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Olefin Rearrangements Assisted by a Molecular Metal−Oxo Surface: The Chemistry of Calix[4]arene Tungsten(IV)

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Abstract: This report deals with the olefin rearrangements achieved on a W-calix[4]arene oxo fragment that mimicks a heterogeneous metal−oxo surface both in the results and the chemical pathways. The olefin complexation by the W(IV)-calix[4]arene fragment has been achieved, generating the $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}]$-$\text{d}^2$ from the reduction of $[cis\text{-(Cl)}_2\text{W}\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}]$, **1**, in the presence of the appropriate olefin. With this method, $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}(\eta^2\text{-C}_2\text{H}_4)]$, **2**, $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}(\eta^2\text{-MeC}_2\text{H}_3)]$, **3**, and $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}(\text{C}_6\text{H}_{10})]$, **4**, have been obtained. In the latter complex the very labile cyclohexene can be replaced by another olefin, such as *trans*-stilbene in $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}(\eta^2\text{-Ph}_2\text{C}_2\text{H}_2)]$, **5**. The ethylene complex, **2**, undergoes deprotonation with LiBu, leading to the corresponding anionic alkylidyne $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}{\equiv}\text{CMe}]\text{Li}$, **6**, which can be protonated, not back to the starting olefin complex, but rather to the corresponding alkylidene $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}{=}\text{C(H)Me}]$, **7**. Complexes **6** and **7** are interrelated by a reversible protonation−deprotonation reaction. The overall transformation of **2** into **7** is the isomerization of ethylene to alkylidene. The intermediacy of a metallacyclopropene in the deprotonation of **2** to give **6** has been proved by the isolation of $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W(PhCHCPh)}]\text{Li}$, **8**, from the deprotonation of **5**. Compounds **5** and **8** are interrelated by a reversible protonation−deprotonation reaction, while the reaction of **8** with MeOTf led, rather, to the alkylation of one of the calix[4]arene oxygen atoms in $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_3\text{-(OMe)}\}\text{W(PhCHCPh)}]$, **9**. The ethylene, **2**, and propylene, **3**, complexes undergo an electron-transfer-catalyzed reaction with ethylene and propylene to the corresponding metallacyclopentanes $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}\{\text{CH}_2\text{CH(R}')\text{CH(R)CH}_2\}]$, [R = R′ = H, **11**; R = Me, R′ = H, **12**; R = R′ = Me, **13**]. Complexes **2**, **3**, **11**, and **13** undergo a reversible one-electron reduction by Na to $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}(\eta^2\text{-C}_2\text{H}_3\text{R})]\text{Na}$, [R = H, **14**; R = Me, **15**] and to $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}\{\text{CH}_2\text{CH(R}')\text{CH(R)CH}_2\}]\text{Na}$, [R = R′ = H, **16**; R = R′ = Me, **17**]. Complexes **16** and **17** can be reoxidized by $\text{Cp}_2\text{FeBPh}_4$ back to **11** and **13**, which do not undergo reversible decoupling of the olefins. The metallacyclopentane complex **11** undergoes deprotonation to $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}\{\text{CH(CH}_2)_2\text{CH}_2\}]\text{Li}$, **18**. Both **11** and **18** photochemically rearrange to the corresponding alkylidene $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}{=}\text{C(H)Pr}^n]$, **19**, and alkylidyne $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}\text{W}{\equiv}\text{CPr}^n]\text{Li}$, **20**.

Introduction

A molecular approach to a solid-state surface[1] active in driving the transformation of organic−inorganic substrates should allow for the following: (i) a geometrically and chemically similar environment of the active site; (ii) the successful achievement of the same kinds of transformations for the same substrate; and (iii) the transformation occurring through a close chemical pathway, which, in the case of heterogeneous systems, takes advantage of the polyfunctionality of a surface.

The present report will stress the analogies between a metal−oxo surface[1,2] and the molecular model exemplified by a metalla calix[4]arene fragment,[3] both active in assisting a variety of ethylene and terminal olefin rearrangements through acid−base pathways. Trying to summarize and simplify the rearrangements of ethylene assisted by a metal−oxo surface, we compiled Charts 1 and 2.[1,2]

A number of peculiarities of the O_4 set of donor atoms from a calix[4]arene skeleton should be mentioned at this stage: (i) the electron-rich oxygen donor atoms, being able to function as basic sites,[1,2] force the metalla calix[4]arene to behave as a bifunctional system; and (ii) the pre-organized arrangement of

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(1) (a) Thomas, J. M.; Thomas, W. J. *Principles and Practice of Heterogeneous Catalysis*; VCH: Weinheim, Germany, 1997. (b) Cox, P. A. *Transition Metal Oxides, an Introduction to their Electronic Structure and Properties*; Oxford University Press: New York, 1992. (c) Gates, B. *Catalytic Chemistry*; Wiley: New York, 1992. (d) *Mechanisms of Reactions of Organometallic Compounds with Surfaces*; Cole-Hamilton, D. J., Williams, J. O., Eds.; Plenum: New York, 1989. (e) Kung, H. H. *Transition Metal Oxides: Surface Chemistry and Catalysis*; Elsevier: Amsterdam, The Netherlands, 1989. (f) Kiselev, V. F.; Krylov, O. V. *Adsorption and Catalysis on Transition Metals and Their Oxides*; Springer: Heidelberg, Germany, 1989. (g) Hoffmann, R. *Solid and Surfaces, A Chemist's View of Bonding in Extended Strucures*; VCH: Weinheim, Germany, 1988. (h) Campbell, I. M. *Catalysis at Surfaces*; Chapman & Hall: London, U.K., 1988. (i) *Catalyst Design, Progress and Perspectives*, Hegedus, L., Ed.; Wiley: New York, 1987. (j) Bond, G. C. *Heterogeneous Catalysis, Principles and Applications*, 2nd ed.; Oxford University Press: New York, 1987.

(2) (a) Corker, J.; Lefebvre, F.; Lecuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J.-M. *Science* **1996**, *271*, 966. (b) Niccolai, G. P.; Basset, J.-M. *Appl. Catal., A* **1996**, *146*, 145. (c) Vidal, V.; Theolier, A.; Thivolle-Cazat, J.; Basset, J.-M.; Corker, J. *J. Am. Chem. Soc.* **1996**, *118*, 4595.

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Chart 1. Ethylene Rearrangements over a Metal−Oxo Surface

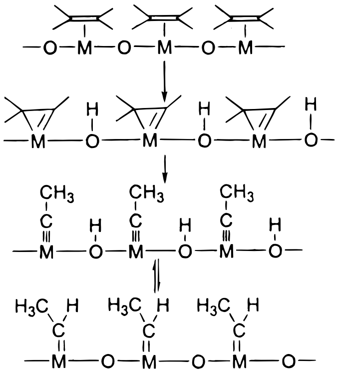
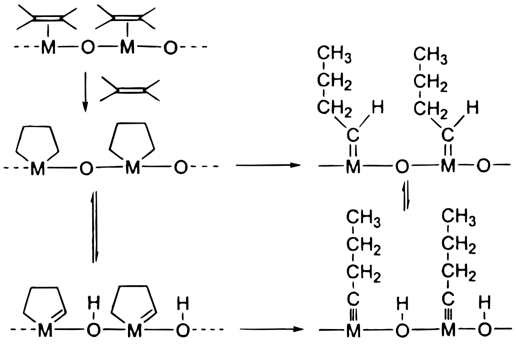


Chart 2. Ethylene Rearrangements over a Metal−Oxo Surface



the oxygen donor atoms makes available at the metal one σ and two π frontier orbitals appropriate for the stabilization of M−C multiple bonds,[4] as in Schrock's trisamidoamine systems.[5]

Here, we report full details on olefin rearrangements occurring on the metal-oxo surface defined by the W{p-Bu^t-calix[4]arene} fragment. The following points will be addressed, both experimentally and through Extended Hückel calculations: (i) the preparation of olefin complexes; (ii) the deprotonation of η^2-olefins to give η^2-vinylidenes (metallacyclopropenes), rearranging in the case of terminal olefins to alkylidynes; (iii) the coupling of terminal olefins at a W(V) metal center, proceeding by electron-transfer catalysis; (iv) the photochemical rearrangements of the metallacyclopentane and the derived metallacyclopentene to the corresponding alkylidene and alkylidyne; and (v) the assistance of the basic O-donor atoms in reactions with electrophiles.

The preceding paper dealing with the preparation of anionic W-calix[4]arene alkylidynes and their chemistry[6] contains the basic information for the present report. Other results have been published elsewhere.[7]

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. All solvents were purified by standard methods and freshly distilled prior to use. NMR spectra were recorded on 200-AC or DPX-400 Bruker instruments; IR spectra were recorded with a Perkin-Elmer FT 1600 spectrophotometer. GC analyses were carried out using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a TCD detector and a Carboxen 1006 capillary column. Photolyses were performed in a "Solarbox" (Cofomegra S.R.L.) equipped with a Xenon lamp (540 Wm^{-2} at 340 nm) using standard laboratory glassware. Magnetic-susceptibility measurements were made with an MPMS5 SQUID susceptometer (Quantum Design Inc.) operating at a magnetic-field strength of 1−5 kG. Corrections were applied for diamagnetism calculated from Pascal constants. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the magnetic susceptibility per metal atom. Magnetic susceptibility data were collected in the temperature range 2−300 K. The synthesis of **1** was performed as reported.[8]

Synthesis of 2. Compound **1**·2(C_7H_8) (15.2 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 room temperature 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 room temperature for 2 days. Some solid was filtered off, and the remaining toluene solution 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 ($CDCl_3$, 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 ($CDCl_3$, 298 K, ppm): δ 70.0 (C_2H_4; J_{CW} = 31 Hz).

Synthesis of 3. Compound **1**·2(C_7H_8) (4.55 g, 4.20 mmol) and Na (0.184 g, 8.00 mmol) were suspended in THF (150 mL) at −25 °C, the flask was saturated with propylene (vac/C_3H_6 cycles), and the mixture was stirred at −25 °C for 2 days and then allowed to stand at room temperature 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 (50 mL) was added to the residue, and the volatiles were evaporated again. The residue was dissolved in toluene (150 mL), and the solution was allowed to stand at room temperature for 3 days. The solid was filtered off, and the toluene solution was evaporated to dryness to give a brown solid, which was washed with pentane (60 mL) and dried in vacuo to give **3**·0.5(C_5H_{12}) (2.52 g, 66%). Anal. Calcd for $C_{49.5}H_{64}O_4W$: C, 65.56; H, 7.11. Found: C, 65.5; H, 7.13. ^1H NMR ($CDCl_3$, 298 K, ppm): δ 7.12 (s, 8H, ArH), 4.40 (d, 4H, J = 12.4 Hz, *endo*-CH_2), 3.92 (m, 1H, C_3H_6), 3.56 (dd, 1H, J = 9.6, 12.2 Hz, C_3H_6), 3.37 (d, 3H, J = 6.6 Hz, C_3H_6), 3.25 (d, 4H, J = 12.4 Hz, *exo*-CH_2), 2.97 (dd, 1H, J = 9.6, 14.0 Hz, C_3H_6), 1.24 (s, 39H, Bu^t, pentane), 0.9 (m, 3H, pentane). ^{13}C NMR ($CDCl_3$, 298 K, ppm): δ 69.8 ($\mathit{C}H_2CHCH_3$), 84.1 ($CH_2\mathit{C}HCH_3$).

