Ethylene Rearrangements to M−C, M=C, and M≡C Functionalities over a Tungsten−Oxo Surface Illustrated by the W(IV) Calix[4]arene Fragment

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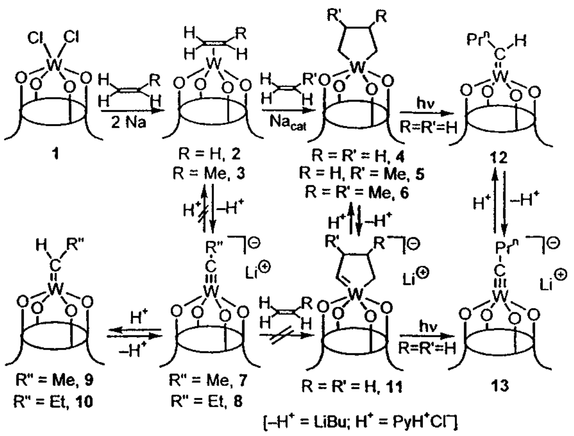
Generation of M−C, M=C, and M≡C functionalities directly from hydrocarbons has been recognized for a long time as a superior feature of heterogeneous catalysts over homogeneous catalysts.[1] Our molecular approach to metal−oxo surfaces[2] uses the preorganized O_4 set of donor atoms derived from calix[4]arene tetraanion.[3] Herein, we report how the d^2 [{*p*-Bu^t-calix[4]-(O_4)}W] fragment assists a variety of ethylene rearrangements, which are very close to those often supposed to occur on metal oxides or other active surfaces.[1] Such rearrangements (Scheme 1) are driven by light, acids, bases, or occur under reducing conditions.

Reductions of **1**, in the absence of any trapping agent, led to a variety of W−W bonded dimers.[3b] However, in the presence of ethylene or propylene, [{*p*-Bu^t-calix[4]-(O)$_4$}W] is intercepted, forming **2**[4] and **3**, which are rare examples of high-valent alkene complexes.[5] Their deprotonation with LiBu at −80 °C in toluene led, via plausible anionic vinyl intermediates, to the corresponding alkylidynes **7**[6] and **8**, which undergo protonation (PyHCl) to the corresponding alkylidenes **9**[7] and **10**. The outcome of this deprotonation−protonation sequence is the isomerization of an η^2-olefin to an alkylidene. This rearrangement, which has been proposed[8] to occur in heterogeneous systems, has seldom been observed in solution.[9]

Scheme 1



Although the reversible coupling of two alkenes at a d^2 metal center is a common process,[10] complexes **2** and **3** do not react wih ethylene and propylene unless a catalytic amount (10%) of Na metal is added. The coupling of two alkenes seems to proceed by an electron-transfer catalysis[11] occurring via the intermediacy of a W(V)−alkene complex.[12] Once formed, the metallacycles **4**−**6**[13] showed an unprecedented irreversibility to the metal−alkene precursor. This irreversibility is supported by the absence

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(4) Procedure for **2**: Compound **1** (15.28 g, 14.0 mmol) and Na (0.609 g, 26.5 mmol) were suspended in THF (150 mL) at −25 °C, the flask was saturated with ethylene (vac/C_2H_4 cycles), and the mixture was stirred at −25 °C for 2 days and then allowed to stand at RT for 1 day, giving a suspension of a white solid in a dark brown solution. The solid was filtered off, volatiles were removed in vacuo, toluene (80 mL) was added to the residue, and volatiles were evaporated again. The residue was dissolved in toluene (350 mL), and the solution was allowed to stand at RT for 2 days. A bit of solid was filtered off, and toluene was evaporated to dryness to give brown **2**, which was washed with pentane (60 mL) and dried in vacuo (8.48 g, 71%). Anal. Calcd for $C_{46}H_{56}O_4W$: C, 64.49; H, 6.59. Found: C, 64.19; H, 6.93. ^1H NMR ($CDCl_3$, 400 MHz, 298 K, ppm): δ 7.13 (s, 8H, ArH), 4.41 (d, 4H, J = 12.4 Hz, *endo*-CH_2), 3.39 (s, 4H, C_2H_4), 3.26 (d, 4H, J = 12.4 Hz, *exo*-CH_2), 1.17 (s, 36H, Bu^t). ^{13}C NMR ($CDCl_3$, 400 MHz, 298 K, ppm): δ 70.0 (C_2H_4, J_{CW} = 31 Hz).

