2); N(2)–O(3), 2.68 (2); N(2)–O(6), 2.70 (2); N(3)–O(1), 2.80 (2); N(3)–O(5), 2.75 (2); N(1)–Cl, 3.21 (1); N(2)–Cl(a), 3.21 (1);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



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

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.

(2) (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297. (b) Herrmann, W. A.; Herdtweck, E.; Floel, M.; Kulpe, J.; Kusthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165.

(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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