Synthesis of 4. Cyclohexene (6.39 g, 77.8 mmol) and Na (1.08 g, 47.0 mmol) were suspended in THF (420 mL) at −25 °C and then degassed (vac/N_2 cycles). **1**·2(C_7H_8) (25.7 g, 23.7 mmol) was added, and the mixture was stirred at −25 °C for 36 h, then at 0 °C for the same time, and finally allowed to stand at room temperature for 4 h, giving a brown suspension. The solid was filtered off, THF was evaporated to dryness, and Et_2O (150 mL) was added to the residue.

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(3) (a) Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 85. (b) Castellano, B.; Zanotti-Gerosa, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1996**, *15*, 4894. (c) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9198. (d) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9709. (e) Caselli, A.; Giannini, L.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1997**, *16*, 5457. (f) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chim. Acta* **1998**, *270* (1−2), 298. (g) Castellano, B.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1998**, *17*, 2328.

(4) (a) Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2825, (b) Giusti, M.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1997**, *16*, 5610. (c) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 437.

(5) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9.

(6) Giannini, L.; Solari, E.; Dovesi, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.*, 2784.

(7) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 823.

(8) (a) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1991**, *30*, 4465. (b) Giannini, L.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.*, in press.

Brown **4**·($C_4H_{10}O$) was then collected and dried in vacuo (12.9 g, 55.3%). Anal. Calcd for $C_{54}H_{72}O_5W$: C, 65.85; H, 7.37. Found: C, 65.84; H, 7.42. ^1H NMR ($CDCl_3$, 298 K, ppm): δ 7.11 (s, 8H, ArH), 4.64 (m, 2H, C_6H_{10}), 4.35 (d, 4H, $J = 12.4$ Hz, *endo*-CH_2), 4.26 (m, 2H, C_6H_{10}), 4.18 (m, 2H, C_6H_{10}), 3.46 (m, 4H, Et_2O), 3.23 (d, 4H, $J = 12.4$ Hz, *exo*-CH_2), 1.61 (m, 2H, C_6H_{10}), 1.44 (m, 2H, C_6H_{10}), 1.21 (s, 36H, Bu^t) overlapping with 1.19 (m, 6H, Et_2O).

Synthesis of 5. Complex **4**·($C_4H_{10}O$) (10.6 g, 10.7 mmol) and *trans*-stilbene (1.93 g, 10.7 mmol) were suspended in toluene (170 mL), and the mixture was heated to and maintained at 60 °C for 30 h to give a dark red-brown suspension. Some solid was filtered off the warm mixture. Volatiles were removed in vacuo and pentane (80 mL) was added to the brown residue. The solution was cooled to − 20 °C to yield 5.62 g (5.33 mmol, 50%) of **5**·0.5(C_7H_8). Anal. Calcd for $C_{61.5}H_{68}O_4W$: C, 70.01; H, 6.50. Found: C, 69.96; H, 6.80. ^1H NMR ($CDCl_3$, 298 K, ppm): δ 7.52 (m, 4H, $C_{14}H_{12}$), 7.35 (m, 4H, $C_{14}H_{12}$), 7.05 (m, 8H, ArH), 6.91 (m, 2H, $C_{14}H_{12}$), 4.79 (s, 2H, PhC*H*C*H*Ph), 3.93 (d, 4H, $J = 12.3$ Hz, *endo*-CH_2), 3.02 (d, 4H, $J = 12.3$ Hz, *exo*-CH_2), 2.35 (s, 1.5H, tol), 1.17 (s, 36H, Bu^t). ^{13}C NMR ($CDCl_3$, 298 K, ppm): δ 82.3 (W(Ph*C*H*C*HPh), $J_{CW} = 27$ Hz).

Synthesis of 6 and Protonation to 7. LiBu (2.35 mL, 1.77 N, 4.16 mmol) was added to a toluene suspension (110 mL) of **2** (3.76 g, 4.39 mmol) at −70 °C and stirred overnight while slowly warming to room temperature. Volatiles were removed by evaporation, and pentane (40 mL) was added to give a brown solution. Upon addition of DME (5 mL), **6**·3($C_4H_{10}O_2$) fell out of solution as a dark green solid and was collected and dried in vacuo (1.6 g, 32%). Anal. Calcd for $C_{58}H_{85}LiO_{10}W$: C, 61.48; H, 7.56. Found: C, 61.52; H, 7.50. ^1H NMR (Py-d_5, 298 K, ppm): δ 7.14 (s, 8H, ArH), 5.20 (d, 4H, $J = 11.6$ Hz, *endo*-CH_2), 3.86 (s, 3H, WCC*H*$_3$), 3.47 (s, 12H, DME), 3.25 (s, 18H, DME, overlapping with d, 4H, *exo*-CH_2), 1.55 (s, 36H, Bu^t). ^{13}C NMR (Py-d_5, 298 K, ppm): δ 269.55 (W*C*CH_3, $J_{CW} = 283.7$ Hz). The reaction of **6** with a stoichiometric amount of PyHCl in THF at room temperature gave clean **7**, as judged by the ^1H NMR of the crude product of reaction (**7** was not isolated because of its high solubility). ^1H NMR (C_6D_6, 298 K, ppm): δ 9.94 (q, 1H, $J = 7.4$ Hz, W═C(*H*)Me), 7.06 (s, 8H, ArH), 5.32 (d, 3H, $J = 7.4$ Hz, W═C(H)C*H*$_3$), 4.93 (d, 4H, $J = 12.6$ Hz, *endo*-CH_2), 3.47 (d, 4H, $J = 12.6$ Hz, *exo*-CH_2), 1.08 (s, 36H, Bu^t).

Synthesis of 8 and Methylation to 9. LiBu (3.2 mL, 1.85 N, 5.92 mmol) was added to a toluene (240 mL) solution of **5**·0.5(C_7H_8) (6.3 g, 5.97 mmol) at −70 °C and stirred overnight while slowly warming to room temperature. Volatiles of the resultant red suspension were evaporated, and the light brown residue was washed with pentane (70 mL) and dried in vacuo to give **8**·(C_7H_8) (2.74 g, 41%). Anal. Calcd for $C_{65}H_{71}LiO_4W$: C, 70.52; H, 6.46. Found: C, 70.66; H, 6.70. ^1H NMR (CD_3CN, 298 K, ppm): δ 7.64 (m, 2H, $C_{14}H_{11}$), 7.49 (m, 2H, $C_{14}H_{11}$), 7.23−7.07 (m, 5H, $C_{14}H_{11}$ overlapping with 5H, tol), 7.03 (s, 8H, ArH), 6.67 (m, 1H, $C_{14}H_{11}$), 6.59 (m, 1H, $C_{14}H_{11}$), 4.36 (d, 4H, $J = 11.2$ Hz, *endo*-CH_2), 2.94 (d, 4H, $J = 11.2$ Hz, *exo*-CH_2), 2.32 (s, 3H, tol), 1.14 (s, 36H, Bu^t). ^{13}C NMR (CD_3CN, 298 K, ppm): δ 253.14 (W*C*PhCHPh, $J_{CW} = 88$ Hz). Crystals suitable for a preliminary X-ray analysis were grown from a THF/heptane solution. MeOTf was added, in a 1:1 molar ratio, to a suspension of **8**·(C_7H_8) in toluene at −60 °C and stirred overnight while slowly warming to room temperature. A light brown solid was filtered off. Volatiles were evaporated to dryness and pentane added. **9** was isolated in low yield as a microcrystalline red compound and characterized by 1D and 2D NMR experiments. ^1H NMR (Tol-d_8, 298 K, ppm): δ 8.02 (m, 2H, $C_{14}H_{11}$), 7.59 (m, 3H, $C_{14}H_{11}$), 7.30−6.70 (m, $C_{14}H_{11}$, ArH, tol), 4.73 (d, 1H, CH_2), 4.44 (d, 1H, CH_2), 4.23 (d, 1H, CH_2), 3.62 (s, 3H, calix[4]-(O)$_3$(OC*H*$_3$)), 3.48 (d, 1H, CH_2), 3.26 (d, 1H, CH_2), 3.20 (d, 1H, CH_2), 3.04 (d, 1H, CH_2), 2.74 (d, 1H, CH_2), 1.43 (s, 18H, Bu^t), 0.80 (s, 9H, Bu^t), 0.74 (s, 9H, Bu^t). ^{13}C NMR (Tol-d_8, 298 K, ppm): δ 272.21 (W*C*PhCHPh), 69.42 (calix[4]-(O)$_3$(O*C*H_3)). Reaction of **8**·(C_7H_8) with a stoichiometric amount of PyHCl in THF at room temperature led to the starting material **5**, as determined by ^1H NMR.

Synthesis of 10. PyHCl (0.34 g, 2.94 mmol) and **2** (2.56 g, 2.99 mmol) were stirred in THF (100 mL) for 2 days at room temperature to give a light brown suspension. A bit of solid was filtered off. Volatiles were evaporated to dryness, and the residue was washed with pentane (50 mL) and dried in vacuo to give **10**·0.5(C_4H_8O)·0.5(C_5H_{12}) (1.99 g, 64%). Anal. Calcd for $C_{55.5}H_{72}ClNO_{4.5}W$: C, 63.82; H, 6.95; N, 1.34. Found: C, 63.50; H, 7.26; N, 1.25. ^1H NMR ($CDCl_3$, 298 K, ppm): δ 16.07 (bs, 1H, Py*H*), 7.76 (br, 1H, Py), 7.17 (m, 4H, ArH), 7.03 (br, 2H, Py), 6.95 (br, 2H, Py), 6.66 (m, 4H, ArH), 4.25 (d, 2H, $J = 14.4$ Hz, *endo*-CH_2), 3.85 (d, 2H, $J = 14.4$ Hz, *endo*-CH_2), 3.73 (m, 2H, THF), 3.45 (br, 4H, C_2H_4), 3.29 (d, 2H, $J = 14.4$ Hz, *exo*-CH_2) overlapping with 3.22 (d, 2H, $J = 14.4$ Hz, *exo*-CH_2), 1.83 (m, 2H, THF), 1.43 (s, 18H, Bu^t), 1.27 (m, 3H, pent), 0.87 (m, 3H, pent), 0.73 (s, 18H, Bu^t). ^1H NMR ($CDCl_3$, 250 K, ppm): δ 15.94 (bs, 1H, Py*H*), 7.80 (m, 1H, Py), 7.15 (m, 4H, ArH) overlapping with 7.13 (m, 2H, Py), 6.90 (m, 2H, Py), 6.66 (m, 4H, ArH), 4.18 (d, 2H, $J = 14.2$ Hz, *endo*-CH_2), 3.80 (d, 2H, $J = 14.6$ Hz, *endo*-CH_2), 3.73 (m, 2H, THF), 3.47 (m, 2H, C_2H_4), 3.29 (d, 2H, $J = 14.6$ Hz, *exo*-CH_2) overlapping with 3.24 (d, 2H, $J = 14.2$ Hz, *exo*-CH_2), 3.12 (m, 2H, C_2H_4), 1.84 (m, 2H, THF), 1.40 (s, 18H, Bu^t), 1.24 (m, 3H, pent), 0.84 (m, 3H, pent), 0.70 (s, 18H, Bu^t). ^{13}C NMR ($CDCl_3$, 250 K, ppm): δ 84.93 (C_2H_4); 71.95 (C_2H_4). Crystals suitable for an X-ray analysis were grown from a DME solution. Reaction of **10**·0.5(C_4H_8O)·0.5(C_5H_{12}) with a stoichiometric amount of BuLi in toluene at −70 °C led to the starting material **2**, as determined by ^1H NMR.