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(6) ^1H NMR for **7** (Py-d_5, 400 MHz, 298 K, ppm): δ 7.16 (s, 8H, ArH), 5.23 (d, 4H, J = 11.7 Hz, *endo*-CH_2), 3.91 (s, 3H, WCCH_3), 3.25 (d, 4H, J = 11.7 Hz, *exo*-CH_2), 1.16 (s, 36H, Bu^t). ^{13}C NMR (Py-d_5, 400 MHz, 298 K, ppm): δ 269.3 (WCCH_3).

(7) ^1H NMR for **9** (C_6D_6, 400 MHz, 298 K, ppm): δ 9.93 (q, 1H, J = 7.4 Hz, WC*H*CH_3), 7.06 (s, 8H, ArH), 5.34 (d, 3H, J = 7.4 Hz, WCHCH_3), 4.93 (d, 4H, J = 12.2 Hz, *endo*-CH_2), 3.23 (d, 4H, J = 12.2 Hz, *exo*-CH_2), 1.09 (s, 36H, Bu^t).

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(12) Cyclic voltammetry of both **2** and **4** shows a reversible 1 e^- reduction wave at about −1 V (−1.08 and −0.91 V, respectively).

(13) Procedure for **4**: Compound **1** (4.42 g, 4.0 mmol) and Na (0.194 g, 8.4 mmol) were suspended in THF (150 mL) at −25 °C, the flask was saturated with ethylene (vac/C_2H_4 cycles), and the mixture was stirred at −25 °C for 1 day, at 0 °C for 12 h, and finally at RT for 1 day. A yellow solid was removed, the resulting red filtrate was taken to dryness, and pentane (50 mL) was added to the residue. Orange **4** was then collected and dried in *vacuo* (2.76 g, 77%). Anal. Calcd for $C_{48}H_{60}O_4W$: C, 65.16; H, 6.83. Found: C, 64.99; H, 7.05. ^1H NMR ($CDCl_3$, 400 MHz, 298 K, ppm): δ 7.18 (s, 8H, ArH), 4.31 (d, 4H, J = 13.2 Hz, *endo*-CH_2), 3.80 (m, 4H, C_4H_8), 3.60 (m, 4H, C_4H_8), 3.38 (d, 4H, J = 13.2 Hz, *exo*-CH_2), 1.28 (s, 36H, Bu^t). ^{13}C NMR ($CDCl_3$, 400 MHz, 298 K, ppm): δ 88.0 (W{*C*$H_2CH_2CH_2$*C*H_2}; J_{CW} = 72 Hz), 36.47 (W{CH_2*C*H_2*C*H_2CH_2}).

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of any alkene redistribution on heating **4** and **6** together in solution and by the regioselective obtention of **5** from the reaction of **2** with propylene. The metallacycle **4** undergoes, under mild conditions, some remarkable transformations, such as the deprotonation (LiBu) to the metallacyclopentene **11**,[14] which can be reversibly protonated (PyHCl) back to the starting material. The reversible protonation−deprotonation/alkylidene−alkylidyne relationship [**7**↔**9**, **8**↔**10**, **12**↔**13**] seems to be restricted to the use of calix[4]arene as ancillary ligand.[3d,15] Both acid−base interrelated metallacycles **4** and **11**, which are thermally stable, rearrange when irradiated (Xe lamp) to the known alkylidene[3d] **12** and alkylidyne **13**, respectively. Although the photochemical generation of alkylidenes from dialkyls is well established,[16] it has never been observed on a metallacycle, where such a reaction leads to an isomerization; even more interesting is the rearrangement of **11** to **13**, which represents the first example of the photochemical generation of an alkylidyne.

