Genesis, Redox, and Acid−Base Relationships among W−C, W═C, and W≡C Functionalities over an Oxo Surface Modeled by Calix[4]arene

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Abstract: This report deals with the chemistry of anionic W-alkylidynes generated over the oxo surface defined by a calix[4]arene tetraanion. The exhaustive alkylation of [*cis*-$(Cl)_2$W{*p*-Bu^t-calix[4]−$(O)_4$}] (**1**), with an excess of alkylating agent led to [{*p*-Bu^t-calix[4]−$(O)_4$}W≡C−R][M] (R = Ph, M = $^1/_2$ Mg, **2**; R = Pr^n, M = Li, **3**; R = $SiMe_3$, M = Li, **4**). The protonation [PyHCl] of **2** and **3** led to the corresponding alkylidenes [{*p*-Bu^t-calix[4]−$(O)_4$}W═C(H)R] (R = Ph, **7**; R = Pr^n, **8**), which were reversibly deprotonated back to the starting akylidynes using LiBu. The reaction of **2**−**4** with $AgNO_3$ led to dimetallic alkylidenes [{*p*-Bu^t-calix-[4]−$(O)_4$}W═C(R)Ag)] (R = Ph, **12**; R = Pr^n, **13**; R = $SiMe_3$, **14**). The alkylation of **3** and **4** with MeOTf occurred at the carbon in **4** and at both carbon and oxygen in **3** leading to [{*p*-Bu^t-calix[4]−$(O)_4$}W═C(Me)-$SiMe_3$] (**9**) and to a mixture of [{*p*-Bu^t-calix[4]−$(O)_4$}W═C(Me)Pr^n], (**10**) and [{*p*-Bu^t-calix[4]−$(O)_3$-(OMe)}W≡C−Pr^n] (**11**), respectively. The functionalization of the anionic alkylidynes was achieved by reacting **2** with electrophiles such as PhCHO leading to [{{*p*-Bu^t-calix[4]−$(O)_4$}W═C(Ph)-C(H)(Ph)-O}$_2$Mg(thf)] (**15**) and with Ph_2C═C═O forming [{{*p*-Bu^t-calix[4]−$(O)_4$}W═C(Ph)-C(═CPh_2)-O}$_2$Mg] (**16**). An indirect, but synthetically quite versatile, functionalization is the oxidation of **2** with I_2 producing [{*p*-Bu^t-calix[4]−$(O)_4$}-W═C(Ph)-I] (**20**). The alkylidenes **7** and **8** were unexpectedly unreactive in the presence of olefins and aldehydes, e.g., PhCHO, which formed a reversible adduct binding inside the calix[4]arene cavity. However, the trans labilization of the alkylidene functionality was achieved by reacting **7** with Bu^{t}NC, a reaction leading to *cis*-stilbene and the W═W dimer [{μ-*p*-Bu^t-calix[4]−$(O)_4$}$_2$W$_2$(CNBu^t)$_2$] (**18**). The one-electron oxidation of **2** by Cp_2FeBPh_4 followed two different pathways via the common free-radical intermediate [{*p*-Bu^t-calix-[4]−$(O)_4$}W═C·(Ph)], leading to either **7** (hydrogen abstraction) or [{*p*-Bu^t-calix[4]−$(O)_4$}$_2$W$_2$(μ^2-η^2:η^2-Ph_2C_2)], (**19**). The nature of the anionic alkylidynes, the reaction pathways with electrophiles, and the one-electron oxidation reactions were analyzed using extended Hückel calculations.

Introduction

Our approach to metal−alkylidene[1] and metal−alkylidyne[2] chemistry is essentially focused on the attempt to make a bridge between homogeneous and heterogeneous systems[3] using a preorganized quasi-planar tetraanionic O_4 set of oxygen donor atoms derived from the deprotonated form of calix[4]arene.[4] To make this approach most significant we chose a metal, i.e., tungsten, which has played a major role in both heterogeneous and homogeneous systems since the discovery of the metathesis reaction,[5] and whose ligands of preference contain oxygen donor atoms.[6,7] One might wonder what might be the consequence of using the calix[4]arene as ancillary ligand in metal−alkylidene and metal−alkylidyne chemistry. The metal bonded to the nearly planar calix[4]arene skeleton in its cone conformation displays three frontier orbitals, one σ and two π, particularly appropriate for stabilizing the M−C multiple bond functionality (see Extended Hückel Calculations); thus alkylidenes and alkylidynes may form spontaneously from conventional alkylation reactions. The other unique role of calix[4]arene, which makes comparisons with the heterogeneous metal−oxide systems[8] valuable, is the basic surrounding of the metal where the oxygen donor