Synthesis of 11. Compound **1**·2(C_7H_8) (4.33 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, then at 0 °C for 12 h, and finally at room temperature for 1 day. A yellow solid was filtered off, the resulting red solution taken to dryness, and pentane (50 mL) was added to the residue. Orange **11** was then collected and dried in vacuo (2.76 g, 78%). Anal. Calcd for $C_{48}H_{60}O_4W$: C, 65.16; H, 6.83. Found: C, 64.99; H, 7.05. ^1H NMR ($CDCl_3$, 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 ($CDCl_3$, 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}). Crystals suitable for an X-ray study were grown from solutions in DME at room temperature. The reaction can also be run starting from isolated **2**, as described in the following for **12**. **11** is thermally very stable ($CDCl_3$, 12h, 80 °C), does not show any shift in the NMR signals upon addition of CH_3CN, and is stable in THF and $CDCl_3$ to PyHCl. An NMR sample ($CDCl_3$) containing a mixture of **11** and **13** (vide infra) was heated 12 h at 80 °C without any change in the ^1H NMR and ^{13}C NMR spectra, which showed only the two starting materials.

Synthesis of 12. Na (0.01 g, 0.4 mmol) was added to a solution of **2** (3.20 g, 3.73 mmol) in THF (120 mL) at −25 °C, the flask was saturated with propylene (vac/C_3H_6 cycles), and the mixture was stirred at −25 °C for 1 day, then at room temperature for 12 h, at −25 °C for 12 h, and finally at room temperature for 1 day. Volatiles were removed in vacuo, benzene (50 mL) was added to the residue and then evaporated to dryness, yielding orange **12**, which was washed with pentane (45 + 15 mL) and dried in vacuo (2.54 g, 76%). Anal. Calcd for $C_{49}H_{62}O_4W$: C, 65.48; H, 6.95. Found: C, 65.11; H, 7.31. ^1H NMR ($CDCl_3$, 298 K, ppm): δ 7.16 (s, 8H, ArH), 4.30 (d, 4H, $J = 13$ Hz, *endo*-CH_2) overlapping with 4.29 (m, 1H, C_5H_{10}), 4.14 (m, 1H, C_5H_{10}), 3.96 (m, 1H, C_5H_{10}), 3.49 (m, 1H, C_5H_{10}), 3.35 (m, 1H, C_5H_{10}) overlapping with 3.35 (d, 4H, $J = 13$ Hz, *exo*-CH_2), 3.22 (m, 1H, C_5H_{10}), 2.74 (m, 1H, C_5H_{10}), 1.27 (s, 36H, Bu^t) overlapping with 1.27 (3H, C_5H_{10}). ^{13}C NMR ($CDCl_3$, 298 K, ppm): δ 95.4 (W{*C*H_2CH(CH_3)CH_2CH_2}; $J_{CW} = 71$ Hz), 84.83 (W{CH_2CH(CH_3)CH_2*C*H_2}; $J_{CW} = 69$ Hz). **12** is thermally very stable ($CDCl_3$, 12h, 80 °C).

Synthesis of 14 and 15. Complex **2** (5.29 g, 6.17 mmol) was stirred with Na (0.141 g, 6.13 mmol) in THF (120 mL) overnight to give a dark green solution. DME (10 mL) was added and volatiles evaporated. The light green residue was washed with pentane (45 mL) and dried in vacuo to give **14**·3($C_4H_{10}O_2$) (2.84 g, 40%). Anal. Calcd for $C_{58}H_{86}NaO_{10}W$: C, 60.57; H, 7.54. Found: C, 60.61; H, 7.57. $\mu_{eff} = 1.04\ \mu_B$ at 298 K. Following the same procedure using **3**·0.5(C_5H_{12}) (2.47 g, 2.72 mmol) as starting material, **15**·2($C_4H_{10}O_2$) was obtained (2.2 g, 75%). Anal. Calcd for $C_{55}H_{78}NaO_8W$: C, 61.51; H, 7.32. Found: C, 61.56; H, 7.63. $\mu_{eff} = 1.25\ \mu_B$ at 298 K.

Synthesis of 16. Complex **11** (2.15 g, 2.43 mmol) was stirred with Na (0.056 g, 2.43 mmol) in THF (120 mL) overnight to give a red solution. DME (10 mL) was added and volatiles evaporated. The yellow residue was washed with pentane (45 mL) and dried in vacuo to give **16**·3($C_4H_{10}O_2$) (2.26 g, 79%). Anal. Calcd for $C_{60}H_{90}NaO_{10}W$: C, 61.17; H, 7.70. Found: C, 61.16; H, 7.79. $\mu_{eff} = 1.4\ \mu_B$ at 298 K. Crystals suitable for X-ray analysis were grown from THF/*n*-hexane.

Synthesis of 13 by Stepwise Reduction, Coupling and Oxidation. Complex **15**·2($C_4H_{10}O_2$) (2.35 g, 2.19 mmol) was suspended in THF (160 mL) at −25 °C. The flask was saturated with propylene (vac/C_3H_6 cycles), and the mixture was stirred overnight at this temperature, then at 0 °C during the day and at room temperature for one night, to give a solution of **17**. The flask was degassed (vac/N_2 cycles), Cp_2FeBPh_4 (1.14 g, 2.26 mmol) was added at −25 °C, and the new mixture was stirred for 1 day at this temperature and then allowed to stand at room temperature for 3 h. Volatiles were evaporated to dryness, and benzene (200 mL) was added to give a mixture of a white and a yellow solid in a red solution. Upon heating, the yellow solid dissolved, and the white solid was filtered off the boiling suspension. Benzene was removed in vacuo, and the orange residue was washed with pentane (55 mL) and dried in vacuo to give **13** (1.04 g, 52%). Anal. Calcd for $C_{50}H_{64}O_4W$: C, 65.79; H, 7.06. Found: C, 65.70; H, 7.29. ^1H NMR ($CDCl_3$, 298 K, ppm): δ 7.23 (s, 8H, ArH), 4.36 (d, 4H, $J = 13$ Hz, *endo*-CH_2), 4.25 (m, 2H, C_6H_{12}), 3.42 (d, 4H, $J = 13$ Hz, *exo*-CH_2), 3.18 (m, 2H, C_6H_{12}), 2.66 (m, 2H, C_6H_{12}), 1.33 (s, 36H, Bu^t) overlapping with 1.30 (d, 6H, C_6H_{12}). ^{13}C NMR ($CDCl_3$, 298 K, ppm): δ 93.8 (W{*C*H$_2$CH(Me)CH(Me)*C*H$_2$}, $J_{CW} = 69.3$ Hz), 48.6 (W{CH$_2$*C*H(Me)-*C*H(Me)CH$_2$}).

Synthesis of 18. BuLi (1.5 mL, 1.67 N, 2.5 mmol) was added to a toluene (80 mL) solution of **11** (2.14 g, 2.4 mmol) at room temperature. The reaction mixture was filtered, DME (10 mL) was added, and then volatiles were removed in vacuo. Pentane (50 mL) was added to the residue, and pale brown **18**·($C_4H_{10}O_2$)·(C_5H_{12}) was collected and dried in vacuo (1.2 g, 47%). The reaction is quantitative, as shown by the clean NMR of the reaction mixture (sample taken after DME addition). Anal. Calcd for $C_{57}H_{81}LiO_6W$: C, 65.01; H, 7.75. Found: C, 65.41; H, 7.55. ^1H NMR (Py-d$_5$, 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). ^1H NMR (Py-d$_5$, 298 K, ppm): δ 13.27 (t, 1H, $J = 3.5$ Hz, C_4H_7), 7.28 (brd, 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). ^1H NMR (Py-d$_5$, 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$_5$, 298 K, ppm): δ 279 (W{*C*HCH$_2$CH$_2$CH$_2$}). Reaction of **18**·($C_4H_{10}O_2$)·(C_5H_{12}) with a stoichiometric amount of PyHCl in THF at room temperature led to the starting material **11**, as determined by ^1H NMR.

Synthesis of 19. Method A: Photochemical Route. A solution of **11** (7.76 g, 8.77 mmol) in toluene (200 mL) was irradiated with a Xe lamp (540 W/m^2 at 340 nm) for 26 h. Volatiles were removed in vacuo, pentane (60 mL) was added to the residue, and pale brown **19** was collected and dried in vacuo (5.62 g, 72%). Anal. Calcd for $C_{48}H_{60}O_4W$: C, 65.16; H, 6.83. Found: C, 64.85; H 6.64. ^1H NMR (C_6D_6, 300 K, ppm): δ 10.0 (t, $J = 7.5$ Hz, 1H, WC(*H*)Pr), 7.07 (s, 8H, ArH), 5.47 (m, 2H, WCHC*H*$_2$CH$_2$CH$_3$), 4.95 (d, $J = 12.2$ Hz, 4H, *endo*-CH_2), 3.24 (d, $J = 12.2$ Hz, 4H, *exo*-CH_2), 1.69 (m, 2H, WCHCH$_2$C*H*$_2$CH$_3$), 1.15 (t, $J = 7.2$ Hz, 3H, WCHCH$_2$CH$_2$C*H*$_3$), 1.08 (s, 36H, Bu^t). ^{13}C NMR (C_6D_6, 300 K, ppm): δ 272 (W*C*(H)Pr, $J_{CW} = 180$ Hz, $J_{CH} = 142$ Hz), 41.6 (WCH*C*H$_2$CH$_2$CH$_3$), 29.5 (WCHCH$_2$*C*H$_2$-CH$_3$), 14.5 (WCHCH$_2$CH$_2$*C*H$_3$).

