

mechanism in the literature for the metal hydride catalyzed isomerism of internal to terminal alkynes.

The hydrido-alkylidyne species, $[\text{ReH}_2(\equiv\text{CCH}_2\text{R})(\text{mq})(\text{PPh}_3)_2]^+$, provide an interesting alternative class of rhenium(VII) alkylidynes to the important Schrock complexes, in which imido, alkoxide, and/or alkylidene ancillary ligands are also present.^{19,20} The mechanism of the formation of the hydrido-alkylidyne complexes is under investigation, as are studies exploring the synthetic scope of these reactions and the reactivity of the resulting complexes.

Acknowledgment. Support from the National Science Foundation, through Grant Nos. CHE88-07444 and CHE91-07578 to R.A.W. and Grant No. CHE86-15556 for the purchase of the microVAX II computer and diffractometer, is gratefully acknowledged.

Supplementary Material Available: Listings of atomic positional parameters for the structure of $\text{ReH}(\equiv\text{C}-n\text{-C}_4\text{H}_9)(\text{mq})(\text{PPh}_3)_2$ (Table S1) (3 pages). Ordering information is given on any current masthead page.

(19) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* 1983, 1506, 1505.

(20) (a) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* 1990, 112, 2448. (b) Weinstock, I. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* 1991, 113, 135.

Oxo-Alkyls of Cr^V and Cr^{VI}

Seok-Kyun Noh, Robert A. Heintz, Brian S. Haggerty, Arnold L. Rheingold, and Klaus H. Theopold*

Department of Chemistry and Biochemistry
University of Delaware
Newark, Delaware 19716

Received September 9, 1991

Transition-metal complexes featuring both alkyl and oxo ligands command a growing share of attention of organometallic chemists.¹ The chemistry of such oxo-alkyls is relevant to stoichiometric and catalytic oxidations of organic molecules mediated by transition metals.² While high-valent chromium reagents have a long history of use as oxidants in organic synthesis,³ no chromium alkyls containing oxo ligands (Cr=O) have been reported.⁴ Our exploration of the reactivity of paramagnetic organochromium compounds⁵ has now yielded several of these molecules. Herein we describe the synthesis, structural characterization, and pre-

(1) (a) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* 1988, 28, 339. (b) Herrmann, W. A. *Angew. Chem.* 1988, 100, 1269; *Angew. Chem., Int. Ed. Engl.* 1988, 27, 1297.

(2) (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (b) Jørgensen, K. A.; Schiøtt, B. *Chem. Rev.* 1990, 90, 1483.

(3) (a) Etard, A. L. *Compt. Rend.* 1880, 90, 534. (b) Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry*; Springer Verlag: Berlin, 1984. (c) Wiberg, K. B. In *Oxidation in Organic Chemistry*; Wiberg, K. B., Ed.; Academic Press: New York, 1965.

(4) For some organometallic chemistry of chromium in very high oxidation states, see: (a) Danopoulos, A. A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* 1989, 8, 2657. (b) Sullivan, A. C.; Wilkinson, G.; Mottevali, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* 1988, 53. (c) Danopoulos, A. A.; Leung, W.-H.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* 1990, 9, 2625. (d) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* 1988, 110, 8234. (e) Meijboom, N.; Schaverien, C. J.; Orpen, A. G. *Organometallics* 1990, 9, 774. For related Mo and W oxo-alkyls, see: (f) Legzdins, P.; Phillips, E. C.; Rettig, S. J.; Sanchez, L.; Trotter, J.; Yee, V. C. *Organometallics* 1988, 7, 1877. (g) Legzdins, P.; Phillips, E.; Sanchez, L. *Organometallics* 1989, 8, 940. (h) Faller, J. W.; Ma, Y. J. *Organomet. Chem.* 1988, 340, 59. (i) Faller, J. W.; Ma, Y. *Organometallics* 1988, 7, 559.

(5) (a) Theopold, K. H. *Acc. Chem. Res.* 1990, 23, 263. (b) Thomas, B. J.; Noh, S. K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* 1991, 113, 893.

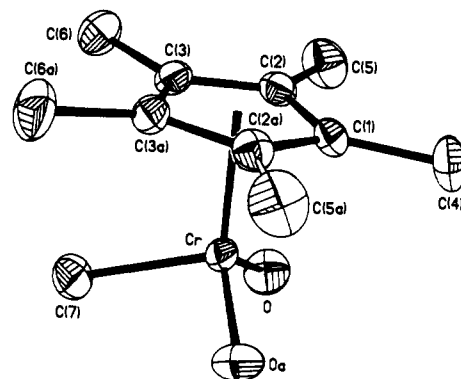


Figure 1. Molecular structure of $\text{Cp}^*\text{Cr}^{\text{VI}}(\text{O})_2\text{CH}_3$ (**2**). Selected bond distances: Cr-O, 1.605 (3) Å; Cr-C(7), 2.054 (5) Å. Interatomic angles: C(7)-Cr-O, 97.5 (1)°; O-Cr-O_a, 109.4 (2)°.