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atoms can assist the protonation−deprotonation of alkylidynes and, in general, their reaction with electrophiles. The so-called macrocyclic stabilization[9] would help greatly in keeping the metal−calix[4]arene fragment resistant to protic acids and strong electrophiles. We should also mention that the use of a tetraanionic macrocycle would lead to anionic alkylidynes, thus providing the best entry to functionalized alkylidenes. Anionic alkylidynes would also allow one to set up a novel redox chemistry in the field.

This report covers the topics outlined above: (i) the genesis of W-anionic alkylidynes; (ii) their reversible protonation and deprotonation reactions; (iii) their metalation with carbophilic metals leading to dimetallic alkylidenes; (iv) their unusual transformation into functionalized alkylidenes using appropriate electrophiles such as aldehydes and ketenes; (v) their oxidative coupling to μ^2-η^2:η^2-acetylene derivatives.

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 instrument. 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. For H_2 detection, Ar was used instead of He as carrier gas. GC/MS analyses were carried out on a Hewlett-Packard 5890A gas chromatograph using a Petrocol DH capillary column coupled with an HP 5970 mass-selective detector. Li and Mg alkylating agents were either purchased (Fluka, Aldrich) or prepared by standard methods. $Zn(CH_2Ph)_2$ was prepared according to the literature.[10] The synthesis of **1** has been performed as previously reported.[11] Photolyses were performed in a Solarbox (Cofomegra S.R.L.) equipped with a xenon lamp (540 W m^{-2} at 340 nm), using standard laboratory glassware.

Synthesis of 2. $Mg(CH_2Ph)_2$ (52 mL, 1.22 N, 63.4 mmol) was added to a toluene (350 mL) suspension of **1**·2(C_7H_8) (23.0 g, 21.2 mmol) at −25 °C. The resulting red solution was allowed to warm to 0 °C overnight and then to room temperature. Toluene was evaporated and THF (500 mL) added to give an ochre mixture, which was stirred at room temperature for 2 days. Bright yellow **2**·6(C_4H_8O) was then collected, washed with THF (3 × 50 mL), and dried in vacuo (17.0 g, 59%). Anal. Calcd for $C_{75}H_{105}Mg_{0.5}O_{10}W$: C, 66.11; H, 7.77. Found: C, 65.80; H, 8.15. ^{1}H NMR (Py-d_5, 300 K, ppm): δ 7.27 (s, 8H, ArH), 7.10 (m, 2H, ArH), 7.03 (m, 2H, ArH), 6.65 (m, 1H, ArH), 5.26 (d, J = 11.6 Hz, 4H, *endo*-CH_2), 3.62 (m, 24H, THF), 3.33 (d, J = 11.6 Hz, 4H, *exo*-CH_2), 1.59 (m, 24H, THF), 1.22 (s, 36H, Bu^t). ^{13}C NMR (Py-d_5, 300 K): δ 267.9 ppm. The X-ray analysis was carried out on the compound recrystallized from pyridine, [{{*p*-Bu^t-calix[4]−$(O)_4$}-W≡C−Ph}·$^1/_2${$Mg(Py)_6$}]·2Py.

Synthesis of 3. LiBu (33 mL, 1.70 N, 56.1 mmol) was added to a toluene (250 mL) suspension of **1**·2(C_7H_8) (20.3 g, 18.9 mmol) at −30 °C, stirred overnight at that temperature, and then allowed to reach room temperature. THF (50 mL) was added, giving a suspension. Volatiles were removed in vacuo, and Et_2O (250 mL) was added to the residue. The mixture was filtered and, after the addition of DME (40 mL), taken to dryness. **3**·2($C_4H_{10}O_2$)·0.5LiCl was collected from pentane (100 mL) and further washed with 50 mL of the same solvent (10.2 g, 49.4%). Anal. Calcd for $C_{56}H_{79}Cl_{0.5}Li_{1.5}O_8W$: C, 61.58; H, 7.29. Found: C, 61.54; H, 7.44. ^{1}H NMR (Py-d_5, 300 K): 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_2CH_3$), 3.48 (s, 8H, DME), 3.25 (s, 12H, DME), overlapping with 3.23 (d, J = 11.6 Hz, 4H, *exo*-CH_2), 1.80 (m, 2H, $WCCH_2CH_2CH_3$), 1.46 (t, J = 7.2 Hz, 3H, $WCCH_2CH_2CH_3$), 1.16 (s, 36H, Bu^t). ^{13}C NMR (Py-d_5, 300 K): δ 276.6 (W*C*(Pr), J_{CW} = 278 Hz), 48.3 ($WCCH_2CH_2CH_3$), 27.0 ($WCCH_2CH_2CH_3$), 14.5 ($WCCH_2CH_2CH_3$). Photolysis in DME of the deprotonated form of **5** leads to **3**·3($C_4H_{10}O_2$), free of LiCl.[12]