Synthesis of 19. Method B: (Reversible) Protonation Route. PyHCl (0.22 g, 1.9 mmol) was added to a solution of **20**·3($C_4H_{10}O_2$) (2.2 g, 1.9 mmol) in Et_2O (100 mL) and the mixture stirred for 2 h. A white solid was filtered off, volatiles were removed in vacuo and pentane added to the residue. **19** was then collected as a brown solid and dried in vacuo (0.97 g, 58%). Anal. Calcd for $C_{48}H_{60}O_4W$: C, 65.16; H, 6.83. Found: C, 64.85; H, 6.64. ^1H NMR (C_6D_6, 300 K): identical to the one reported above. The reaction of **19** with a stoichiometric amount of BuLi (in toluene at −30 °C) led to pure **20**, as determined by ^1H NMR spectroscopy.

Synthesis of 20. A solution of **18**·($C_4H_{10}O_2$)·(C_5H_{12}) (4.0 g, 3.8 mmol) in DME (100 mL) was irradiated with a Xe lamp (540 W/m^2 at 340 nm) for 24 h to give a suspension of a yellow solid in a brown solution. Volatiles were removed in vacuo, pentane (60 mL) was added to the residue, and pale brown **20**·3($C_4H_{10}O_2$) was collected, washed with pentane (15 mL), and dried in vacuo (3.1 g, 70%). Anal. Calcd for $C_{60}H_{89}LiO_{10}W$: C, 62.06; H, 7.72. Found: C, 62.54; H, 7.76. ^1H NMR (Py-d$_5$, 300 K, ppm): δ 7.15 (s, 8H, ArH), 5.20 (d, $J = 11.6$ Hz, 4H, *endo*-CH_2), 4.08 (t, $J = 6.6$ Hz, 2H, WCC*H*$_2$CH$_2$CH$_3$), 3.48 (s, 12H, DME), 3.25 (s, 18H, DME) overlapping with 3.23 (d, $J = 11.6$ Hz, 4H, *exo*-CH_2), 1.80 (m, 2H, WCCH$_2$C*H*$_2$CH$_3$), 1.46 (t, $J = 7.2$ Hz, 3H, WCCH$_2$CH$_2$C*H*$_3$), 1.16 (s, 36H, Bu^t). ^{13}C NMR (Py-d$_5$, 300 K, ppm): δ 276.6 (W*C*(Pr), $J_{CW} = 278$ Hz), 48.3 (WC*C*H$_2$CH$_2$-CH$_3$), 27.0 (WCCH$_2$*C*H$_2$CH$_3$), 14.5 (CCH$_2$CH$_2$*C*H$_3$).

X-ray Crystallography for Complexes 3, 10, 11, and 16. Single crystals suitable for X-ray diffraction were grown from common organic solvents (Table 1). Data for **3** and **10** were collected on a Mar345 image plate detector diffractometer, while those for **11** and **16** were collected on a Siemens SMART CCD diffractometer using Mo *K*α radiation. The solutions and refinements were carried out using the programs SHELX76[9] and SHELX93.[10] The details of the X-ray data collection, structure solution, and refinement are given in the Supporting Information.[11]

Results

d^2-W Ion Bound to a Tetraoxo Surface Complexing Olefins. As reported elsewhere, the reduction of [*cis*-(Cl)$_2$W-{*p*-Bu^t-calix[4]-(O)$_4$}], **1**, with alkali metals in THF led to metal−metal bonded species.[12,8b] Suitable substrates can intercept the d^2 [W(calix)] fragment, preventing the formation of such dimers, which represent a "thermodynamic sink" for our system.

As outlined in Scheme 1, the reduction of **1** below −20 °C in THF saturated with ethylene or propylene led to the corresponding η^2-olefin complexes **2** and **3**. The η^2-cyclohexene complex **4** was obtained by a similar procedure. The latter exhibits a high thermal lability: new olefin complexes can be readily obtained by heating solutions of **4** in toluene (50 °C, 12 h) in the presence of a slight excess of the new olefin (provided that the desired product is more thermally stable than **4**). The η^2-trans-stilbene complex **5** was most conveniently prepared by this route, the direct synthesis being limited by competitive reaction of the free olefin with Na.

All η^2-olefin species **2**−**5** exhibit an effective C_{4v} symmetry in solution (NMR). The C_2H_4 ligand in **2** gives rise to a single signal both in ^1H NMR and in the ^{13}C NMR (at 70 ppm). The latter shows a coupling constant to ^{183}W of 31 Hz, in agreement with that reported by Chisholm for dimeric (W═W) η^2-(C_2H_4)W alkoxo species (27−37 Hz)[13] and not far from values reported for high-valent W imido η^2-olefin mononuclear species (21−23 Hz).[14] Figure 1 reports the C−H heterocorrelate (short-range HSQC)[15] spectrum of **2**, including (along the axes) the pattern

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[9] Sheldrick, G. M. SHELX76. Program for crystal structure determination. University of Cambridge, Cambridge, England, 1976.

[10] Sheldrick, G. M. SHELXL93. Program for crystal structure refinement. University of Göttingen, Göttingen, Germany, 1993.

[11] See the paragraph at the end of the paper regarding Supporting Information.

[12] Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 753.

[13] (a) Barry, J. T.; Chacon, S. T.; Chisholm, M. H.; Huffman, J. C.; Streib, W. E. *J. Am. Chem. Soc.* **1995**, *117*, 1974. (b) Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5284.

[14] Clark, G. R.; Nielson, A. J.; Rickard, C. E. F.; Ware, D. C. *J. Chem. Soc., Dalton Trans.* **1990**, 1173.

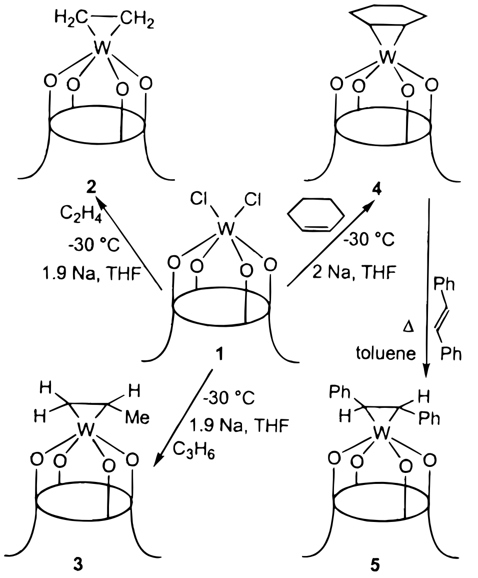
[15] Braun, S.; Kalinowski, H.-O.; Berger, S. *100 and More Basic NMR Experiments, a Practical Course*; VCH: Weinheim, Germany, 1996.

Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes **3**, **10**, **11**, and **16**.

complex	**3**	**10**	**11**	**16**
formula	$C_{47}H_{58}O_4W \bullet 2C_7H_8$	$C_{46}H_{56}ClO_4W \bullet C_5H_6N \bullet C_4H_{10}O_2$	$C_{48}H_{60}O_4W$	$C_{48}H_{60}O_4W \bullet C_{16}H_{34}NaO_5 \bullet C_4H_8O$
a, Å	13.111(6)	19.758(4)	12.9481(8)	15.057(1)
b, Å	14.900(4)	18.543(4)	13.1863(8)	26.792(2)
c, Å	15.294(3)	13.856(3)	13.7972(9)	19.170(1)
α, °	89.50(2)	90	97.822(6)	90
β, °	83.19(5)	99.52(3)	103.845(8)	91.63(1)
γ, °	70.28(5)	90	108.501(8)	90
V, Å^3	2791.1(18)	5006.6(19)	2110.8(3)	7730.2(9)
Z	2	4	2	4
formula weight	1055.1	1062.5	884.8	1286.4
space group	$P\bar{1}$ (n. 2)	Cc (n. 9)	$P\bar{1}$ (n. 2)	$P2_1/n$ (n. 14)
t, °C	22	−83	22	22
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.255	1.410	1.392	1.105
μ, cm^{-1}	21.54	24.57	28.34	15.75
transmission coeff	0.878−1.000	0.606−1.000	0.628−1.000	0.796−1.000
R^a	0.079	0.045 [0.048]^b	0.027	0.079
wR_2	0.209	0.118 [0.126]	0.065	0.200
GOF	1.095	1.043	1.221	1.277
N-observed^c	7078	8148	5840	6945
N-independent^d	9498	10 455	5899	10 933
N-refinement^e	7078	8148	5870	6945
variables	583	576	485	693

[a] Calculated on the observed reflections having $I > 2\sigma(I)$ for **3**, **11** and $I > 3\sigma(I)$ for **10**, **16**. [b] Values in square brackets refer to the "inverted" structure. [c] N-observed is the total number of the independent reflections having having $I > 2\sigma(I)$ for **3**, **11** and $I > 3\sigma(I)$ for **10**, **16**. [d] N-independent is the number of independent reflections. [e] N-refinement is the number of reflections used in the refinement having $I > 0$ for **11**, $I > 2\sigma(I)$ for **3**, $I > 3\sigma(I)$ for **10** and **16** and corrected for absorption.

Scheme 1



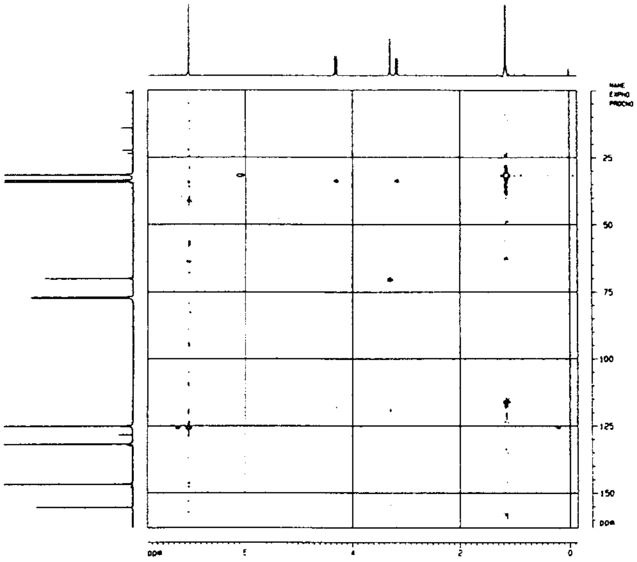


Figure 1. gsHSQC spectrum of **2**.

observed in ^{1}H NMR and ^{13}C NMR. The structure of the *endo*-MeCN adduct of **2**, [**2**•MeCN], was reported in a related communication[7] details are given here for the structure of **3**.

