Reaction of $Cp_2Ta(CH_2)CH_3$ with Methyl- and Phenylrhenium Pentacarbonyl: "Wittig-like" Metathesis of Bound Carbon Monoxide to a $C{=}CH_2$ (Vinylidene) Group and NMR Evidence for the Intervention of a Zwitterionic Intermediate

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Despite their importance in catalysis and organotransition-metal chemistry, reactions that deoxygenate carbon monoxide (CO) and convert it directly into longer chain hydrocarbons are not well understood.[1] We recently reported a reaction between Schrock's tantalum alkylidene complex[2] $Cp_2Ta(CH_2)CH_3$ (Cp = η^5-C_5H_5) and $Re_2(CO)_{10}$ that resulted in CO/CH_2 deoxygenation and coupling, leading to a bound methylacetylide ligand.[3] We have now found that treatment of $Cp_2Ta(CH_2)CH_3$ with methyl- and phenylrhenium pentacarbonyl leads to a dramatically different product, a complex containing alkenyl and oxotantalum groups bound to a rhenium center. We provide evidence that this process occurs by the novel and potentially general reaction sequence illustrated in Scheme I: initial "Wittig-like" attack of the tantalum-bound CH_2 group on a CO ligand to give an oxametallacycle, followed by ring opening to a zwitterion and cleavage to oxotantalum and vinylidene complexes. The vinylidene is then trapped by rapid migratory insertion of the alkyl or aryl group to give an alkenyl complex.

Treatment of the tantalum alkylidene complex $Cp_2Ta(CH_2)(CH_3)$ (**1**)[2] with 1 equiv of the methyl- or phenylrhenium pentacarbonyl complexes $RRe(CO)_5$ (R = CH_3, **2a**; Ph, **2b**) above 0 °C yielded the bridging oxo complexes $Cp_2(CH_3)Ta(\mu\text{-}O)Re(CR{=}CH_2)(CO)_4$ (R = Me, **3a**; Ph, **3b**)[4,5] (Scheme II). This reaction occurs at room temperature and in the absence of light, requiring only seconds to provide a high yield of product (>90% by ^{1}H NMR spectroscopy). Compounds **3a** and **3b** were isolated in 61% and 67% yield, respectively, in pure crystalline form by slow diffusion of pentane into a benzene solution, followed by slow cooling to −30 °C. The ^{1}H NMR spectrum of **3b** suggested its identity as an alkenyl complex by showing two doublets attributable to inequivalent vinylic protons, and the ^{13}C NMR spectrum also shows phenylvinyl resonances. The IR spectra of **3a** and **3b** have absorbances at 833 and 831 cm^{-1}, respectively, which we assign to the M–O–M′ bridging oxo stretches.

To confirm these inferences, an X-ray crystallographic analysis of **3b** was performed. Details of the determination and structural data are provided as supplementary material, and an ORTEP diagram is shown in Figure 1. The length of the Ta=O bond is 1.76(1) Å, while the Re—O bond is 2.15(1) Å, suggesting that the complex possesses a Ta=O double bond and a Re—O donor-acceptor interaction. The Ta—O—Re bond angle of 179.0(6)° is linear within experimental error. A linear structure with a large discrepancy in metal oxo bond lengths between an early and a late transition metal is rare but is generally viewed as being due to a dative interaction between the late metal and the oxygen.[6] The Re center has a pseudooctahedral coordination geometry, and the CH_2 group is directed toward the Cp_2Ta center and the more sterically demanding phenyl group directed away from it.

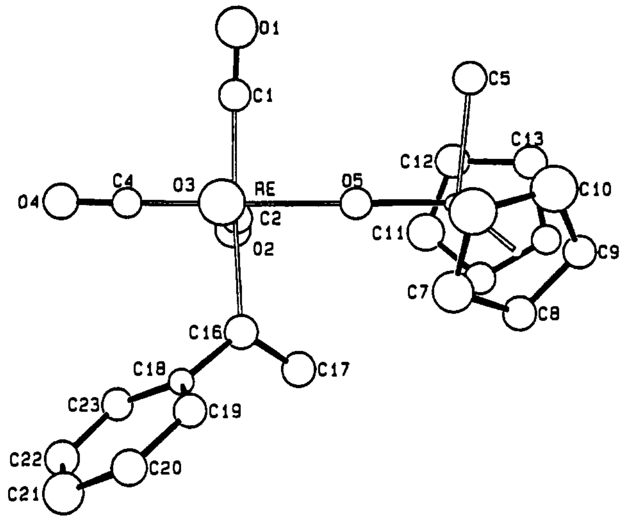
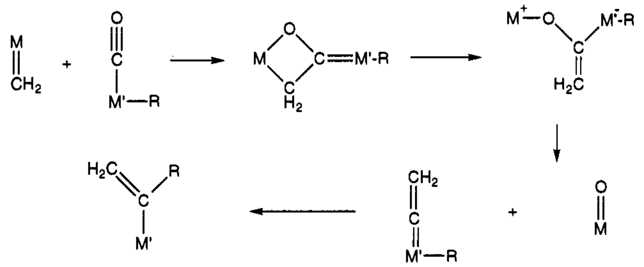


