Reactive Alkoxide Complexes of Groups 6 and 7 Metals

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Summary: Easily available alkoxo complexes [M(OR)(CO)$_3$(bipy)] (M = Mn, Re) and [Mo(OR)(η^3-C_3H_5)(CO)$_2$(phen)] react with dimethylacetylenedicarboxylate (DMAD) to afford the Z-alkenyls resulting from DMAD insertion into the M−OR bonds. Evidence suggesting a nondissociative mechanism is presented.

In contrast with the wealth of information available on the insertion of acetylenes into M−H and M−C bonds, few examples of insertion of acetylenes into metal−heteroatom bonds are known.[1]

Low-valent transition metal alkoxo complexes are still rare, and the mismatch between the electron-rich metal center and the π-donor alkoxide holds potential as a source of reactivity. In the vast field of carbonyl-stabilized, electron-precise middle transition metal compounds, alkoxides are particularly scant. A notable exception is Bergman's work on [Re(OR)(CO)$_3$L$_2$] (L$_2$ = two phosphines or a bidentate phosphine or arsine) complexes, which have been shown to insert CO_2 and CS_2.[2]

Chelating diimines such as 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) ligands are stronger electron donors than diphosphines or diarsines, as reflected in the lower ν_{CO} values of their similar complexes (see below). Since a more electron-rich metal center enhances the reactivity of alkoxide complexes toward electrophiles,[2b] diimine complexes of the type [M(OR)(CO)$_3$(N−N)] are expected to be more reactive than their phosphine or arsine counterparts. The planarity and lack of bulky substituents on the diimine rings should contribute to a higher reactivity by facilitating the approach of the incoming electrophile to the alkoxide group. We therefore reasoned that alkoxo complexes with the diimine ligands could insert a broader range of substrates. Thus, we were pleased to find that [M(OCH$_3$)(CO)$_3$(bipy)] (M = Mn, **1**; Re, **2**), easily available by reaction of sodium methoxide with [M(OTf)(CO)$_3$(bipy)] complexes,[3,4] insert smoothly dimethylacetylenedicarboxylate (DMAD), a reaction so far exclusive of the isoelectronic highly reactive compound [Ir(C$_5$Me$_5$)(OH)(Ph)(PMe$_3$)].[5,6]

The reactions afforded as single products the *Z*-alkenyls **5** and **6** (see Scheme 1), which were characterized spectroscopically and, in the case of **6**, by X-ray diffraction (Figure 1).[7] ^{1}H NMR monitoring of the insertion reaction in CD_2Cl_2 showed **5** and **6** to be the only products.

We wished to extend the combination of ease of preparation and relative stability with a high reactivity displayed by **1** and **2** to other metal−ligand sets. We recently found that carbanionic nucleophiles react with [MoCl(η^3-C_3H_5)(CO)$_2$(N−N)] (N−N = bipy, phen) complexes to yield stable alkyls.[8] Similarly, the reaction of [MCl(η^3-C_3H_5)(CO)$_2$(phen)] (M = Mo, W) with sodium methoxide afforded the new complexes [M(OCH$_3$)(η^3-C_3H_5)(CO)$_2$(phen)] (M = Mo, **3**; W, **4**) which have been characterized spectroscopically.[4] Alkoxide attack to the allyl ligand was not observed, and complexes **3** and **4**

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[1] (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163−1188. (b) Villanueva, L. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1992**, *11*, 2963−2965. (c) Vanderlende, D. D.; Abboud, K. A.; Boncella, J. M. *Inorg. Chem.* **1995**, *34*, 5319−5326. (d) Simpson, R. D.; Bergman, R. G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 220−223. Examples of alkoxocomplexes of groups 6 and 7 in low oxidation states are referenced in this paper. (e) Boncella, J. M.; Eve, T. M.; Rickman, B.; Abboud, K. A. *Polyhedron* **1998**, *17*, 725−736.

[2] (a) Simpson, R. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 781−796. (b) Simpson, R. D.; Bergman, R. G. *Organometallics* **1992**, *11*, 4306−4315. (c) Simpson, R. D.; Bergman, R. G. *Organometallics* **1992**, *11*, 3980−3993. In a previous work, Orchin studied the CO insertion in the Mn−OMe and Re−OMe bonds of related compounds: Mandal, S. K.; Ho, D. M.; Orchin, M. *Inorg. Chem.* **1991**, *30*, 2244−2248.