In complex **3**, a propylene molecule is symmetrically η^2-bonded to the metal atom of a [W(p-Bu^t-calix[4]-(O)$_4$] fragment (Figure 2). Complex **3** crystallizes with two molecules of toluene, one of them as a guest in the calixarene cavity. The W−C [mean value, 2.124(9) Å] and C(45)−C(46) [1.399(17)-Å] bond distances (Table 2) are in good agreement with those observed in [**2**•MeCN]. The plane of the η^2-bonded atoms [W,C-(45),C(46)] is perpendicular, while the plane through the propylenic carbon atoms [C(45),C(46),C(47)] is roughly parallel to the mean O$_4$ plane [dihedral angles 90.7(3) and 23.3(12)°, respectively]. The O$_4$ core is tetrahedrally distorted with tungsten displaced by 0.394(2) Å toward the η^2-bonded atoms (Table 3). The four W−O bond lengths (Table 2) are different, the mean value of the W−O(2) and W−O(4) bond distances [1.844-(4) Å] being significantly shorter than the mean value of the W−O(1) and W−O(3) distances [2.030(4) Å]. The O(1)−W−O(3) bond angle [165.8(3)°] is remarkably larger than that of O(2)−W−O(4) [148.3(3)°]. The coordination polyhedron of the metal, as well as the conformation of the macrocycle, are very close to those observed in five-coordinated complexes containing W═C bonds. In particular, the calixarene unit assumes an elliptical cone section (Table 3).

Acid−Base Behavior of Metallacyclopropane W(Calix) Complexes. The electron-deficient nature of calixarene-supported W(VI) makes α-carbon atoms susceptible to proton abstraction, the resulting carbanion being stabilized by donation to the metal and charge delocalization onto the oxygen atoms.[16]

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(16) (a) *Early Transition Metal Clusters with π-Donor Ligands*, Chisholm, M., Ed.; VCH: New York, 1995. (b) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*, Wiley: New York, 1988.

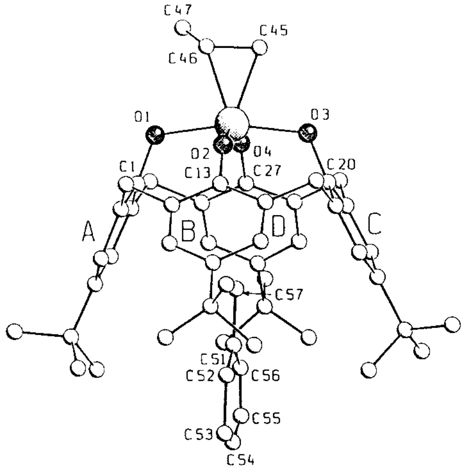


Figure 2. SCHAKAL view of complex **3**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **3** and **10**

	3	**10**
W(1)−Cl(1)		2.413(2)
W(1)−O(1)	2.032(6)	2.036(4)
W(1)−O(2)	1.852(5)	1.907(4)
W(1)−O(3)	2.028(6)	2.056(4)
W(1)−O(4)	1.835(5)	1.901(4)
W(1)−C(45)	2.127(12)	2.231(9)
W(1)−C(46)	2.122(12)	2.190(6)
O(1)−C(1)	1.353(12)	1.345(8)
O(2)−C(13)	1.355(11)	1.390(7)
O(3)−C(20)	1.381(10)	1.311(9)
O(4)−C(27)	1.388(8)	1.371(7)
C(45)−C(46)	1.399(17)	1.366(13)
C(46)−C(47)	1.39(3)	
C(45)−W(1)−C(46)	38.5(4)	36.0(3)
O(3)−W(1)−O(4)	88.7(2)	83.3(2)
O(2)−W(1)−O(4)	148.3(3)	164.1(2)
O(2)−W(1)−O(3)	88.1(3)	83.6(2)
O(1)−W(1)−O(4)	87.8(3)	83.4(2)
O(1)−W(1)−O(3)	165.8(3)	73.9(2)
O(1)−W(1)−O(2)	87.6(3)	84.2(2)
W(1)−O(1)−C(1)	119.0(5)	126.4(4)
W(1)−O(2)−C(13)	147.4(6)	126.1(4)
W(1)−O(3)−C(20)	118.9(5)	129.0(4)
W(1)−O(4)−C(27)	146.2(6)	126.7(3)
W(1)−C(45)−C(46)	70.6(6)	70.4(5)
W(1)−C(46)−C(45)	71.0(6)	73.6(4)
W(1)−C(46)−C(47)	118.8(10)	
C(45)−C(46)−C(47)	123.3(13)	

The reaction of complex **5** with BuLi in toluene at low temperature (−80 °C) led to the clean deprotonation of the 1,2-disubstituted η^2 olefin to give an anionic η^2-vinyl species, **8** (Scheme 2). The η^2-vinyl functionality was first identified by its characteristic ^{13}C NMR signal at 253 ppm. This value was very close to the one recently reported by Schrock for an analogous, but neutral, compound supported by a triamidoamine ligand (246 ppm).[17] The value of J_{WC}, 88 Hz, although lower than expected for a W−C multiple bond, was consistent with that found in the mentioned triamidoamine complex (67.9 Hz).[17] The bond connectivity of **8** was confirmed by several X-ray analyses, although none is published.[18]

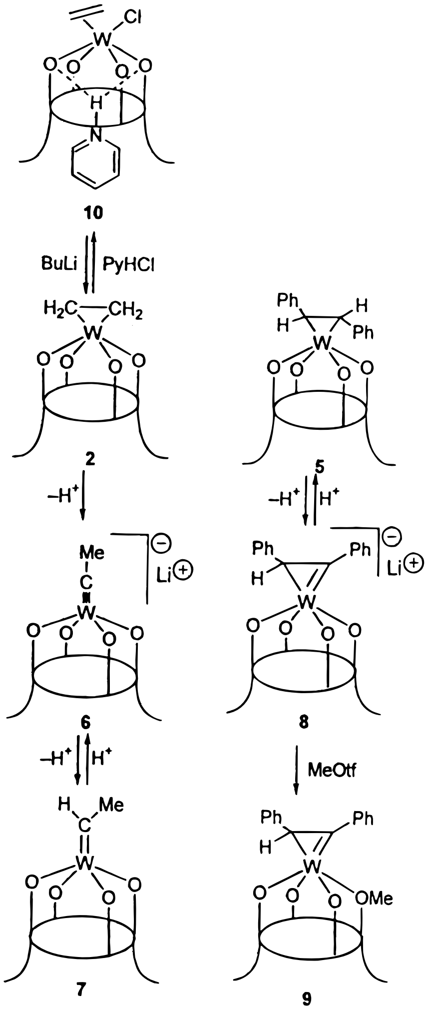
The attempted deprotonation of the terminal olefin in **2** led to the alkylidyne **6**, most likely via an anionic vinyl intermediate, analogous to **8**, undergoing an irreversible 1,2 proton shift.

Table 3. Comparison of Relevant Conformational Parameters within Calixarene for Complexes **3**, **10**, **11**, and **16**

	3	**10**	**11**	**16**
(a) Distances (Å) of Atoms from the O_4 Mean Plane				
O(1)	0.166(7)		−0.261(3)	−0.264(8)
O(2)	−0.110(6)		0.240(3)	0.371(10)
O(3)	0.119(6)		−0.217(3)	−0.339(10)
O(4)	0.110(6)		0.238(3)	0.382(10)
W	0.394(2)		0.575(1)	0.532(1)
(b) Dihedral Angles (deg) between Planar Moieties [a]				
E ∧ A	114.5(2)	179.7(2)	159.7(1)	167.9(3)
E ∧ B	133.3(2)	115.4(2)	128.3(1)	116.2(3)
E ∧ C	116.7(2)	173.3(1)	116.6(1)	121.9(4)
E ∧ D	131.2(2)	116.2(2)	124.1(1)	116.3(4)
A ∧ C	128.8(2)	173.2(2)	96.3(1)	108.8(4)
B ∧ D	95.6(3)	128.4(2)	107.3(1)	127.3(4)
(c) Contact Distances (Å) between *Para* Carbon Atoms of Opposite Aromatic Rings				
C(4)...C(17)	7.500(11)	10.766(12)	9.083(8)	9.55(2)
C(10)...C(24)	9.080(12)	7.530(9)	8.525(7)	7.63(2)

[a] E (reference plane) refers to the least-squares mean plane defined by the C(7), C(14), C(21), and C(28) bridging methylenic carbon atoms.

Scheme 2



Protonation (PyHCl) of **6** gave the corresponding alkylidene **7** (the same kind of reactions can be done also starting from **3**). Complexes **6** and **7** were identified by their characteristic spectroscopic features, i.e., a signal at 283.7 ppm, with a J_{CW} = 283.7 Hz, in the ^{13}C NMR spectrum of **6** and a quartet at 9.93 ppm (J = 7.8 Hz, 1H) in the ^{1}H NMR of **7**. The outcome

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[17] Dobbs, D. A.; Schrock, R. R.; Davis, W. M. *Inorg. Chim. Acta* **1997**, *263*, 171.

of this deprotonation−protonation sequence is the isomerization of an η^2 olefin to an alkylidene. Such a rearrangement, which was proposed[19] to occur in heterogeneous systems, was seldom observed in solution.[20] More common are examples of the reverse rearrangement.[21] The transformation of a terminal olefin into a carbyne ligand by reaction with an osmium complex has been recently reported.[22]

A fundamental point both in molecular and surface chemistry is that of the involvement of donor atoms (from the ancillary ligand or the surface) in acid/base reactions.[23] We have investigated the reaction of H^+ (from PyHCl) and Me^+ (from MeOTf) with the anionic vinylidene **8** (Scheme 2): although protonation gave back the starting material as the only product observed in solution (^{1}H NMR), the reaction with MeOTf led to a neutral vinylidene, **9**, alkylated at the oxygen and not at the carbon center (at least when performing the reaction at −80 °C in toluene). This suggests that the oxygen atoms are the preferred site of attack of electrophiles on **8**, under kinetic control. We can suppose that protonation also occurs first on oxygen atoms and that the resulting protonated analogue of **9**, as a result of the high mobility of H^+, readily rearranges to the observed product. The structure of **9** was assigned on the basis of its spectroscopic (NMR) features: (i) presence in ^{13}C NMR spectrum of a signal at 272.2 ppm, characteristic of a C−W multiple bond, as the one of the η^2-vinyl functionality; (ii) overall C_S symmetry of the calixarene moiety; (iii) signals typical of OMe functionality in ^{1}H and ^{13}C NMR spectra (3.62 and 69.4 ppm, respectively), which do not correlate with any other signal in both H−H and H−C TOCSY[15] experiments.

In the neutral η^2-ethylene complex, **2**, the bound carbon atoms have no carbanionic character, and reaction with PyHCl led to complex **10** (Scheme 2) by addition of Cl^- to the W atom, while the proton is shared between two oxygen donor atoms and the nitrogen (pyridine) inside the cavity. Accordingly, it gives a rather broad signal at 16 ppm in ^{1}H NMR. It is reasonable to suggest that, in the absence of any strong base (i.e., pyridine), the protonation would proceed exclusively to the oxygen donor atoms.