Figure 1. ORTEP diagram for the molecular structure of $Cp_2(CH_3)Ta(\mu\text{-}O)Re(CPh{=}CH_2)(CO)_4$ (**3b**). Selected bond distances (Å): Ta–O5, 1.761(11); Ta–C5, 2.214(17); Re–O5, 2.147(11); Re–C16, 2.234(17); C16–C17, 1.34(2). Selected bond angleSPCLN Ta-O5-Re, 179.0(6)°. $C_{23}H_{20}O_5ReTa$ crystallizes in the orthorhombic space group *Pbca*; a = 12.375(2), b = 20.892(2), and c = 16.906(2) Å; $\alpha = \beta = \gamma = 90°$. Of 2851 reflections collected (−104 °C, Mo Kα: $3.0 < 2\theta < 45.0°$), 2224 ($F^2 > 3\sigma(F^2)$) were refined to R = 0.047, R_w = 0.054. Only the Ta and Re atoms were refined anisotropically.

Scheme I



The two most likely mechanisms for this reaction, illustrated in Scheme II, differ in the relative timing of the migratory insertion and CO deoxygenation steps that must occur in the conversion of **2** to **3**. It is unlikely that the reaction proceeds by initial loss of CO from the Re center because such dissociation normally requires light or relatively high temperatures.[7] A more likely mechanism (path A in Scheme II) proceeds by "Wittig-type" metathesis of the Ta=CH_2 moiety and a ReC≡O group, leading to oxametallacycle **4**. Fragmentation of the metallacycle (probably via zwitterion **5**; see below) leads to the oxotantalum species **6** and the alkyl- or arylrhenium vinylidene complex **7**. The vinylidene complex then undergoes rapid solvent-induced migratory insertion to give THF solvate **8**. At this point, the solvent

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[1] Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell Univ. Press: Ithaca, NY, 1981.

[2] Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

[3] Proulx, G.; Bergman, R. G. *Science* **1993**, *259*, 661.

[4] Anal. Calcd for $C_{18}H_{18}O_5TaRe$: C, 31.72; H, 2.66. Found: C, 31.99; H, 2.66. NMR data for $Cp_2(CH_3)Ta(\mu\text{-}O)Re(CCH_3{=}CH_2)(CO)_4$ (**3a**): ^{1}H NMR (400 MHz, THF-d_8) δ 6.19 (s, 10H, C_5H_5), 5.99 (dq, 1H, $^2J_{HH}$= 4.6 Hz, $^4J_{HH}$= 1.0 Hz, CCH_2), 4.98 (dq, 1H, $^2J_{HH}$ = 4.6 Hz, $^4J_{HH}$= 1.0 Hz, CCH_2), 2.29 (t, 3H, $^4J_{HH}$= 1.0 Hz, CCH_3), 0.91 (s, 3H, $TaCH_3$); ^{13}C {^{1}H} NMR (101 MHz, THF-d_8) δ 195.4 (s, ReCO), 194.8 (s, ReCO), 193.9 (s, ReCO), 166.3 (s, ReC=CH_2), 122.2 (s, CCH_2), 111.7 (s, C_5H_5), 38.7 (s, CCH_3), 15.8 (s, $TaCH_3$); MS (FAB) *m/z* 682 (M$^+$), 654 (M$^+$–CO), 626 (M$^+$–2CO).