[3] The ν_{CO} bands of **2** occur at 1999, 1882, and 1861 cm^{-1} in KBr, in which medium the complex [Re(OCH$_3$)(CO)$_3$(PMe$_3$)$_2$] absorbs at 2012 and 1921 cm^{-1} (see ref 2b). This indicates the more electron-rich nature of the diimine complex.

[4] The methoxo complexes **1**−**4** were prepared by reaction of complexes ([M(OTf)(CO)$_3$(bipy)], M = Mn, Re (in turn prepared by reaction of the bromides with silver triflate); [MCl(η^3-C_3H_5)(CO)$_2$(phen)], M = Mo, W) with sodium methoxide in dicloromethane. Full experimental details are given as Supporting Information.

[5] Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7888−7889. For insertion of acetylenes into Rh−O bonds of a bidentate phosphine-alkoxide ligand see: Yamamoto, Y.; Hang, X. H.; Ma, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 1965−1968.

[6] To a solution of **1** (0.050 g, 0.153 mmol) in THF (20 mL) was added DMAD (19 μL, 0.153 mmol). After stirring for 10 min the volatiles were removed in vacuo and the residue was washed with hexane (2 × 10 mL) to afford the complex **5**. Yield: 0.057 g, 80%. IR (THF): 2009, 1915 (ν_{CO}), 1731, 1713. ^{1}H NMR (CD_2Cl_2): 9.03, 8.05, 7.95, 7.43 [m, 2H each, bipy], 3.59 [s, 3H, CO_2Me], 3.53 [s, 3H, CO_2Me], 2.85 [s, 3H, OMe]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 223.79 [2CO], 215.57 [CO], 175.01 and 167.04 [O=*C*−OCH$_3$], 162.14 [C=C], 155.30, 154.34 [bipy], 147.72 [C=C] 137.62, 125.54, 121.79 [bipy], 59.96 [O*C*H$_3$], 51.58 and 50.13 [COO*CH*$_3$].

[7] X-ray data for **6**: crystal dimensions 0.25 × 0.22 × 0.20 mm, monoclinic, $P2_1/c$, $a = 9.224(1)$ Å, $b = 16.112(2)$ Å, $c = 14.820(2)$ Å, $\beta = 97.487(3)°$, $V = 2183.6(6)$ Å^3, $Z = 4$, $T = 295$ K, $\rho_{calcd} = 1.824$ g cm^{-3}, $\mu = 5.613$ mm^{-1}, $F(000) = 1160$, $\theta_{max} = 23.28°$, *hkl* ranges −10 to 10, −17 to 17, −10 to 16; 9623 data collected, 3137 unique data ($R_{int} = 0.0214$), 2807 data with $I > 2\sigma(I)$, 283 parameters refined, GOF(F^2) = 1.108, final *R* indices R1 = 0.0372, wR2 = 0.0898; max./min. residual electron density 1.328 (0.100)/−0.968 (0.100) e Å^3.

[8] Pérez, J.; Riera, L.; Riera, V.; García-Granda, S.; García-Rodriguez, E. *J. Am. Chem. Soc.* **2001**, *123*, 7469−7470.

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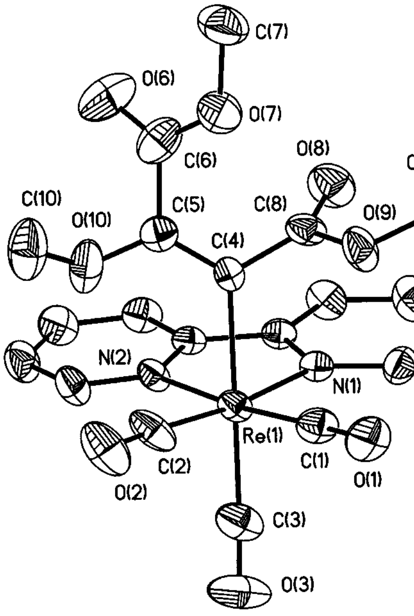
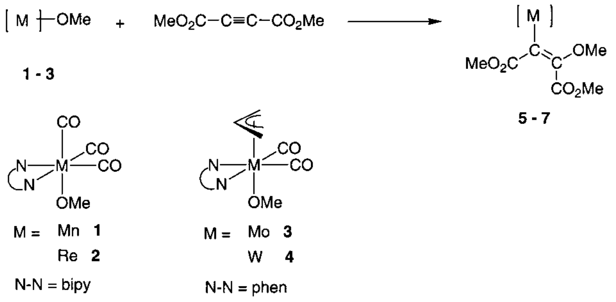


Figure 1. Molecular structure of **6** with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Re(1)−C(4) 2.198(8), C(4)−C(5) 1.333(12), C(5)−O(10) 1.297(12); C(5)−C(4)−C(8) 119.4(8), C(5)−C(4)−Re(1) 123.5(6), C(8)−C(4)−Re(1) 117.0(6), O(10)−C(5)−C(4) 124.6(9), O(10)−C(5)−C(6) 114.4(9), C(4)−C(5)−C(6) 120.5(9).