The ethylene ligand is rather fluctuational at room temperature, giving a broad, featureless signal in ^{1}H NMR, while at low temperature (250 K) two resolved multiplets are observed in ^{1}H NMR, corresponding to two signals in ^{13}C NMR. This is consistent with the conformation observed in the X-ray structure, where the two C atoms of ethylene and the chlorine atom are coplanar, assuming a meridional disposition, rather than a facial disposition, most commonly observed when more than two substituents are bound to a metal−calixarene moiety.[3] It is important to notice that such a conformation would be the appropriate one to drive 1,2 insertion and reductive coupling, if we managed to substitute Cl respectively with an R group or another olefin. We might speculate that the monoreduced form of olefin complexes might attain such a distorted calixarene conformation (with K^+ taking the place of PyH^+ in the cavity), thus making possible the olefin coupling.

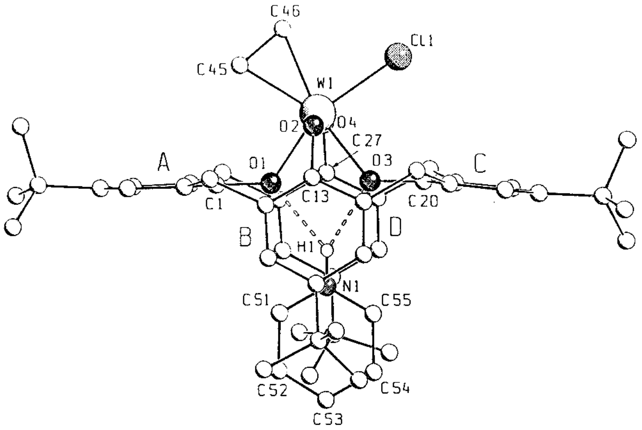

Figure 3. SCHAKAL view of complex **10**.

Complex **10** consists of the $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}W(\eta^2\text{-}C_2H_4)(Cl)]^-$ anion and the pyridinium cation, $[PyH]^+$. The pyridinium cation enters the calixarene cavity pointing the N−H bond toward the center of the cavity (Figure 3). This gives rise to a bifurcated hydrogen bond involving the O(1) and O(3) oxygen atoms from the O_4 set of donor atoms as indicated by the following geometry: N(1)···O(1), 2.828(9) Å; H(1)···O(1), 2.12 Å; N(1)−H(1)···O(1), 138.5°; N(1)···O(3), 2.756(9) Å; H(1)···O(3), 1.99 Å; N(1)−H(1)···O(3), 147.7°. The ethylene molecule shows a slightly asymmetric η^2-bonding mode, the W−C(45) bond distance [2.231(9) Å] being just significantly longer than that of W−C(46) [2.190(6) Å]. These values are remarkably longer than those observed in **3** and **2**·MeCN. The geometry of the WC_2 fragment (Table 2) is in agreement with that generally found for η^2-bonded ethylene. The W−Cl bond distance [2.413(2) Å] is remarkably longer than in **1**[8b] and $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}W(Cl)_2K(thf)_2]$[8b] (mean values 2.320(1) and 2.351(2) Å, respectively). The W−O(1) and W−O(3) bond lengths involving the oxygen atoms interacting with the pyridinium proton are remarkably longer [mean value 2.046(10) Å] than the other two [mean value 1.904(3) Å]. The planarity of the O_4 set of donor atoms is completely removed, the calix[4]arene assuming a flattened conformation with the A and C rings nearly parallel to each other [173.2(2)°] and to the reference plane [dihedral angles 179.7(2) and 173.3(1)°, respectively] (Table 3). W(1), Cl(1), C(45), and C(46) are coplanar (max deviation 0.004(9) Å for C(46)). The latter plane forms a dihedral angle of 0.4(1)° with the plane defined by W(1), O(1), and O(3). Thus, C(45)−C(46), Cl(1), O(1), and O(3) define the equatorial plane of the coordination octahedron (max out-of-plane 0.010(6) Å for C(45), W(1) out-of-plane 0.007(4) Å). The pyridinium cation enters the macrocycle pointing the N−H(1) bond toward the center of the cavity along with the calixarene axis. The W···H(1) separation is 3.28 Å. The guest ring is oriented in such a way to be perpendicular to the A and C rings [dihedral angles 86.6(2) and 87.7(2)°, respectively] and roughly parallel to the B and D rings [dihedral angles 22.3(2) and 29.4(2)°, respectively]. The electronic structure of η^2-olefin and η^2-vinyl (metallacyclopropane/ene) species will be further discussed in the section dedicated to extended Hückel calculations.

The Reductively Induced Olefin Coupling. The reversible coupling of two alkenes at a d^2 metal center is quite common

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[18] Crystal data of **8**: $C_{86}H_{119}LiO_{11}W$, M = 1519.60, monoclinic, space group $P2_1/n$, $a = 19.874(2)$, $b = 15.9150(14)$, $c = 30.005(3)$ Å, $\beta = 101.077(8)°$, $V = 9313.3(15)$ Å^3, Z = 4, $D_{calcd} = 1.084$ g/mL^3, $F(000) = 3200$, λ(Mo Kα) = 0.71073 Å, $\mu = 1.289$ mm^{-1}; crystal dimensions 0.61 × 0.48 × 0.29. Diffraction data were collected on a KUMA CCD at 143 K. For 11 179 observed reflections [$I > 2\sigma(I)$] the conventional R is 0.1616 (wR_2 = 0.4237 for 13 431 independent reflections).

[19] Iwasawa, Y.; Hamamura, H. *J. Chem. Soc., Chem. Commun.* **1983**, 130.

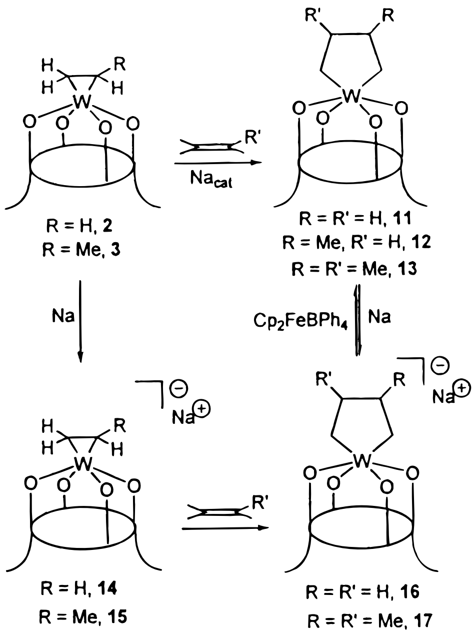
[20] (a) Miller, G. A.; Cooper, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 709. (b) Freundlich, J. S.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6476. (c) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3643.

[21] (a) Freudenberg, J. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 1937. (b) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157.

[22] Spivak, G. J.; Coalter, J. N.; Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999.

[23] Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Shih, K.-Y.; O'Donohgue, M. B.; Davis, W. M.; Reiff, W. M. *J. Am. Chem. Soc.* **1997**, *119*, 11876.

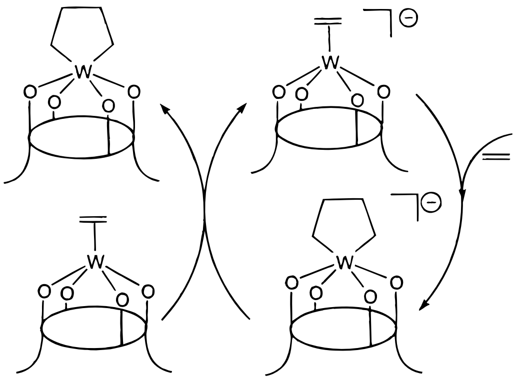
Scheme 3



in the chemistry of groups IV and V elements,[24] but seems to be a much more difficult process for W(IV).[25] Complexes **2** and **3** did not react with an excess of olefin; however, in the presence of catalytic amounts of Na, a regioselective and irreversible reaction leading to metallacyclopentanes **11**−**13** took place, as outlined in Scheme 3. The irreversibility of the coupling was proved by the clean synthesis of complex **12** (thermally stable in $CDCl_3$ at 70 °C for 12 h) in the reaction of **2** with propylene, catalyzed by 10% Na. It was further tested mixing **11** and **13** in $CDCl_3$: no trace of **12** was visible (^{13}C NMR) even after prolonged heating ($CDCl_3$, 70 °C for 12 h).

As the coupling of two alkenes at a W(calix) center requires the intermediacy of a W(V)−alkene complex, the mechanism can be described as an "electron−transfer catalysis"[26] (Scheme 4). This hypothesis is supported by cyclic voltammetry of **2** and **11**, showing a reversible one-electron reduction wave near −1 V (−1.08 and −0.91 V, respectively).[27] Moreover, the coupling of two propylene units was achieved performing stoichiometric reactions following, step by step, the proposed electron-transfer catalysis cycle. W(V) species **14**−**16** were isolated and fully characterized. Their magnetic behavior (SQUID analysis) is consistent with the hypothesis of a metal-centered radical ion, with an almost temperature-independent μ_{eff} of 1.0−1.4 μ_B, resulting from a strong spin−orbit coupling typical of W(V) species.[28]

Scheme 4



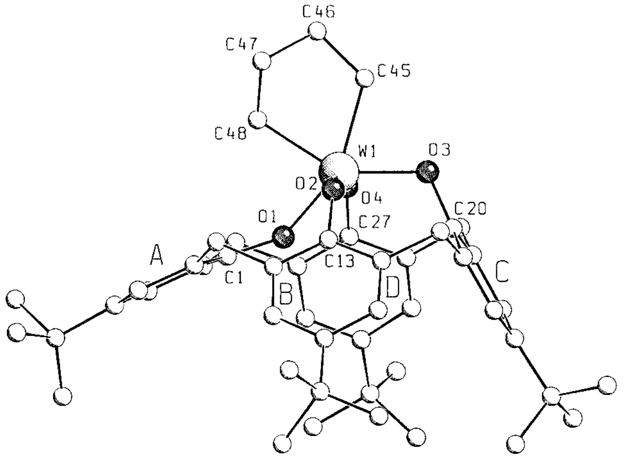


Figure 4. SCHAKAL view of complex **11**. Disorder affecting the butyl groups associated to the A and B rings has been omitted for clarity.

The calix moiety of complexes **11**−**13** exhibits an apparent C_{4v} symmetry in the NMR, even at low temperatures (200 K). The regiochemistry of complex **12** was assigned on the basis of NMR experiments. All the H of the metallacycle fragments appear as separate multiplets. In the ^{13}C NMR spectrum, two signals of C atoms bound to W (easily identified by the W satellites) are present. Each of these carbon atoms is bound to two hydrogen atoms, as can be deduced by a Heteronuclear Correlation spectrum (short-range HSQC,[15] set to show one-bond interactions) showing cross-peaks between each carbon and two hydrogen atoms. As a consequence, the Me group must be carried by a carbon not directly bound to tungsten. The regiochemistry of the metallacycle obtained by the coupling of two propylene units, **13**, assigned by analogous NMR experiments, confirms the selective formation of W−C bonds with the least encumbered olefin end. This is the regiochemistry, easily explained on steric grounds, usually observed for olefin coupling at a d^2 metal center. The apparent C_{4v} symmetry in the NMR spectrum of **13** supports the anti arrangement of the two methyl groups in the metallacycle.