Synthesis of 4. $LiCH_2SiMe_3$ (5.63 g, 60 mmol) was added to a suspension of **1**·2(C_7H_8) (21.7 g, 20.0 mmol) in toluene (250 mL) at −25 °C and allowed to warm to 0 °C overnight. After the addition of DME (30 mL), volatiles were removed in vacuo and Et_2O (600 mL) was added to the residue. LiCl was filtered off, and after further addition of DME (30 mL), the yellow solution was taken to dryness. Bright yellow **4**·2($C_4H_{10}O_2$) was collected from pentane (100 mL), further washed with pentane (3 × 25 mL), and dried in vacuo (15.6 g, 71%). Anal. Calcd for $C_{56}H_{81}LiO_8SiW$: C, 61.08; H, 7.41. Found: C, 61.12; H, 7.86. ^{1}H NMR (Py-d_5, 300 K, ppm): δ 7.15 (s, 8H, ArH), 5.25 (d, J = 11.6 Hz, 4H, *endo*-CH_2), 3.47 (s, 8H, DME), 3.25 (s, 12H, DME), overlapping with, 3.26 (d, J = 11.6 Hz, 4H, *exo*-CH_2), 1.16 (s, 36H, Bu^t), 0.24 (s, 9H, $SiMe_3$). ^{13}C NMR (Py-d_5, 300 K): δ 308.1 (W*C*($SiMe_3$)). Crystals suitable for X-ray analysis were obtained from cooling THF/toluene solutions. When the reaction was performed by the addition of $LiCH_2SiMe_3$ (0.87 g, 9.2 mmol) to a suspension of **1**·2(C_7H_8) (3.3 g, 3.0 mmol) in frozen Et_2O (80 mL), which was then allowed to melt and then warm under stirring to room temperature in a closed Schlenk tube, no H_2 could be detected by GC analysis of the gas phase. NMR analysis of the yellow suspension showed clean **4**. Clean **4** was also obtained performing the reaction in THF at −30 °C.

Reacting **4**·2($C_4H_{10}O_2$) (3.08 g, 2.80 mmol) with PyHCl (0.334 g, 2.89 mmol) in Et_2O at room temperature, [{*p*-Bu^t-calix[4]−$(O)_4$}-W=C(H)Si$(CH_3)_3$] was cleanly formed. ^{1}H NMR (C_6D_6, 300 K): δ 10.35 (s, 1H, WC(*H*)Si$(CH_3)_3$), 7.07 (s, 8H, ArH), 4.98 (d, J = 12.2 Hz, 4H, *endo*-CH_2), 3.26 (d, J = 12.2 Hz, 4H, *exo*-CH_2), 1.08 (s, 36H, Bu^t), 0.48 (s, 9H, W=C(H)Si*Me*$_3$). Due to its extreme solubility, this alkylidene was not isolated. The reaction of [{*p*-Bu^t-calix[4]−$(O)_4$}W=C(H)Si$(CH_3)_3$] with a stoichiometric amount of BuLi (in toluene at −30 °C) led to pure **4**, as determined by ^{1}H NMR spectroscopy.