Scheme 1



have a stable geometry with mutually trans methoxide and allyl ligands. Complex **3** reacted with DMAD in dichloromethane at room temperature to give the insertion product **7**, characterized spectroscopically[9] and by X-ray diffraction (see Scheme 1 and Figure 2),[10] in which a *Z*-alkenyl ligand like those present in **5** and **6** (obtained as the single product, as observed when the reaction was monitored by ^{1}H NMR) was found.[11]

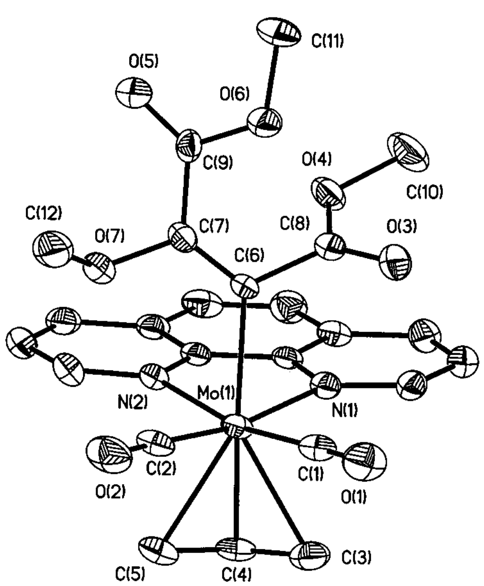


Figure 2. Molecular structure of **7** with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo(1)−C(6) 2.272(5), C(6)−C(7) 1.327(7), C(7)−O(7) 1.405(6); C(7)−C(6)−C(8) 117.6(4), C(7)−C(6)−Mo(1) 127.7(4), C(8)−C(6)−Mo(1) 114.8(3), C(6)−C(7)−O(7) 120.4(5), C(6)−C(7)−C(9) 125.9(4), O(7)−C(7)−C(9) 113.0(4).

Bergman found that nucleophilic attack by the undissociated alkoxide is the most plausible mechanism for the insertion of electrophiles into Re−O bonds of the aforementioned phosphine or arsine complexes.[2,12] This seems to be also the case for the reaction of DMAD with **1**−**3**. Thus, we prepared the complex [Re(OEt)(CO)$_3$(bipy′)] (bipy′ = 4,4′-dimethyl-2,2′-bipyridine) (**8**) and found it to insert DMAD. A mixture of **2** and **8** was dissolved in CD_2Cl_2, and NMR monitoring during a 40 min period (during which time DMAD insertion with either complex reaches completion) showed the absence of exchange products. The nonobserved crossover products have been independently synthesized (see Supporting Information), and their methoxide ^{1}H NMR signals were found to be distinguishable from those of the observed products. Similar negative crossover experiments were conducted with the molybdenum complexes.[13]

Although alkoxide dissociation does not seem to occur prior to reaction with DMAD, the cost of M−OMe bond cleavage is crucial to the reaction. Thus, although the tungsten alkoxide **4** shows IR bands at lower wavenumbers than the molybdenum analogue **3**, indicating more back-bonding and therefore a more basic alkoxide,

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(9) Following the procedure described for **5** and **6**, to a solution of **3** (0.050 g, 0.12 mmol) in CH_2Cl_2 (20 mL) was added DMAD (20 μL, 0.16 mmol) to give in 45 min the complex **7**. Yield: 0.052 g, 86%. IR (CH_2Cl_2): 1941, 1832 (ν_{CO}), 1703, 1689. ^{1}H NMR (CD_2Cl_2): 9.07, 8.43 [m, 2H each, phen], 7.90 [s, 2H, phen], 7.77 [m, 2H, phen], 3.56 [s, 3H, CO_2Me], 3.38 [s, 3H, CO_2Me], 3.18 [d (6.5), 2H, H_{syn}], 2.89 [s, 3H, OMe], 2.75 [m, 1H, CH of η^3-C_3H_5], 1.61 [d (9.6), 2H, H_{anti}]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 228.88 [CO], 174.44 and 171.47 [O=*C*−OCH_3], 162.03 and 152.22 [C=C], 153.55, 144.91, 137.20, 129.90, 127.35, and 124.37 [phen], 76.20 [C^2 of η^3-C_3H_5], 59.05 [O*C*H_3], 57.89 [C^1 and C^3 of η^3-C_3H_5], 51.31 and 50.31 [COO*C*H_3].