The structures of complex **11** (Figure 4) and of the anion in complex **16** (Figure 5) have been confirmed by X-ray single-crystal structure analyses and are discussed together because of their structural similarities. Hereafter, the values in square brackets will refer to **16**. The W−C bond distances are not significantly different from each other {mean values 2.182(4) [2.182(11)] Å} and fall in the range of values expected for W−C σ bonds.[29] The C−C bond distances within the metallacyclopentane ring are consistent with a single-bond character (Table

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[24] (a) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1771. (b) Hill, J. E.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 3428. (c) Takahashi, T.; Tamura, M.; Saburi, M.; Uchida, Y.; Negishi, E.-I. *J. Chem. Soc., Chem. Commun.* **1989**, 852. (d) Erker, G.; Czisch, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059. (e) Schrock, R. R.; McLain, S.; Sancho, J. *Pure Appl. Chem*. **1980**, *52*, 729. (f) McLain, S.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558.

[25] High-valent W oxo and imido olefin complexes were prepared in the presence of excess olefin. See, e.g., (a) ref 14. (b) Su, F.-M.; Cooper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545. (c) Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261. Reversible ethylene coupling at a d^2-W center has been reported: Wang, S.-Y. S.; VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1998**, *17*, 2628.

[26] Collmann, 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 4, p 259.

[27] Osella, D.; Ravera, M.; Giannini, L.; Floriani, C., unpublished results.

[28] Bordreaux, E. A.; Mulay, N. L. *Theory and Applications of Molecular Paramagnetism*; Wiley: New York, 1976; p 148.

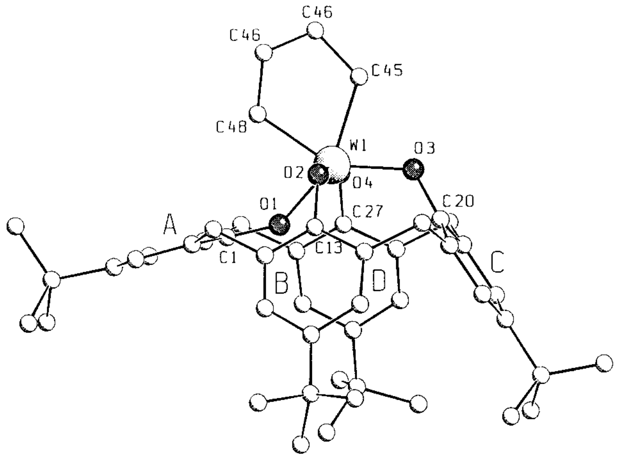

Figure 5. SCHAKAL view of the anion in complex **16**. Disorder affecting the butyl groups associated to the A, B, C, and D rings has been omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (°) for Complexes **11** and **16**

	11	**16**
W(1)−O(1)	1.924(3)	1.924(8)
W(1)−O(2)	1.859(2)	2.024(9)
W(1)−O(3)	1.988(3)	1.974(9)
W(1)−O(4)	1.865(3)	2.000(9)
W(1)−C(45)	2.190(6)	2.182(16)
W(1)−C(48)	2.173(6)	2.182(14)
O(1)−C(1)	1.349(5)	1.309(13)
O(2)−C(13)	1.373(4)	1.362(17)
O(3)−C(20)	1.385(6)	1.348(18)
O(4)−C(27)	1.378(6)	1.368(17)
C(45)−C(46)	1.496(8)	1.53(3)
C(46)−C(47)	1.511(10)	1.40(4)
C(47)−C(48)	1.498(10)	1.53(3)
C(45)−W(1)−C(48)	73.0(2)	74.4(5)
O(3)−W(1)−O(4)	89.6(1)	92.3(4)
O(2)−W(1)−O(4)	158.0(1)	167.7(4)
O(2)−W(1)−O(3)	88.8(1)	91.3(4)
O(1)−W(1)−O(4)	82.0(1)	84.1(4)
O(1)−W(1)−O(3)	130.8(1)	129.4(4)
O(1)−W(1)−O(2)	82.4(1)	84.6(3)
W(1)−O(1)−C(1)	149.0(2)	145.3(7)
W(1)−O(2)−C(13)	136.8(3)	120.1(8)
W(1)−O(3)−C(20)	114.1(2)	121.7(7)
W(1)−O(4)−C(27)	134.8(2)	121.6(8)
W(1)−C(45)−C(46)	113.3(4)	117.8(13)
C(45)−C(46)−C(47)	106.2(5)	109.4(16)
C(46)−C(47)−C(48)	105.1(5)	111.7(17)
W(1)−C(48)−C(47)	119.0(4)	114.1(12)

4). The metal lies on the equatorial plane, being displaced by only 0.017(1) [0.002(1)] Å. The O_4 core shows remarkable tetrahedral distortions, tungsten protruding by 0.575(1) [0.532(1)] Å toward the alkyl ligand (Table 3). The W−O bond distances fall in a rather wide range, and the most significant differences concern O(2) and O(4), the mean value of the W−O(2) and W−O(4) bond lengths being 1.861(2) Å in **11** vs 2.012(6) Å in **16**, as a probable consequence of the decreased oxidation number of the metal. The W−O(1) {1.924(3) [1.924(8)] Å} and W−O(3) {1.988(3) [1.974(9)] Å} equatorial bond distances are intermediate and seem not to be affected by the change of the oxidation state (Table 4). The significant difference between these last distances reflects the asymmetry shown by the macrocycle which assumes a half flattened conformation: the A ring is pushed outward with respect to the cavity, coming out to be roughly parallel to the reference plane (Table 3).

The Deprotonation and Photochemical Opening of Metallacycles. The metallacycle **11** undergoes, under mild conditions, some remarkable transformations such as the deprotonation (LiBu) to the metallacyclopentene **18**, which can be reversibly protonated (PyHCl) back to the starting material (Scheme 3). Probably because of the higher rigidity due to the metal−carbon double bond, **18** is less fluctuational than **11**: the calix moiety exhibits a C_s symmetric spectrum below −20 °C. The presence of a tungsten−carbon double bond is supported by a triplet at 13.27 ppm (1H, $J = 3.9$ Hz) in the ^{1}H NMR and by a signal at 279 ppm in the ^{13}C NMR spectrum; these data compare well with those of the analogous metallacyclopentene supported by a triamidoamine ligand recently reported by Schrock (11.3 and 265 ppm, respectively).[30]

Both acid−base interrelated metallacycles, **11** and **18**, which are thermally stable, rearrange when irradiated (Xe lamp) to the alkylidene **19** and alkylidyne **20**, respectively. Although the photochemical generation of alkylidenes from dialkyls is well-established,[31] it has never been observed on a metallacycle, where such a reaction consists of an isomerization. More interesting still is the rearrangement of **18** to **20**, which represents the first example of the photochemical generation of an alkylidyne. It should be noted that this photochemical path represents the best synthetic approach to both **19** and **20**.

At variance with complex **18**, Schrock's metallacyclopentene is reported as thermally unstable, spontaneously rearranging to the corresponding alkylidyne.[30]

Discussion

Chemical Considerations. This report deals with some very peculiar features of calix[4]arene that make it very different from the continuously referred to Schrock's triamidoamino ligand.[5,30] The major similarity with the latter is the preorganized chemical environment which imposes on the metal a set of frontier orbitals particularly appropriate for driving the system toward the stabilization of metal−carbon multiple bonds. A major difference, however, is the nature of the chemical environment, which allows a completely different synthetic access to metal alkylidenes and alkylidynes. In the present case, they form from olefins rather than from the alkylation reaction of a metal which can be functionalized.

The macrocyclic stability, along with the strength of the C−O bonds, allowed the synthesis of reduced forms of W(IV), as reported in Scheme 1. The reactive d^2 metals generated on an oxo surface can be trapped by unsaturated substrates such as olefins in the form of metallacyclopropanes. Complexes **2**−**5** have been used, as in the present paper, as precursors to W−C multiple bonds or can be employed as a source of the d^2 [W(IV)-calix[4]arene] fragment. However, the latter use requires a good leaving olefin. The kinetic lability of the olefin depends on the substituent at the C═C double bond, the cyclohexene derivative **4** being the most suitable one for this purpose. As a matter of fact, the synthesis of other olefin complexes, inaccessible by

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[29] Woodward, S.; Winter, M. J. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 5, Chapter 5.

[30] Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Dobbs, D. A.; Shih, K.-Y.; Davis, W. M. *Organometallics* **1997**, *16*, 5195.

[31] (a) Van der Schaaf, P. A.; Hafner, A.; Mühlebach, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1845. (b) Chamberlain, L. R.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Dalton Trans.* **1987**, 155. (c) Chamberlain, L. R.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1987**, 163. (d) Chamberlain, L. R.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1984**, *106*, 1847.

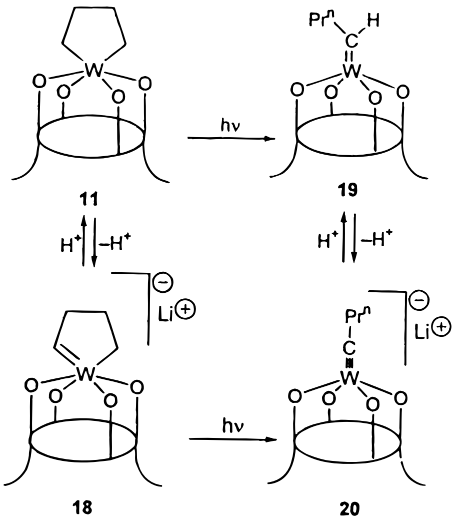
the reductive method, can be carried out replacing cyclohexene in **4**. Attempts to labilize the metal−olefin bond via an additional ligand to the metal was, unexpectedly, unsuccessful. On the contrary, in the case of **2** the addition of MeCN or Bu^{t}NC led, rather, to a stabilization of the metal−olefin interaction.