Synthesis of 5. $MgBr(CH_2)_4MgBr$[13] (15 mL, 0.365 M in THF, 5.47 mmol) was added to a suspension of **1**·2(C_7H_8) (5.70 g, 5.25 mmol) in toluene (150 mL) at −25 °C, to give a red solution, which was allowed to warm to room temperature overnight. Dioxane (1 mL) was added, volatiles were evaporated in vacuo, and the residue was extracted with Et_2O (150 mL) for 3 days. Solvent was evaporated and orange **5**·($C_4H_{10}O$) washed with pentane, collected, and dried in vacuo (2.25 g, 45%). Anal. Calcd for $C_{52}H_{70}O_5W$: C, 65.13; H, 7.36. Found: C, 64.84; H, 7.53. ^{1}H NMR (C_6D_6, 298 K, ppm): δ 7.15 (s, 8H, ArH), 4.47 (d, 4H, J = 13.2 Hz, *endo*-CH_2), 3.99 (m, 4H, C_4H_8), 3.60 (m, 4H, C_4H_8), 3.27 (d, 4H, J = 13.2 Hz, *exo*-CH_2), 1.28 (s, 36H, Bu^t).

Synthesis of 6. $LiCH_2SiMe_3$ (15 mL, 0.254 M in toluene, 3.81 mmol) was added to a suspension of **1**·2(C_7H_8) (4.13 g, 3.8 mmol) in THF (100 mL) at −10 °C. The mixture was stirred at 0 °C overnight, warmed to room temperature, and filtered. THF was evaporated in vacuo down to ∼50 mL, Et_2O was added, and the mixture was allowed to stand overnight at −25 °C, to give **6**·3(C_4H_8O) as red needles which were collected and dried in vacuo (2.4 g, 56%). Anal. Calcd for $C_{56}H_{76}Cl_2LiO_7W$: C, 59.90; H, 6.82. Found: C, 59.95; H, 6.78. ^{1}H NMR (CD_3CN, 298 K, ppm): δ 12.2 (s, 4H), 5.50 (s, 4H), 3.69 (m, THF), overlapping with 3.67 (s), 1.86 (m, 12H, THF), 1.41 (s, 18H, Bu^t), 1.32 (s, 18H, Bu^t).

6·3(C_4H_8O) (1.19 g, 1.06 mmol) was reacted with $LiCH_2SiMe_3$ (8.4 mL, 0.254 M in toluene, 2.13 mmol) in toluene (50 mL) at −30 °C. After stirring at this temperature overnight and at room temperature for 2 h, a yellow suspension was obtained. ^{1}H NMR analysis revealed only a minor amount of **4** (20−30%), the main products gave signals spread over 30 ppm.

Synthesis of 7. Method A. $Zn(CH_2Ph)_2$ (3.16 g, 12.7 mmol) was added to a suspension of **1**·2(C_7H_8) (13.1 g, 12.1 mmol) in toluene (500 mL). The resulting mixture was stirred at room temperature over-

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night, at 50 °C for 2 h, and at 70 °C for 5 h. Bu^n_4NCl (3.51 g, 12.6 mmol) was added, and the suspension was stirred for 2 h at 100 °C. A solid was filtered off the hot mixture, volatiles were evaporated, and pentane (300 mL) was added. The product was collected and dried in vacuo (7.37 g, 66%). Anal. Calcd for $C_{51}H_{58}O_4W$: C, 66.67; H, 6.36. Found: C, 66.65; H, 6.76.

Synthesis of 7. Method B. Cp_2FeBPh_4 (2.37 g, 4.69 mmol) was added to a suspension of **2**·6(C_4H_8O) (5.81 g, 4.26 mmol) in Et_2O (230 mL) at −20 °C. The resultant mixture was stirred at this temperature overnight and then at room temperature to give a yellow-orange suspension. The solid was extracted overnight with its own mother liquors, volatiles were then evaporated to dryness, and pentane was (50 mL) added to the residue. The orange solid was collected and dried in vacuo (2.86 g, 73.1%). Anal. Calcd for $C_{51}H_{58}O_4W$: C, 66.67; H, 6.36. Found: C, 66.86; H, 6.63.