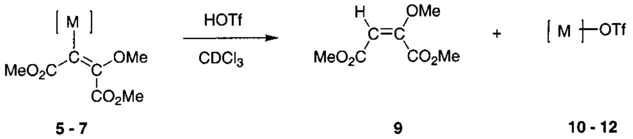
(10) Data for **7**: crystal dimensions 0.41 × 0.32 × 0.18 mm, triclinic, $P\bar{1}$, $a = 10.198(2)$ Å, $b = 10.487(3)$ Å, $c = 13.233(3)$ Å, $\alpha = 74.658(4)°$, $\beta = 73.658(4)°$, $\gamma = 63.303(4)°$, $V = 1197.4(5)$ Å^3, $Z = 2$, $T = 295$ K, $\rho_{calcd} = 1.515$ g cm^{-3}, $\mu = 50.594$ mm^{-1}, $F(000) = 556$, $\theta_{max} = 23.28°$, *hkl* ranges −9 to 11, −11 to 10, −14 to 13; 5377 data collected, 3446 unique data ($R_{int} = 0.0280$), 3100 data with $I > 2\sigma(I)$, 310 parameters refined, GOF(F^2) = 1.096, final *R* indices R1 = 0.0586, wR2 = 0.1448; max./min. residual electron density 1.346 (0.120)/−1.112 (0.120) e Å^3.

(11) To our knowledge, the only insertion reactions of group 6 alkoxides are those reported by Darensbourg with anionic zerovalent tungsten complexes, which insert CO_2: (a) Darensbourg, D. J.; Sanchez, K. M.; Reibenspies, J. H.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 7094−7103. (b) Darensbourg, D. J.; Mueller, B. L.; Reibenspies, J. H.; Bischoff, C. H. *Inorg. Chem.* **1990**, *29*, 1789−1791. (c) Darensbourg, D. J.; Mueller, B. L.; Bischoff, C. J.; Chojnacki, S. S.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 2418−2424.

(12) It should be noted that the alkoxo complexes reported here do not have sites for acetylene coordination previous to insertion, a feature in common with the tungsten compounds of ref 11.

(13) Negative crossover experiments have been used to support a nondissociative mechanism, see ref 2 and: Bergman, R. G. *Polyhedron* **1995**, *14*, 3227−3237. Preparation and data of the ethoxo complexes are included in the Supporting Information.

Scheme 2



5 - 7 **9** **10 - 12**

complex **4** fails to insert DMAD, likely as a result of the W−OR bond being stronger than Mo−OR. Insertion of DMAD being faster with **1** than with **2** falls in the same trend.

The reaction of the insertion products **5**−**7** with triflic acid cleanly cleaves the metal−$C_{alkenyl}$ bond, thus allowing demetalation of the olefin **9**[14,15] and the potential recycling of the metallic precursors (see Scheme 2).

The reactivity of compounds **1**−**4** with other electrophiles is being investigated and will be reported in a forthcoming publication.

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Supporting Information Available: Complete details for the synthesis of all compounds, spectroscopic data, and X-ray crystallographic data for **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Feit, B.; Haag, B.; Kast, J.; Schmidt, R. R. *J. Chem. Soc., Perkin Trans. 1* **1986**, 2027−2036.

(15) Reaction of **5**−**7** with HOTf: The alkenyl (**5**, **6**, or **7**) was dissolved in $CDCl_3$ (0.5 mL) in a 5 mm NMR tube, which was then capped with a rubber septum. The stoichiometric amount of HOTf was injected. The ^1H NMR spectrum of this sample showed the signals of the triflato complexes (**10**, **11**, and **12**, respectively) as well as the signals of the free olefin **9**. ^1H NMR data of **9** ($CDCl_3$): 5.21 [s, 1H], 3.89 [s, 3H, OMe], 3.74 [s, 3H, CO_2Me], 3.71 [s, 3H, CO_2Me]. Integration of the olefin and triflato complexes showed a 1:1 ratio.