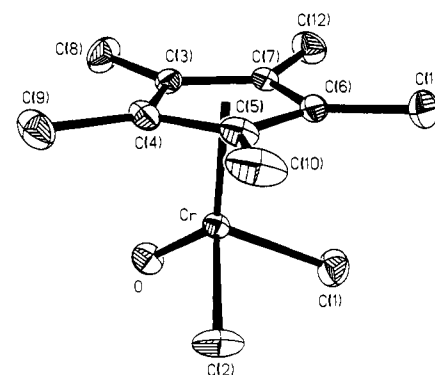
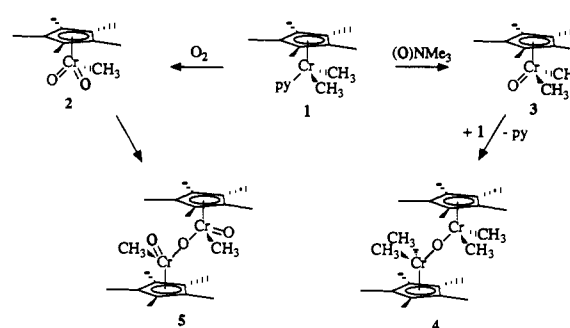


Figure 2. Molecular structure of $\text{Cp}^*\text{Cr}^{\text{V}}(\text{O})(\text{CH}_3)_2$ (**3**). Selected bond distances (values in parentheses refer to the second molecule in the asymmetric unit): Cr-C(1), 2.044 (6) Å (2.041 (6) Å); Cr-C(2), 2.042 (5) Å (2.045 (5) Å); Cr-O, 1.579 (3) Å (1.581 (3) Å). Interatomic angles: C(1)-Cr-C(2), 90.8 (2)° (89.2 (2)°); C(1)-Cr-O, 100.4 (2)° (101.9 (2)°); C(2)-Cr-O, 101.3 (2)° (101.0 (2)°).

Scheme I



liminary reactivity studies of oxo-alkyls of chromium in its highest oxidation states (V and VI).

Admission of an excess (>1.5 equiv) of dry dioxygen to cooled (-78 °C) ether solutions of $\text{Cp}^*\text{Cr}^{\text{III}}(\text{py})(\text{CH}_3)_2$ (**1**) ($\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$, py = pyridine), followed by slow warming to room temperature, induced a sequence of color changes (from brown through green to red). Evaporation of the solvent, extraction of the solid residue with pentane, and recrystallization from the same solvent yielded dark red crystals of $\text{Cp}^*\text{Cr}^{\text{VI}}(\text{O})_2\text{CH}_3$ (**2**) in 40% yield (Scheme I).⁶ Sharp NMR resonances in the expected range attested to the diamagnetic nature of **2**,

(6) **2**: ¹H NMR (C_6D_6) δ 1.53 (s, 15 H), 1.35 (s, 3 H); ¹³C NMR (C_6D_6) δ 120.1, 25.6, 10.5; IR (KBr) 3015 (m), 2978 (sh), 2953 (sh), 2920 (s), 2857 (m), 1443 (m), 1375 (s), 1358 (m), 1121 (m), 951 (m, sh), 914 (s), 804 (m) cm^{-1} ; UV-vis (THF) 472 nm (ϵ 1630), 350 (4310), 233 (14280); MS (70 eV) 234 (M^+ , 28), 202 (52), 134 (77) 119 (100); HRMS calcd for $\text{C}_{11}\text{H}_{18}\text{CrO}_2$ 234.0712, found 234.0715; mp 93 °C.

consistent with its d^0 electronic configuration. The dioxo moiety gave rise to two bands in the IR spectrum, a strong one (ν_{sym}) at 914 cm^{-1} and a weaker shoulder (ν_{asym}) at 951 cm^{-1} .