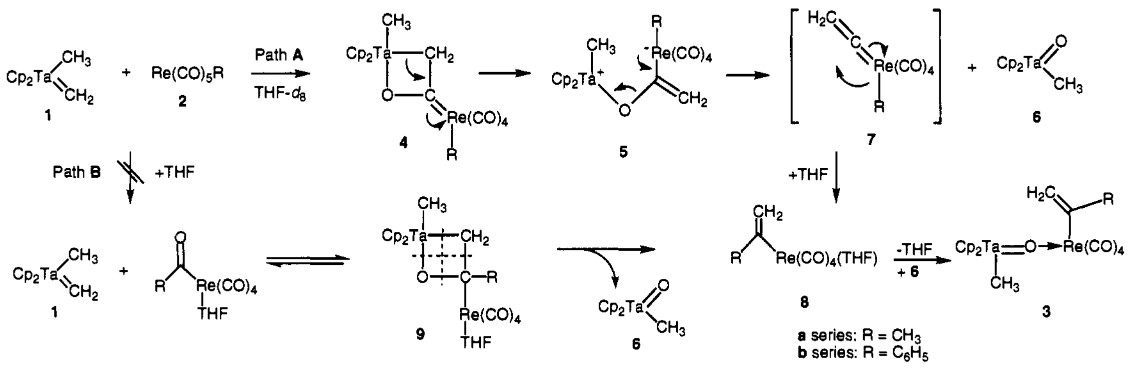
[5] Anal. Calcd for $C_{23}H_{20}O_5TaRe$: C, 37.15; H, 2.71. Found: C, 37.23; H, 2.71. NMR data for $Cp_2(CH_3)Ta(\mu\text{-}O)Re(CPh{=}CH_2)(CO)_4$ (**3b**): ^{1}H NMR (400 MHz, C_6D_6) δ 7.46 (d, 2H, $^3J_{HH}$ = 7.0 Hz, *o*-C_6H_5), 7.30 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *p*-C_6H_5), 7.06 (t, 2H, $^3J_{HH}$ = 7.3 Hz, *m*-C_6H_5), 6.53 (d, 1H, $^2J_{HH}$ = 4.6 Hz, CCH_2), 5.74 (d, 1H, $^2J_{HH}$ = 4.6 Hz, CCH_2), 5.28 (s, 10H, C_5H_5), 0.65 (s, 3H, $TaCH_3$); ^{13}C{^{1}H} NMR (101 MHz, THF-d_8) δ 194.0 (s, ReCO), 193.8 (s, ReCO), 193.1 (s, ReCO), 173.2 (s, $ReCCH_2$), 159.7 (s,CCH_2), 128.3 (s, *i*-C_6H_5), 126.5 (s, *o*-C_6H_5), 125.8 (s, *m*-C_6H_5), 124.2 (s, *p*-C_6H_5), 110.2 (s, C_5H_5), 15.9 (s, $TaCH_3$); MS (FAB) *m/z* 744 (M$^+$), 716 (M$^+$–CO), 688 (M$^+$–2CO), 632 (M$^+$–4CO).

[6] Pilato, R. S.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 1986 and references cited there.

[7] For example, see: Hieber, W.; Braun, W.; Beck, P. *Chem. Ber.* **1960**, *93*, 903.

0002-7863/93/1515-9802$04.00/0

Scheme II



molecule is displaced by the tantalum oxo linkage in **8** to form the stable bridging oxo complex **3**.

The second possible reaction pathway (path B in Scheme II) involves initial migration of the alkyl or aryl group to a CO ligand. Subsequently, the tantalum alkylidene complex attacks the acyl species much as the (η^5-C_5Me_5) analog of **1** has been shown to attack aldehydes.[8]

Preliminary isotope tracer and low-temperature NMR monitoring experiments have allowed us to distinguish between these mechanistic alternatives. In one experiment, $CH_3Re(CO)_5$ (**2a**) was replaced with its perdeuterated analog, $CD_3Re(CO)_5$ (**2a-*d*$_3$**). The complex obtained was $Cp_2(CH_3)Ta(\mu$-$O)Re(CCD_3{=}CH_2)(CO)_4$ (>98% trideuterated), demonstrating that the vinyl methyl group is transferred essentially exclusively from the $Re(CH_3)$ rather than from the $Cp_2Ta(CH_2)(CH_3)$ center. In a second experiment, a solution of **1** and **2a** were mixed in a sealed NMR tube at −50 °C and then warmed slowly. At −35 °C, the ^1H NMR spectrum showed the formation of a new material whose concentration builds up only under these low-temperature conditions. Although we thought at first that this species might be metallacycle **4**, its proton NMR spectrum[9] and the X-ray structure of a perfluoroalkyl analogue[10] are more consistent with its assignment as the zwitterion **5a** (Scheme II). At −5 °C this first observable intermediate began to decompose and two new thermally unstable products began to appear. One is the previously characterized $Cp_2(CH_3)Ta{=}O$ (**6**).[3] NMR data on the second of these products is consistent with its assignment as the 2-propenylrhenium THF-*d*$_8$ complex $(CO)_4Re(CMe{=}CH_2)$(THF-*d*$_8$) (**8a**).[11] Upon further warming of the solution, resonances for **5a**, **6**, and **8a** disappear as resonances for the isolable product **3a** began to appear.[12] At room temperature, the only product remaining was **3a** in >90% yield. These observations are clearly more consistent with path A than with path B in Scheme II.[13]

