Metal Formates via Oxidation of Metal Carbonyl Hydrides

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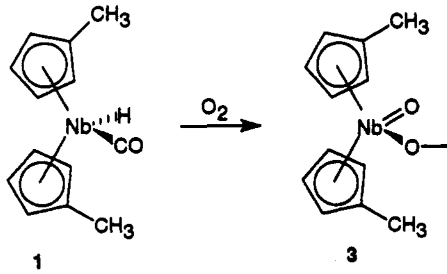
*Summary: The reaction of the metal carbonyl hydrides (η^5-$C_5H_4CH_3)_2M(CO)H$ (M = Nb (**1**), Ta (**2**)) with dioxygen produces the metal formato complexes (η^5-$C_5H_4CH_3)_2Nb(O)(\eta^1$-$O_2CH)$ (**3**) and (η^5-$C_5H_4CH_3)_2Ta(O)(\eta^1$-$O_2CH)$ (**4**), apparently through the intermediacy of the corresponding CO_2 complexes (η^5-$C_5H_4CH_3)_2M(\eta^2$-$CO_2)H$.*

The activation of carbon monoxide by transition-metal centers forms the basis of numerous commercially and synthetically important catalytic processes.[1] The study of stoichiometric reactions of metal carbonyl complexes, in turn, has provided valuable mechanistic models for these catalytic reactions.[2] Although presently of lesser practical importance, the potential utility of metal-catalyzed transformations of carbon dioxide has also stimulated considerable interest in its organometallic chemistry.[3] Metalloformates [M–OC(O)H] have been implicated as important intermediates in catalytic reactions of both of these carbon oxides, e.g. in the water–gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$),[4] and in carbon dioxide hydrogenation to formic acid[5] and its derivatives.[6]

Recently, in connection with our studies of carbon *dioxide* activation by metal complexes a new class of atom addition reactions of coordinated carbon *monoxide* was discovered (producing metal–CO_2[7] and –COS[8] complexes) which serves as a model for the initial stage of catalytic oxidation and sulfurization of carbon monoxide, respectively. We now report novel findings on the aerobic oxidation of the hydridometal carbonyls $Cp'_2M(CO)H$ (Cp′ = η^5-$CH_3C_5H_4$; M = Nb (**1**), Ta (**2**)) which results instead in the generation of metalloformates by a heretofore unrecognized pathway.

Treatment of a red-brown toluene solution of (η^5-$C_5H_4CH_3)_2Nb(CO)H$[9] (**1**) with an equimolar amount of O_2 at 20 °C resulted in a color change to yellow within 15 min, accompanied by disappearance of the carbonyl absorption of **1** at 1892 cm^{-1} and appearance of a new band at 1667 cm^{-1}. Workup and crystallization gave the colorless, unstable solid **3**,[10] which was associated with the latter IR band and whose ^1H NMR spectrum exhibited a 1 H singlet at 9.03 ppm (in addition to resonances associated with the MeCp ring) and a $^{13}\{^1H\}$ NMR resonance at 166.9 ppm. Importantly, when (η^5-$C_5H_4CH_3)_2Nb(^{13}CO)H$ was oxidized, the ^1H NMR resonance of **3** at 9.03 ppm appeared as a doublet with $J(^{13}C–H)$ = 206 Hz. These spectroscopic data together clearly indicate the presence of an η^1-formato ligand in **3**.[11] The (lack of) color, the strongly deshielded Cp′NMR resonances, and the appearance of a MS molecular ion at *m/e* 312 lead us to formulate **3** as the Nb(V) oxo–formate species (η^5-$C_5H_4CH_3)_2Nb(O)(\eta^1$-$O_2CH)$ (eq 1).[12]



(1)

Parallel experiments conducted with the tantalum analog (η^5-$C_5H_4CH_3)_2Ta(CO)H$[9] (**2**) extended the generality of and provided mechanistic insight into this novel assembly of CO, H, and O fragments into formate. Thus, injection of an equimolar amount of O_∞ into a violet toluene solution of **2** at 20 °C resulted in a gradual color change to yellow accompanied by disappearance of the M—CO

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(1) (a) *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1968, 1977; Vols. I and II. (b) *Catalytic Activation of Carbon Monoxide*; Ford, P.C., Ed.; ACS Symposium Series 152; American Chemical Society: Washington, DC, 1981.