Final proof of the structure was obtained by X-ray crystallography; the result is shown in Figure 1.⁷ **2** is a monomeric half-sandwich and possesses a crystallographic mirror plane. Although the pentamethylcyclopentadienyl ligand is clearly η^5 -bonded, its endocyclic C-C bonds show some bond length alternation toward a localized diene, and the Cr-C distances range from 2.19 to 2.37 Å. This distortion toward an η^1 structure is probably a manifestation of the strong trans influence of the oxo ligand. The Cr-C_{methyl} bond (2.05 Å) is only slightly shorter than comparable bonds in chromium(III) derivatives (2.09 Å on average),^{5a} and the two symmetry-equivalent Cr-O distances (1.61 Å) fall squarely within the range found for known chromium oxo complexes (1.51-1.65 Å).⁸

Reaction of **1** with 0.5 equiv of O_2 under similar reaction conditions produced a dark green solution. Evaporation of the solvent yielded a solid residue from which a light green compound could be sublimed (room temperature, ca. 10^{-4} Torr) in very low yield. The same compound is produced in higher yield (52%) by reaction of **1** with trimethylamine *N*-oxide (Scheme 1). Spectroscopic and analytical data of this compound were consistent with the formula $\text{Cp}^*\text{Cr}^{\text{V}}(\text{O})(\text{CH}_3)_2$ (**3**).⁹ In particular, the compound exhibited one strong band ($\nu_{\text{Cr=O}}$ 976 cm^{-1}) in the IR spectrum, which was shifted to 935 cm^{-1} upon use of $^{18}\text{O}_2$ in the synthesis. The magnetic susceptibility of **3** was measured in the temperature interval 4-290 K using a Faraday balance. The complex is paramagnetic, and the data were fitted with a Curie-Weiss expression.¹⁰ The effective magnetic moment (corrected for diamagnetism, no detectable TIP) of **3** at 285 K is $1.76 \mu_{\text{B}}$, consistent with the d^1 configuration of pentavalent chromium.

The result of an X-ray structure determination of **3** is depicted in Figure 2.¹¹ The crystal contains two independent—albeit chemically equivalent—molecules in the asymmetric unit; they do not contain any crystallographically imposed symmetry elements. By comparison with **2**, the Cp* ligands of **3** exhibit no significant C-C bond length alternation, and the Cr-C_{ring} distances span a slightly smaller range. The average of the four Cr-C_{methyl} distances (2.043 (6) Å) does not differ significantly from that of **2**, while the Cr-O bonds of **3** are slightly shorter (average of 1.580 (3) Å).

Mixing equal amounts of **1** and **3** led to the formation of a dark green compound accompanied by liberation of pyridine (detected by ^1H NMR spectroscopy). On the basis of the spectroscopic data, we tentatively assign the structure $[\text{Cp}^*\text{Cr}^{\text{IV}}(\text{CH}_3)_2]_2(\mu_2\text{-O})$ (**4**) to this paramagnetic complex.¹² Considering the great oxidizing

power of chromium in its highest oxidation states, the considerable stability of the complexes described above is remarkable. C_6D_6 solutions of **2** decompose only slowly at room temperature ($t_{1/2}$ ca. 10 days), yielding mostly diamagnetic $[\text{Cp}^*\text{Cr}^{\text{V}}(\text{O})(\text{CH}_3)]_2(\mu_2\text{-O})$ (**5**).¹³ The same compound is produced in a rapid reaction of **2** with triphenylphosphine. Chromium-based catalysts are used for the polymerization of small olefins;¹⁴ however, neither **2** nor **3** showed any reaction with ethylene at room temperature and ambient pressure. The metal-carbon bond of **2** is not cleaved by methanol, indicating the highly covalent nature of the bond.

These results underscore the emerging notion that strongly π -donating oxo ligands greatly stabilize organometallic compounds in unusually high formal oxidation states and render their metal-carbon bonds nonpolar. It is our belief that the complexes described herein are only the tip of an iceberg laden with fascinating high-valent organochromium compounds. We are currently exploring this possibility.

Acknowledgment. We thank Prof. F. DiSalvo (Cornell University) for the use of his Faraday balance. This research was supported by the National Science Foundation (CHE-9096251).

Supplementary Material Available: Tables of X-ray structure determinations of $\text{Cp}^*\text{Cr}(\text{O})_2\text{CH}_3$ and $\text{Cp}^*\text{Cr}(\text{O})(\text{CH}_3)_2$, including crystal data, atomic coordinates, anisotropic thermal parameters, and bond distances and angles (16 pages). Ordering information is given on any current masthead page.

(13) **5**: ^1H NMR (C_6D_6) δ 1.79 (s, 15 H), 1.21 (s, 3 H); IR (KBr) 2986 (m), 2911 (s), 1435 (m), 1377 (s), 1161 (w), 1109 (m), 1020 (m), 937 (s), 826 (s), 819 (w) cm^{-1} ; MS (70 eV) 452 (M^+ , 6), 288 (47), 134 (79), 119 (100). Anal. Calcd for $\text{C}_{22}\text{H}_{36}\text{Cr}_2\text{O}_5$: C, 58.39; H, 8.02. Found: C, 57.48; H, 7.53. The crystal structure of **5** has been determined and will be reported in a full paper.