All of the compounds in Scheme 1 have been fully characterized (**9**, and **10** by NMR only). The X-ray structure has been established for **2**, analyzed as the acetonitrile adduct **14**, and **4**.[17] The structural prototypes of the W−alkylidene and W−alkylidyne bonded to calix[4]arene have been recently reported.[3d] The picture of **14** (see Figure 1) shows a symmetrically bonded η^2-ethylene in the metallacyclopropane form [C45−C46, 1.401(4) Å] having trans to it an acetonitrile hosted[3i] in the cavity [W−N, 2.291(3) Å], while the calix[4]arene has a regular cone conformation with the metal 0.277(1) Å out of the O_4 plane. The hexacoordination of the metal in **4** (see Figure 2), with two ligands (see the W−C bonds) cis rather than trans as in **2**, and the asymmetric bonding mode of the metallacyclopentane led to a significant distortion of the W-calix[4]arene fragment, the equatorial plane of the octahedron being defined by O1, O3, C45, and C48. The complex is very fluctional, exhibiting an apparent C_{4v} symmetric NMR spectrum, even at low temperatures (200 K). A lower fluxionality is observed for the deprotonated metallacylopentene **11**, which has a ^{1}H NMR spectrum of C_s symmetry below 253 K (above 320 K, the calix moiety has an apparent C_{4v} symmetry).

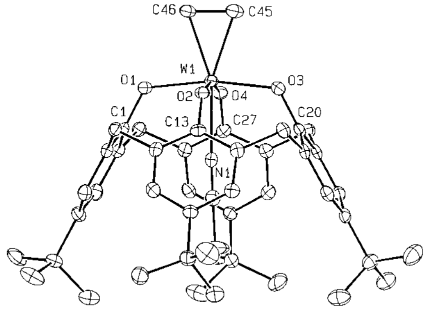

Figure 1. ORTEP drawing of complex 14 (30% probability ellipsoids). Selected bond distances (Å): W1−O1, 2.036(2); W1−O2, 1.867(2); W1−O3, 2.024(2); W1−O4, 1.873(2); W1−N1, 2.291(3), W1−C45, 2.141(4); W1−C46, 2.150(4); C45−C46, 1.401(4). Bond angles (deg): C45−W1−C46, 38.1(1); W1−O1−C1, 123.7(2); W1−O2−C13, 137.6(2); W1−O3−C20, 123.6(2); W1−O4−C27, 137.1(2).

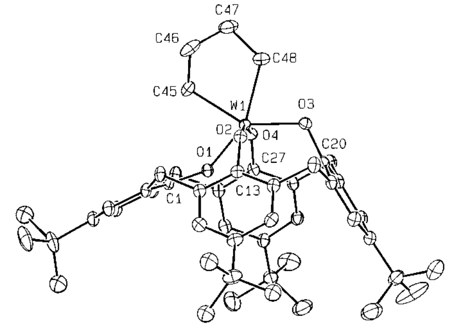

Figure 2. ORTEP drawing of complex 4 (50% probability ellipsoids). Selected bond distances (Å): W1−O1, 1.924(3); W1−O2, 1.858(2); W1−O3, 1.987(3); W1−O4, 1.866(3); W1−C45, 2.174(6); W1−C48, 2.192(6); C45−C46, 1.494(11); C46−C47, 1.510(11); C47−C48, 1.496(9). Bond angles (deg): C45−W1−C48, 72.9(2); W1−O1−C1, 149.0(3); W1−O2−C13, 136.9(3); W1−O3−C20, 114.1(2); W1−O4−C27, 134.8(2). Disorder involving the *tert*-butyl groups has been omitted for clarity.

Scheme 1 gives the overall picture of the fundamental transformations undergone by ethylene and propylene on a W(IV)−oxo calix[4]arene surface. Although some of these transformations are known for different metal fragments, the occurrence both on a single fragment and on a metal−oxo surface is unprecedented.