Synthesis of 7. Method C. PyHCl (0.665 g, 5.75 mmol) and **2**·6(C_4H_8O) (7.55 g, 5.54 mmol) were stirred in Et_2O (200 mL) overnight to give a dark suspension. After an addition of toluene (70 mL), the mixture was taken to dryness and toluene (160 mL) was added to the residue. A white solid was filtered off, and volatiles were evaporated to give brown **7**·(C_7H_8), which was washed with pentane (40 mL) and dried in vacuo (4.58 g, 82%). Anal. Calcd for $C_{58}H_{66}O_4W$: C, 68.91; H, 6.58. Found: C, 68.94; H, 6.76. ^{1}H NMR ($CDCl_3$, 298 K, ppm): δ 10.16 (s, 1H, WC(*H*)Ph), 7.63 (m, 2H, Ph), 7.21 (m, 2H, Ph), overlapping with, 7.20 (s, 8H, ArH), 6.90 (m, 1H, Ph), 4.70 (d, 4H, J = 12.2 Hz, *endo*-CH_2), 3.38 (d, 4H, J = 12.2 Hz, *exo*-CH_2), 2.40 (s, 3H, tol), 1.29 (s, 36H, Bu^t). ^{1}H NMR (Py-d_5, 300 K): δ 10.98 (s, 1H, WC(*H*)Ph), 7.52 (m, 4H, Ph), 7.33 (s, 8H, ArH), 6.82 (m, 1H, Ph), 5.08 (d, 4H, J = 12.2 Hz, *endo*-CH_2), 3.45 (d, 4H, J = 12.2 Hz, *exo*-CH_2), 2.20 (s, 3H, tol), 1.16 (s, 36H, Bu^t). ^{1}H NMR (C_6D_6, 300 K, ppm): δ 10.20 (s, 1H, WC(*H*)Ph), 7.30 (m, 2H, Ph), 7.17 (m, 2H, Ph), 7.08 (s, 8H, ArH), 6.55 (m, 1H, Ph), 4.99 (d, 4H, J = 12.2 Hz, *endo*-CH_2), 3.24 (d, 4H, J = 12.2 Hz, *exo*-CH_2), 2.10 (s, 3H, tol), 1.08 (s, 36H, Bu^t). ^{13}C NMR (C_6D_6, 300 K): δ 260.5 (W*C*(Ph)H). Crystals suitable for X-ray analysis were obtained by extraction in Et_2O, using the methodology reported in ref 14.

Complex **7** was found to be exceedingly thermally (12 h, 80 °C) and photochemically stable. It was coordinated by PhCHO in toluene and C_6D_6 solutions. IR of a 1:1 mixture (tol, ν_{max} cm^{-1}): 1705.8 (m), 1683.4 (m), 1660 (m). ^{1}H NMR, excess PhCHO: 9.93 ppm W=C(*H*)-Ph (vs 10.20 ppm without added ligands), PhC*H*O very broad at 8.9 ppm (vs 9.67 ppm for free PhC*H*O). At room temperature, bright yellow [{*p*-Bu^t-calix[4]−$(O)_4$}W=O] became visible after 24 h. Solutions containing **7** and PhC(Me)O in a 1:1 ratio or in excess of the ketone showed NMR and IR spectra consisting of those of the two components superimposed.

Synthesis of 8. PyHCl (0.22 g, 1.9 mmol) was added to a solution of **3**·2($C_4H_{10}O_2$)·0.5LiCl (2.07 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 was added to the residue. **8** was then collected as a brown solid and dried in vacuo (0.97 g, 57%). Anal. Calcd for $C_{48}H_{60}O_4W$: C, 65.16; H, 6.84. Found: C, 64.85; H, 6.64. ^{1}H NMR (C_6D_6, 300 K): δ 10.0 (t, J = 7.5 Hz, 1H, WC(Pr)*H*), 7.07 (s, 8H, ArH), 5.47 (m, 2H, WCHC$H_2$$CH_2$$CH_3$), 4.95 (d, J = 12.2 Hz, 4H, *endo*-CH_2), 3.24 (d, J = 12.2 Hz, 4H, *exo*-CH_2), 1.69 (m, 2H, WCHCH_2C$H_2$$CH_3$), 1.15 (t, J = 7.2 Hz, 3H, WCC$H_2$$CH_2CH_3$), 1.08 (s, 36H, Bu^t). ^{1}H NMR (Py-d_5, 300 K): δ 10.7 (br d, 1H, W=C(*H*)-Pr), 7.33 (s, 8H, ArH), 5.63 (m, 2H, WCHC$H_2$$CH_2$$CH_3$), 4.90 (d, J = 12.2 Hz, 4H, *endo*-CH_2), 3.48 (d, J = 12.2 Hz, 4H, *exo*-CH_2), 1.88 (m, 2H, WCCH_2C$H_2$$CH_3$), 1.26 (m, 3H, WCC$H_2$$CH_2CH_3$), overlapping with 1.16 (s, 36H, Bu^t). ^{13}C NMR (C_6D_6, 300 K): δ 272 (W*C*(Pr)H, J_{CW} = 180 Hz, J_{CH} = 142 Hz), 41.6 (WC$CH_2$$CH_2$$CH_3$), 29.5 (WCC$H_2$$CH_2$$CH_3$), 14.5 (WCC$H_2CH_2CH_3$).