(14) (a) Clark, A. *Catal. Rev.* **1969**, *3*, 145. (b) Karol, F. J.; Karapinka, G. L.; Wu, C.; Dow, A. W.; Johnson, R. N.; Carrick, W. L. *J. Polym. Sci. A-1* **1972**, *10*, 2621. (c) Karol, F. J.; Brown, G. L.; Davison, J. M. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 413.

Biradical Character of a Closed-Shell Heteroaromatic Quinone

Toyonari Sugimoto,* Masashi Sakaguchi, Hiroshi Ando, Tomohiro Tanaka, and Zen-ichi Yoshida*

Department of Synthetic Chemistry
Kyoto University, Yoshida, Kyoto 606, Japan

Jun Yamauchi*

College of Liberal Arts and Science
Kyoto University, Yoshida, Kyoto 606, Japan

Yasushi Kai,* Nobuko Kanehisa, and Nobutami Kasai*

Department of Applied Chemistry
Osaka University, Yamadaoka, Osaka 565, Japan

Received October 21, 1991

There are so far very few definitive demonstrations of biradical contribution to the ground state of individual closed-shell organic molecules.¹ Tschitschibabin's hydrocarbon (**1**)² is one example, although opinions differ as to whether the compound exists as a singlet, a triplet, or a mixture of the two spin states.³⁻⁵ The

(7) Crystal data for **2**: $\text{C}_{11}\text{H}_{18}\text{CrO}_2$, orthorhombic, *Pnma*; $a = 12.6097$ (23), $b = 12.6518$ (26), $c = 7.4018$ (13) Å; $V = 1180.9$ (3) Å³, $Z = 4$; $R(F) = 3.77\%$. Despite the similarity in a and b , photographic and diffraction experiments determined that the highest symmetry was orthorhombic. Two octants of data (2360 reflections, max $2\theta = 50^\circ$) were merged, yielding 913 observed ($4\sigma F_o$) data. All non-hydrogen atoms were refined anisotropically, and hydrogen positions were included as idealized contributions.

(8) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988; p 163.

(9) **3**: ^1H NMR (C_6D_6) δ 4.9 (br); IR (KBr) 2967 (s), 2901 (s), 1431 (m), 1379 (m), 1134 (m), 1105 (m), 1024 (w), 976 (s), 802 (w), 513 (m); UV-vis (THF) 773 nm (ϵ 40), 328 (1350), 236 (3240); MS (70 eV) 233 (M^+ , 2), 218 (19), 203 (94), 185 (100); mp 48 °C. Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{CrO}$: C, 61.78; H, 9.07. Found: C, 61.92; H, 9.23. Preliminary ESR studies (X-band) of **3** showed a septet (due to hyperfine coupling to the six equivalent methyl protons with $g = 2.000347$ and $a(^1\text{H}) = 6.3$ G).

(10) The susceptibility data was fitted with a Curie-Weiss expression ($\chi_m = [C/(T - \theta)] + \text{TIP}$). $C = 0.398$, $\theta = -3.3$ K, $\text{TIP} = -7.3 \times 10^{-5}$ emu.

(11) Crystal data for **3**: $\text{C}_{12}\text{H}_{21}\text{CrO}$, monoclinic, *P2₁/c*; $a = 14.438$ (3), $b = 14.188$ (3), $c = 13.499$ (3) Å; $\beta = 114.97$ (2)°; $V = 2506.8$ (9) Å³, $Z = 8$, $R(F) = 5.14\%$. Preliminary photographic and diffraction experiments, which were performed due to similarity in the values of a and b , eliminated symmetries higher than monoclinic. Two octants of data (4888 reflections, max $2\theta = 50^\circ$) yielded 3278 observed ($3\sigma F_o$) data. All non-hydrogen atoms were refined anisotropically, and hydrogen positions were included as idealized contributions.

(12) **4**: ^1H NMR (C_6D_6) δ -14.1 (br s, Cp*); IR (KBr) 2947 (s), 2907 (s), 2880 (s), 1487 (w) 1425 (m), 1377 (s), 1107 (m), 1020 (m), 978 (w), 937 (m), 804 (w), 696 (w) 502 (m); mp 97-99 °C.

(1) Platz, M. S. In *Diradical*; Borden, W. T., Ed.; Wiley: New York, 1982.

(2) Tschitschibabin, A. E. *Ber.* **1907**, *40*, 1810-1819.

(3) Müller, E.; Müller-Rodloff, I. *Justus Liebigs Ann. Chem.* **1935**, *517*, 134-151.

(4) Schwab, G. M.; Agliardi, N. *Chem. Ber.* **1940**, *73B*, 95-98.

(5) Seel, F. *Naturwissenschaften* **1946**, *33*, 60-61.

(6) Seel, F. *Z. Elektrochem.* **1948**, *52*, 182-193.