Migratory insertion reactions of vinyl or alkyl vinylidene species have been recently documented,[14-17] but we believe that the formation of **3b** is the first example of the much stronger metal aryl bond[18,19] undergoing migratory insertion with a vinylidene ligand to form an arylvinyl complex. Also unusual are the rates of the migratory insertion reactions, which occur at temperatures below ambient.[20] To our knowledge, the conversion of **2** to **3** is the first observation of the sequence illustrated in Scheme I, involving oxametallacycle and zwitterion formation from an alkylidene and metal-bound CO, followed by breakdown of the zwitterion intermediate to give a product in which the carbon monoxide oxygen atom has been replaced with a CH_2 group. Further investigations are continuing into the generality and mechanisms of these processes.[21]

Acknowledgment. We are grateful to a referee for an insightful comment on the NMR spectrum and structure of the low-temperature NMR-detectable intermediate in this reaction. We acknowledge the National Science Foundation (Grant No. CHE-9113261) for generous financial support of this work and Dr. F. J. Hollander, director of the U. C. Berkeley X-ray diffraction facility (CHEXRAY), for determination of the X-ray structure.

Supplementary Material Available: Tables containing complete crystal and data collection parameters, positional parameters and estimated standard deviations, and intramolecular distances and angles for **3b** (5 pages). This material is provided with the archival edition of the journal, which is available in many libraries. Alternatively, ordering information is given on any current masthead page.

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[8] Whinnery, L. L.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 7575.

[9] ^1H NMR data for $Cp_2(CH_3)Ta(\mu$-$OC(CH_2))Re(CH_3)(CO)_4$ (**10**) (THF-*d*$_8$, −20 °C): δ 6.52 (10H, s, Cp), 4.32 (1H, s, CH-*H*), 3.82 (1H, s, CH-*H*), 1.16 (3H, s, Ta-C*H*$_3$), −0.49 (3H, s, Re-C*H*$_3$).

[10] The reaction of $Cp_2(CH_3)Ta{=}CH_2$ with $(CO)_5Re(n$-$C_3F_7)$ takes a course similar to that described for **1** and **2**, except that it can be stopped at an earlier stage and the zwitterionic intermediate analogous to **5** isolated and characterized by X-ray diffraction (structure determination performed by Dr. F. J. Hollander). The details of this reaction and X-ray study will be provided in a full paper.

[11] ^1H NMR data for $Re(CCH_3{=}CH_2)(CO)_4$(THF-*d*$_8$) (**13**) (THF-*d*$_8$, 10 °C): δ 6.41 (1H, dq, $^2J = 4$ Hz, $^4J = 1$ Hz, CH-*H*), 5.07 (1H, dq, $^2J =$ 4Hz, $^4J = 1$ Hz, CH-*H*), 2.33 (3H, t, $J = 1$ Hz, C-C*H*$_3$).

[12] The formation of a bridging oxo complex by displacement of a solvent molecule from a late metal species by the oxo ligand of an early metal center has been documented before; see ref 6.

[13] At the suggestion of a referee, we have carried out the low-temperature, NMR-monitored reaction of **1** with **2a** in the presence of excess PMe_3. Under these conditions, zwitterion **5** is again formed at a rate comparable to that observed in the absence of phosphine. Subsequently, however, $CH_3C(CH_2)$-$Re(CO)_4(PMe_3)$ and additional free $Cp_2(CH_3)Ta{=}O$ (**6**) are produced in place of THF complex **8a** and bridging oxo complex **3a**.

[14] Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 68.

[15] Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990,** *382*, 255.

[16] Fryzuk, M. D.; Huang, L.; McManus, N. T.; Paglia, P.; Rettig, S. J.; White, G. S. *Organometallics* **1992**, *11*, 2979.

[17] Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008.

[18] Group VII metal–phenyl bonds have been reported to be about 5 kcal/mol stronger than group VII metal–methyl bonds; see: Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166.

[19] 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.

[20] In a related (alkyl)(aryl)rhenium complex, methyl migration has been reported to occur approximately 30 times faster than the corresponding phenyl group migration; see: Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2723.

[21] In these and related reactions, replacement of a single carbonyl ligand in **2** with a σ-donor (such as PPh_3) shuts down any reaction at room temperature between the late metal and the tantalum methylene complex. Attempts to carry out a number of these reactions at elevated temperature results in decomposition of the methylene complex to a mixture of products. These products are currently under study.