The reaction of **8** with a stoichiometric amount of BuLi in toluene at −30 °C led to pure **3**, as determined by ^{1}H NMR spectroscopy. **8** was found to be thermally (12 h, 60 °C) and photochemically very stable, and it was coordinated by PhCHO in solution. IR of a 1:1 mixture (tol, ν_{max} cm^{-1}): 1705.8 (m), 1683.8 (m), 1660.4 (m). **8** showed major shifts in ^{1}H NMR on addition of Bu^tNC; solutions containing excess of the latter evolve to give M−M bonded dimer **18**. Complex **8** was best obtained by photolysis of **5** in toluene.[12]

Synthesis of 9. MeOTf (0.24 g, 1.46 mmol) was added to a yellow suspension of **4**·2($C_4H_{10}O_2$) (1.60 g, 1.46 mmol) in toluene (120 mL) and stirred overnight to give an orange mixture. Solids were filtered off, volatiles were evaporated, and pentane (40 mL) was added. The resulting solution was kept at 5 °C for 5 days to give ochre crystals of **9**. The product was then collected and dried in vacuo (0.63 g, 45.3%). ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.08 (s, 8H, ArH), 5.64 (s, 3H, Me), 4.58 (d, 4H, J = 12.7 Hz, *endo*-CH_2), 3.26 (d, 4H, J = 12.7 Hz, *exo*-CH_2), 1.18 (s, 36H, Bu^t), 0.50 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 298 K): δ 276 (W*C*(Me)$SiMe_3$, J_{CW} = 166.5 Hz).

Synthesis of 10 and 11. MeOTf (0.25 g, 1.52 mmol) was added to a suspension of **3**·3($C_4H_{10}O_2$) (1.76 g, 1.51 mmol) in toluene (120 mL) and stirred overnight. A white solid was filtered off, volatiles were evaporated, and pentane (40 mL) was added. The resulting solution was kept at 5 °C for 5 days to give a solid, which was collected and dried in vacuo (0.83 g), containing **10** and **11** in roughly equal amounts.

For **10**: ^{1}H NMR (C_6D_6, 300 K, ppm): 7.07 (s, 8H, ArH), 5.41 (s, 3H, W=C(*Me*)Pr), 5.17 (t, 2H, J = 6.85 Hz, WC(CH_3)C$H_2$$CH_2$$CH_3$), 4.93 (d, 4H, *endo*-$CH_2$), 3.24 (d, 4H, *exo*-$CH_2$), 1.73 (m, 2H, WC-($CH_3$)$CH_2CH_2$$CH_3$), 1.27 (t, 3H, WC($CH_3$)$CH_2$$CH_2CH_3$), 1.09 (s, 36H, Bu^t). ^{1}H NMR ($CDCl_3$, 300 K, ppm): 7.13 (s, 8H, ArH), 5.52 (s, 3H, WC(Pr)*Me*), 5.17 (t, 2H, J = 7.3 Hz, WC(Me)C$H_2$$CH_2$$CH_3$), 4.57 (d, 4H, J = 12.2 Hz, *endo*-CH_2), 3.27 (d, 4H, J = 12.2 Hz, *exo*-CH_2), 1.84 (m, 2H, WC(Me)CH_2C$H_2$$CH_3$), 1.28−1.16 overlapping (36H, Bu^t, 3H, WC(Me)$CH_2$$CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 300 K, ppm): δ 28.4 (WC(*Me*)Pr), 46.4 (WC(Me)$CH_2$$CH_2$$CH_3$), 293.0 (W*C*(Me)Pr, J_{CW} = 177 Hz).