The reactivity of the olefin bonded in complexes **2**−**5** is revealed by its acid−base behavior. In particular, the protonation of **2** did not lead to any protolysis of the W−C bond according to the very low nucleophilicity of the carbon residue in the metallacyclopropane fragment, as expected for a W(VI) alkyl derivative.[30] Therefore, the addition of the Cl^- to the metal occurred along with the partial protonation of the oxygen donor atoms inside the cavity by the pyridinium cation. This reaction may be an indication of the assistance of the oxygen donor atoms, as in the case of heterogeneous surfaces, in the protonation of organometallic functionalities. The deprotonation of the olefin in **2** and **5** proceeds as expected from the acidic behavior of an alkyl derivative of W(VI). The deprotonated form leads directly to the corresponding anionic alkylidyne, via the intermediate formation of a metallacyclopropene, which has been isolated in the case of *trans*-stilbene, as the anionic η^2-vinyl **8**. A significant difference is observed in the protonations of **6** and **8**. In the former case, the reaction leads to the corresponding alkylidene with the overall result of the ethylene rearranging to an alkylidene via a deprotonation and protonation pathway. In the case of internal olefins such as *trans*-stilbene, the protonation of **8** gives back the starting olefin complex. When a different electrophile, namely MeOTf, is used, **8** gives rise to an alkylated form at the oxygen (see complex **9** in Scheme 2). It should be pointed out that the oxygen donor atoms can play the role of a basic site in close proximity to the metal center, a peculiarity of the metalla−calix[4]arene fragment, which makes the comparison with a metalla−oxo surface particularly appropriate (see Charts 1 and 2).[1,2]

In this context, we should draw attention to the quite impressive similarity between the olefin rearrangements depicted in Scheme 2 and those supposed to occur on a metal−oxo surface (see Chart 1 in the Introduction), not only in terms of results but also for the similar acid−base pathway through which the olefins rearrange.[1,2] When the ancillary ligands are monodentate aryloxo or alkoxo groups or they contain nitrogen donor atoms, the protonation of organic functionalities, namely alkylidenes or alkylidynes, usually leads to the rearrangement or loss of the ancillary ligand.[32]

The metal-assisted olefin chemistry reported here has another significant peculiarity that justifies the comparison of metalla−calix[4]arenes with a metal−oxo surface. This is the electron-transfer-catalyzed dimerization of ethylene and propylene to the corresponding metallacyclopentane. Unlike many organometallic systems,[24,33] the reductive coupling of an olefin (see Scheme 3) is not a reversible reaction and only occurs in the presence of small amounts of a reducing agent, in our case sodium metal. This led, as a synthetic result, to regiochemically controlled isomers of metallacyclopentanes. With the purpose of supporting the idea of the electron-transfer-catalyzed dimerization of the olefin (see Scheme 4),[26] we ran the reversible one-electron reduction of the metal-olefin complexes **2** and **3** and of the metallacyclopentane **11**−**13** to **14**, **15** and **16**, **17**, respectively. The latter species have been isolated and structurally characterized. The irreversible formation of the metallacyclopentanes from C_2 units under electron-transfer conditions led to the easy access of the C_4 alkylidenes and alkylidynes, which have been obtained from the photochemically assisted transformation of **11** and **18** (see Scheme 5). Once again, Schemes 3 and 5 parallel very closely what is supposed to occur on metal−oxo surfaces as displayed in Chart 2.

Scheme 5



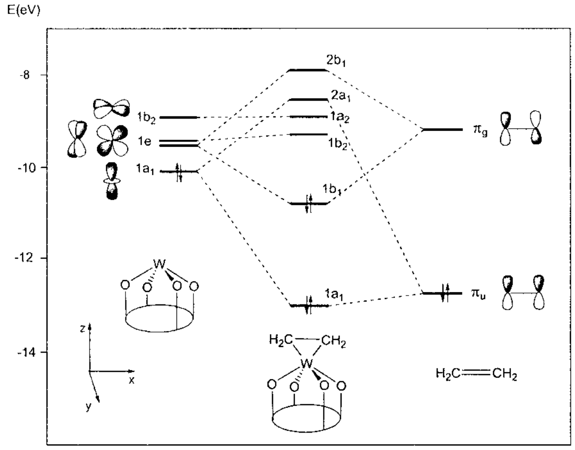


Figure 6. Molecular orbital interaction diagram for $[(calix)W(C_2H_4)]$.

Extended Hückel Analysis of [W(calix[4]arene)] Complexes with Ethylene. Extended Hückel calculations[34] were performed to study the electronic structure and the reactivity pattern of some of the considered complexes. The calix[4]arene ligand has been slightly simplified by replacing it with four phenoxo groups and symmetrizing it to a C_{4v} geometry. This simplified model retains the main features of the whole ligand. In particular, the geometrical constraints on the O_4 set of donors atoms have been maintained by fixing the geometry of the four phenoxo groups to the experimental X-ray values.

The interactions between the [W(calix)] metal fragment and the ethylene moiety is reported in Figure 6. The frontier orbitals of the [W(calix)] fragment in a C_{4v} symmetry have been already discussed[6] and are reported on the left of Figure 6, which shows the bonding interactions expected for this system,[35] i.e., between the $1a_1(d_{z^2})$ and the π_u and between one of the two orbitals of

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[32] Protonation and deprotonation of alkylidynes usually affects the coordination sphere of the metal. See: Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. *Carbyne Complexes*; VCH: Weinheim, Germany, 1988; Chapter 5, pp 189−190.

[33] Ingrosso, G. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Vol. 1, Chapter 10.

[34] (a) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179. (b) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

[35] Hoffmann, R.; Chen, M. M. L.; Thorn, D. L. *Inorg. Chem.* **1977**, *16*, 503.

the 1e set, d_{xz} or π_g. Although extended Hückel calculations do not allow a clear distinction between the metallacyclic or donor−acceptor nature of metal-ethylene complexes,[36,37] the good energy match of the d_π(W) and π^* (C_2H_4) orbitals, the high degree of back-donation (0.76 e), and the high M−C overlap population (0.31 to be compared with 0.11 for a typical donor−acceptor complex such as $[Cl_3Pt(C_2H_4)]^-$)[36] suggest a metallacyclic character for **2**−**5**. This is in agreement with the observed X-ray structure of **3**, which shows short W−C bond lengths (2.14 Å) and a very elongated C−C bond distance (1.40 Å).

It is worth noting that, due to the latter interaction, the d_{xz} is no longer available to the π donation from the calixarene oxygen atoms in the xz plane, thus explaining the strong C_{2v} distortion of the [W(calix)] unit observed in the X-ray structure of **3**, with the two W−O bonds in the metal−ethylene plane ca. 0.2 Å longer than the remaining two W−O bonds in the orthogonal plane. The presence of two orthogonal d_π orbitals equally available for the interaction with the π system of C_2H_4 suggests a small activation barrier for fragment rotation about the z axis. The calculations on the ethylene complex, with the C=C rotated by 45° with respect to the xz symmetry plane, gave an estimate of the energy barrier of only 3 kcal mol^{-1}. This result suggests an essentially free rotation of the organic fragment and is in good agreement with the ^1H NMR of **2**−**5**, indicating an apparent C_{4v} symmetry of the calix[4]arene moiety even at low temperatures.

The easy one-electron reversible reduction of η^2-olefin and metallacyclopentane complexes is easily explained: complex **2** has a low-energy d_{yz} LUMO which can accept an extra electron giving rise to a W(V) radical species. The magnetic analyis of **14** shows an essentially constant magnetic moment in the whole temperature range considered, 2−300 K, with a value of ca. 1.4 μ_B, resulting from spin−orbit coupling, typical of W(V), d^1 species.[28] Analogous considerations apply to the monoanion of metallacycle complex **11**.

We have analyzed the deprotonation of **5** to the metallacyclopropene **8**[38] using $[W(calix)(HCCH_2)]^-$ as a model complex, whose orbital diagram is in Figure 7. On the right we show the main frontier orbitals of the $HCCH_2^-$ moiety, which consist of two filled orbitals of σ and π symmetry (1a′ and 1a″) and a low-lying, empty orbital of π symmetry (2a′). The first and third orbitals resemble the bonding and antibonding π orbitals of ethylene (rehybridized so as to point toward the metal), while the second one is mainly a p_π orbital on the C_α atom. The main bonding interactions are between the $1a_1(d_{z^2})$ and the σ donor 1a′ of $HCCH_2^-$ and between the two d_π metal orbitals and the two vinyl π orbitals 1a″ and 2a′. The former two orbital interactions lead to two M−C bonds and a reduction of the C=C bond order, while the latter leads to an increase of the M−C_α bond order, in agreement with the 1,2-tunstenacyclopropene formulation. It is worth noting that the considered [W(calix)-($HCCH_2$)]$^-$ model complex may be regarded as intermediate in the deprotonation of **2** to **6**, leading to the final alkylidyne product through the hydrogen shift from C_α to C_β. Indeed, in such an η^2 coordination the vinyl complex assumes already an alkylidene-like character, i.e., with an electronic structure intermediate between **2** and the final alkylidyne product **6**. At the same time, the $HCCH_2$ unit assumes a geometry particularly favorable for the hydrogen shift from C_α to C_β, which would require only a movement of H_α in the M−C_α−C_β plane. This suggests a facile C_α to C_β hydrogen shift, in agreement with the experimentally observed direct deprotonation from **2** to **6** without isolation of any intermediate vinyl species.

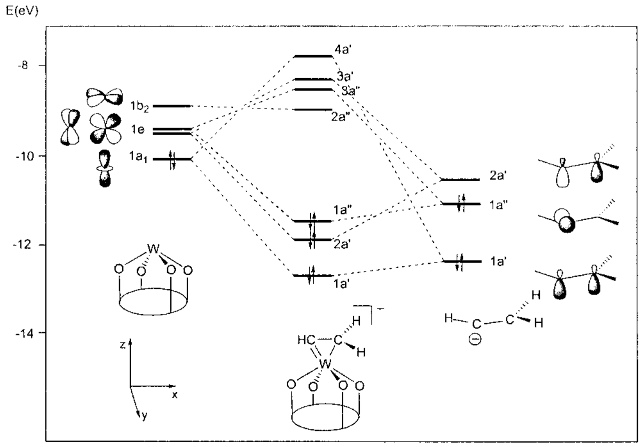

Figure 7. Molecular orbital interaction diagram for $[(calix)W(HCCH_2)]^-$ η^2-vinyl complex.

Conclusions

Although the 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 over homogeneous catalysts, the investigation of the chemistry of the d^2 [{p-Bu^t-calix[4]-$(O)_4$}W] fragment, and in particular of η^2-olefin species, led to the discovery of a variety of olefin rearrangements which are very close to those often supposed to occur on metal oxides or other active surfaces. Such rearrangements are driven by light, acids, or bases, or occur under reducing conditions. This means that they can be controlled and, in perspective, used to generate in situ desired (active) species from (inert) precursors. These rearrangements lead to metallacycles, alkylidenes and alkylidynes, where the organometallic fragment derives from one of the simplest (and cheapest) building blocks of chemistry, i.e., ethylene. The protonation−deprotonation of alkylidene and alkylidynes, beyond their synthetic values as a means to modifing the ligand and access to new complexes, respectively, shed new light on the (underestimated) role of coordinated donor atoms in acid/base reactions, both in homogeneous and surface chemistry. 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 unique and unprecedented.

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Supporting Information Available: ORTEP diagrams and tables giving crystal data and structure refinement, atomic coordinates, isotropic and anisotropic displacement parameters, and bond lengths and angles for **3**, **10**, **11**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) Albright, T. A.; Hoffmann, R.; Thiebeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

(37) For ab initio approaches to the distinction between metallacyclic and donor−acceptor complexes, see: (a) Steigerwald, M. L.; Goddard, W. A., III *J. Am. Chem. Soc.* **1985**, *107*, 5027. (b) Pidun, U.; Frenking, G. *Organometallics* **1995**, *14*, 5325.

(38) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435.