(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 12, pp 619–665.

(3) Reviews: (a) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, Germany, 1988. (b) Ito, T.; Yamamoto, A. In *Organic and Bioorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Halstead Press: New York, 1982; Chapter 3, pp 79–151. (c) Darensbourg, D.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (d) Kolomnikov, I. S.; Lysyak, T. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1990**, *59*, 344.

(4) Slegeir, W. A. R.; Sapienza, R. S.; Easterling, B. In ref 1b, pp 325–343. Darensbourg, D. J.; Rokicki, A. In ref 1b, p 121. King, R. B.; King, A. D., Jr.; Yang, D. B. In ref 1b, pp 123–132.

(5) Tsai, J.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 5117. Graf, E.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1992**, 623.

(6) Darensbourg, D. J.; Ovalles, C. *J. Am. Chem. Soc.* **1987**, *109*, 330 and references cited therein.

(7) Fu, P.-F.; Khan, M. A.; Micholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 6579.

(8) Fu, P.-F.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1993**, *12*, 3790.

(9) $(MeCp)_2Nb(CO)H$ (**1**) and $(MeCp)_2Ta(CO)H$ (**2**) were prepared from $(MeCp)_2MH_3$ (M = Nb, Ta) according to the method described for $Cp_2Nb(CO)H$ and exhibited appropriate NMR, IR, and mass spectra: Foust, D. F.; Rogers, R. D.; Rausch, M. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 5646.

(10) Compound **3** was isolated (12%) by filtration and addition of hexane to the filtrate at −10 °C. **3**: IR (KBr) 1630, 1242 cm^{-1}; ^1H NMR (C_6D_6) δ 9.03 (s, 1 H), 5.90 (m, 2 H), 5.60 (m, 2 H), 5.35 (m, 2 H), 5.09 (m, 2 H), 1.89 (s, 6 H); ^{13}C NMR (C_6D_6) δ 166.9, 119.0, 111.2, 109.7, 107.4, 30.1; MS (EI, 12 eV) *m/e* 312 (M^+, 5), 296 ($M^+ - O$, 49), 266 ($M^+ - O_2CH$, 4). The instability of **3**, manifested by the ready formation of a yellow, noncarbonyl-containing precipitate, prevented its isolation in pure form.

(11) (a) Darensbourg, D. J.; Rockicki, A. *Organometallics* **1982**, *1*, 1685. (b) Darensbourg, D. J.; Fisher, M. B.; Schmidt, R. E. J.; Baldwin, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 1297. (c) Darensbourg, D. J.; Rockicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223. (d) Smith, S. A.; Blake, D. M.; Kubota, M. *Inorg. Chem.* **1972**, *11*, 660. (e) Johnson, B. F. G.; Johnston, R. D.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1971**, *689*. (f) Pu, L. S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1968**, *90*, 3896. (g) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379. (h) Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1980**, *198*, C75. (i) Komiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 784. (j) Kolomnikov, I. S.; Gusev, A. I.; Aleksandrov, G. G.; Lobeeva, T. S.; Struchkov, Y. T.; Vol'pin, M. E. *J. Organomet. Chem.* **1973**, *59*, 349. (k) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* **1972**, *46*, C58.

(12) A green-brown Nb(III) carboxylate, $Cp_2Nb(\eta^1$-$O_2CCMe_3)$, has been reported with ν(OCO) at 1652 cm^{-1} and a ^1H NMR Cp resonance at 5.29 ppm: Pasynskii, A. A.; Skripkin, Y. V.; Kalinnokoc, V. T. *J. Organomet. Chem.* **1978**, *150*, 51.