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Supporting Information Available: Tables giving crystal data and details of the structure determination, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **14** and **4** (12 pages). See any current masthead page for ordering and Internet access instructions.

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(14) NMR for **11**. ^{1}H NMR (Py-d_5, 400 MHz, 243 K, ppm): δ 13.4 (t, 1H, $J = 3.5$ Hz, C_4H_7), 7.48 (s, 2H, ArH), 7.46 (s, 2H, ArH), 6.98 (m, 6H, ArH, C_4H_7), 5.48 (d, 2H, $J = 11.2$ Hz *endo*-CH_2), 4.91 (d, 2H, $J = 12.8$ Hz *endo*-CH_2), 3.45 (m, 6H, *exo*-CH_2, C_4H_7), 2.56 (m, 2H, C_4H_7), 1.42 (s, 9H, Bu^t), 1.27 (s, 9H, Bu^t), 0.77 (s, 18H, Bu^t). ^{1}H NMR (Py-d_5, 400 MHz, 298 K, ppm): δ 13.27 (t, 1H, $J = 3.5$ Hz, C_4H_7), 7.28 (br, 8H, ArH), 7.02 (m, 2H, C_4H_7), 5.16 (brd, 4H, *endo*-CH_2), 3.54 (m, 2H, C_4H_7), 3.47 (d, 4H, $J = 12.7$ Hz, *exo*-CH_2), 2.60 (m, 2H, C_4H_7), 1.37 (brd, 36H, Bu^t). ^{1}H NMR (Py-d_5, 400 MHz, 326 K, ppm): δ 13.19 (t, 1H, $J = 3.5$ Hz, C_4H_7), 7.28 (s, 8H, ArH), 7.02 (m, 2H, C_4H_7), 5.17 (d, 4H, $J = 12.2$ Hz *endo*-CH_2), 3.53 (m, 2H, C_4H_7), 3.45 (d, 4H, $J = 12.2$ Hz, *exo*-CH_2), 2.60 (m, 2H, C_4H_7), 1.19 (s, 36H, Bu^t). ^{13}C NMR (Py-d_5, 400 MHz, 298 K, ppm): δ 279 ($W\{CHCH_2CH_2CH_2\}$).

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(17) Crystal data for **14**: $C_{48}H_{59}NO_4W{\cdot}2C_6H_6$, $M_w = 1054.1$, monoclinic, space group $P2_1/c$, $a = 17.057(4)$ Å, $b = 15.791(3)$ Å, $c = 19.192(4)$ Å, $\beta = 103.86(2)°$, $V = 5018.8(19)$ Å^3, $Z = 4$, $D_{calcd} = 1.395$ g/cm^3, $F(000) = 2176$, μ(Mo Kα) = 0.71068 Å, μ(Cu Kα) = 23.96 cm^{-1}: crystal dimensions 0.20 × 0.25 × 0.44 mm. For 7581 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 143$ K on a Rigaku AFC6S diffractometer ($3° < 2\theta < 55°$) and corrected for absorption the final R is 0.025 (wR2 = 0.067 for the 9191 reflections having $I > 0$ used in the refinement). Crystal data for **4**: $C_{48}H_{60}O_4W$, $M_w = 884.9$, triclinic, space group, $P\bar{1}$, $a = 12.9481(8)$ Å, $b = 13.1863(8)$ Å, $c = 13.7972(9)$ Å, $\alpha = 97.822(6)$, $\beta = 103.845(8)°$, $\gamma = 108.501(8)°$, $V = 2110.8(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.392$ g/cm^3, $F(000) = 908$, λ(Mo Kα) = 1.71068 Å, μ(Mo Kα) = 28.34 cm^{-1}: crystal dimensions 0.23 × 0.30 × 0.52 mm. For 5840 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 295$ K on a Siemens SMART CCD ($5° < 2\theta < 46°$) and corrected for absorption, the final R is 0.029 (wR2 = 0.069 for the 5870 reflections having $I > 0$ used in the refinement). For both **14** and **4** absorption correction was made according to: North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351−359.