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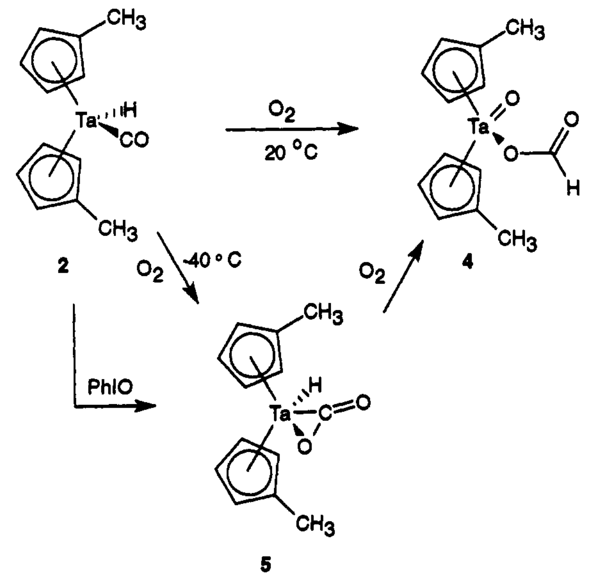
Scheme 1



IR band of **2** (1890 cm^{-1}) and the growth of a new C=O absorption associated with the product **4** at 1630 cm^{-1} (Scheme 1); the latter was shifted to 1595 cm^{-1} when derived from $(\eta^5\text{-}C_5H_4CH_3)_2Ta(^{13}CO)H$, proving its origin from the carbon monoxide carbon. Additional evidence for the identity of **4** as a formate complex was provided by its ^{1}H and ^{13}C NMR spectra[13] (toluene-d_8), which showed diagnostic resonances of the formato group at 8.62 (d, $J(^{13}C\text{-}H) = 195$ Hz) and 171 ppm, respectively. As with the Nb complex **3**, the color (pale yellow) of **4** and the substantial downfield shift of the Cp resonances of **4** relative to those for the starting material **2** (1.0 ppm) suggest a Ta(V) state, i.e. $(\eta^5\text{-}C_5H_4CH_3)_2Ta(O)(\eta^1\text{-}O_2CH)$. The instability of **4** prevented its complete structural characterization.

The demonstrated susceptibility of both M–H[14] and M–CO[15] ligands to attack by O_2 raised the fundamental question of which unit in **1** and **2** reacts first. Low-temperature spectroscopic monitoring of the oxidation of tantalum complex **2** provided the answer. Exposure of a toluene-d_8 solution of **2** to oxygen while it was maintained at −40 °C revealed the generation of the new species **5**, which had (*inter alia*)[16] an IR absorption at 1719 cm^{-1}, a ^{1}H NMR resonance at −5.55 ppm, and a ^{13}C NMR absorption at 201.9 ppm. Together these spectral features indicate that **5** still retains the Ta–H fragment while the Ta–CO unit has been transformed into a $Ta(\eta^2\text{-}CO_2)$ unit;[17] i.e., **5** is $(\eta^5\text{-}C_5H_4CH_3)_2TaH(\eta^2\text{-}CO_2)$. Within 1–2 h at −40 °C in the presence of oxygen the resonances of **5** had largely disappeared, leaving formate complex **4** and other unidentified products. Importantly, **5** could also be generated cleanly by treatment of **2** with PhIO at 20 °C and persisted much longer in solution than **5** obtained from **2** with O_2, consistent with the requirement of additional oxygen for the **5** to **4** conversion.

A number of features of the above results are especially deserving of comment. The conversions **1** → **3** and **2** → **4** represent the first examples of formate generation via oxidation of a hydridometal carbonyl.[18] Furthermore, tantalum complex **5** is the first detected $HM(CO_2)$ complex and its conversion to the formate **4** is suggestive of the involvement of *coordinated* CO_2 in the insertion step.[19] It is interesting to contrast the present reactions, in which CO oxidation is followed by insertion, with oxidations of the corresponding alkylmetal carbonyls, $Cp'_2M(CO)R$,[7] in which the intermediate $Cp'_2M(\eta^2\text{-}CO_2)R$ complexes are isolable and are resistant to insertion, even at elevated temperatures.[21] This observation is consistent with prior studies demonstrating the more facile insertion of olefins and alkynes into the M–H bond of $Cp_2M(CO)Z$ (M = Nb, Ta; Z = H, R)[22] and of the insertion of CO_2 into the M–Z bond of $ZM(CO)_5^-$ (Z = H, R)[20] but contrasts with the more difficult (at least thermodynamically) CO insertions into M–H bonds.[23] Finally, the mechanism of the novel M–CO → M–CO_2 transformation remains in question and further insight awaits the results of continuing investigations.

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[13] **4**: IR (toluene) 1630 cm^{-1}; ^{1}H NMR (toluene-d_8) δ 8.63 (s, 1 H), 5.6–5.4 (m, 8 H), 2.37 (s, 6 H); ^{13}C NMR (C_6D_6) δ 170.0, 85.6, 85.3, 81.5, 79.9, 29.9.

[14] Insertions of O_2 into M–H produce M–OH and/or MOOH, e.g.: (a) Grundy, K. R.; Laing, K. R.; Roper, W. R. *J. Chem. Soc. D* **1970**, 1500. (b) Johnson, L. E.; Page, J. A. *Can. J. Chem.* **1969**, *47*, 4241. (c) Bayston, J. H.; Winfield, M. E. *J. Catal.* **1964**, *3*, 123.

[15] (a) Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235. (b) Atwood, J. D.; Lawson, H. J. *J. Am. Chem. Soc.* **1989**, *111*, 6223. (c) Curtis, M. D.; Han, K. R. *Inorg. Chem.* **1985**, *24*, 378. (d) Kubota, M.; Rosenberg, F. S.; Sailor, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 4558. (e) Roundhill, D. M.; Allen, G. H.; Bechtold, Huber, H.; McIntosh, D.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 975. (g) Zecchina, A.; Spoto, G.; Coluccia, S.; Guglielminotti, E. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1975.

[16] **5**: Ir (toluene) 1719 cm^{-1}; ^{1}H NMR (toluene-d_8, −40 °C) δ 5.05–4.8 (m, 8 H), 2.48 (s, 6 H), −5.55 (s, 1 H); ^{13}C NMR (toluene-d_8, −40 °C) 201.9, 85.7, 85.3, 81.6, 79.9, 30.6.

[17] IR signals (C=O) for $Cp'_2M(\eta^2\text{-}CO_2)R$ (M = Nb, Ta) are at ca. 1720–1740 cm^{-1} and ^{13}C NMR resonances at ca. 200 ppm. M = Nb: Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145. See also ref 7. M = Ta: Rahman, F. A. K.; Nicholas, K. M. Unpublished results. A peroxocarbonyl formulation, $Cp'_2HTaC(=O)OO$, for **5** may also be considered but appears less likely, given the production of **5** from PhIO and **2**.

[18] Existing (nonmetathetical) routes to $L_nM(O_2CH)$ include the following: (a) $L_nM\text{—}H + CO_2$;[11] (b) $L_nM + CO + OH^-$;[4] (c) $L_nM(=O)H + CO$ (Kim, Y.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 8600).

[19] Unlike CO insertions, for which ligand precoordination has been amply demonstrated, coordination of CO_2 preceding insertion into $L_nM\text{-}H$ has not been proven and has been discounted in some cases.[20] Indeed, as noted by a reviewer, the conversion of **5** to **4** could proceed via reaction of a Ta–H species, e.g. $Cp'_2Ta(O)H$, with free CO_2.[18c]

[20] (a) Darensbourg, D. J. In *Enzymatic and Model Carboxylation Reactions for Carbon Dioxide Utilization*; Aresta, M., Schloss, J. V., Eds.; NATO ASI Series 314; Kluwer Academic: Dordrecht, The Netherlands, 1990; pp 43–64. (b) Darensbourg, D. J.; Wiegreffe, H. P.; Wiegreffe, P. W. *J. Am. Chem. Soc.* **1990**, *112*, 9252. Darensbourg, D. J.; Wiegreffe, H. P. *Inorg. Chem.* **1990**, *29*, 592. (c) Bo, C.; Dedieu, A. *Inorg. Chem.* **1989**, *28*, 304.

[21] Fu, P.-F.; Khan, M. A.; Micholas, K. M. *Organometallics* **1991**, *10*, 382.

[22] Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134. Yasuda, H.; Yamamaoto, H.; Arai, T.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1991**, *10*, 4058.

[23] Reference 1b, pp 645–650 and references cited therein.