For **11**: ^{1}H NMR (C_6D_6, 300 K, ppm): δ 7.23 (d, 2H, J = 2.45 Hz, ArH), 7.21 (d, 2H, J = 2.45 Hz, ArH), 6.91 (s, 2H, ArH), 6.85 (s, 2H, ArH), 4.51 (s, 3H, OMe), from 4.97 to 4.91 (t, 2H, WCC$H_2$$CH_2$$CH_3$) overlapping with (d, 2H, *endo*-CH_2), 4.53 (d, 2H, *endo*-CH_2), 3.24 (d, 4H, *exo*-CH_2), 1.79 (m, 2H, WCCH_2C$H_2$$CH_3$), 1.40 (s, 18H, Bu^t), 1.09 (t, 3H, WCC$H_2$$CH_2CH_3$), 0.81 (s, 9H, Bu^t), 0.72 (s, 9H, Bu^t). ^{1}H NMR ($CDCl_3$, 300 K, ppm): δ 7.06 (s, 2H, ArH), 7.05 (d, 2H, J = 2.45 Hz, ArH), 7.02 (s, 2H, ArH), 7.00 (d, 2H, J = 2.45 Hz, ArH), 5.12 (s, 3H, OMe), 4.93 (t, 2H, J = 6.8 Hz, WC$CH_2$$CH_2$$CH_3$), 4.48 (d, 2H, J = 12.7 Hz, *endo*-CH_2), 4.42 (d, 2H, J = 12.7 Hz, *endo*-CH_2), 3.35 (d, 2H, J = 12.7 Hz, *exo*-CH_2), 3.18 (d, 2H, J = 12.7 Hz, *exo*-CH_2), 1.84 (m, 2H, WCCH_2C$H_2$$CH_3$), 1.28−1.16 overlapping (36H, Bu^t, 3H, WCC$H_2$$CH_2CH_3$).^{13}C NMR ($CDCl_3$, 300 K, ppm): δ 301.7 (W*C*CH_2-$CH_2$$CH_3$, J_{CW} = 278 Hz), 80.7 (OCH_3), 49.3 (WC$CH_2$$CH_2$$CH_3$).

Synthesis of 12. $AgNO_3$ (0.70 g, 4.1 mmol) and **2**·6(C_4H_8O) (5.58 g, 4.1 mmol) were suspended in THF (150 mL) and the mixture was stirred overnight, giving a suspension of a gray solid in a red supernatant. Volatiles were removed, and pentane (150 mL) was added. A pale solid was filtered off; the pentane solution was concentrated to 50 mL and kept at −25 °C for 4 days. Deep red **12** was collected from the cold mother liquors and dried in vacuo (2.4 g, 57%). Anal. Calcd for $C_{51}H_{57}AgO_4W$: C, 59.72; H, 5.60. Found: C, 59.95; H, 5.91. ^{1}H NMR (Py-d_5, 300 K): δ 7.50 (m, 2H, Ph), 7.27 (s, 8H, ArH), overlapping with 7.2 (m, 2H, Ph), 6.74 (m, 1H, Ph), 5.26 (d, J = 11.6 Hz, 4H, *endo*-CH_2), 3.36 (d, J = 11.6 Hz, 4H, *exo*-CH_2), 1.19 (s, 36H, Bu^t). ^{13}C NMR (Py-d_5, 298 K): δ 265.6 (W*C*(Ph), J_{CW} = 256 Hz). ^{1}H NMR (C_6D_6, 298 K, ppm): δ 8.12 (m, 2H, Ph), 7.11 (m, 2H, Ph), 6.94 (s, 8H, ArH), 6.81 (m, 1H, Ph), 4.83 (d, 4H, J = 12.7 Hz, *endo*-CH_2), 2.95 (d, 4H, J = 12.7 Hz, *exo*-CH_2), 1.10 (s, 36H, Bu^t). ^{13}C NMR (C_6D_6, 298 K): δ 241.1 ({W*C*(Ph)}{μ-Ag}, J_{CAg} = 58 Hz). ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.49 (m, 2H, Ph), 6.97 (s, 8H, ArH), 6.80 (m, 2H, Ph), 6.61 (m, 1H, Ph), 4.42 (d, 4H, J = 12.5 Hz, *endo*-CH_2), 2.88 (d, 4H, J = 12.5 Hz, *exo*-CH_2), 1.20 (s, 36H, Bu^t). ^{13}C NMR (CD_2Cl_2, 298 K): δ 240.9 ({W*C*(Ph)}{μ-Ag}, J_{CAg} = 60 Hz).

Synthesis of 13. $AgNO_3$ (0.3 g, 1.77 mmol) was added to a solution of **3**·3($C_4H_{10}O_2$) (1.97 g, 1.70 mmol) in THF (100 mL) and the mixture stirred overnight. Volatiles were removed in vacuo, and the residue was extracted with Et_2O (100 mL). The resulting deep red solution was kept at −25 °C for 24 h to yield **13** as red needles (0.5 g, 30%). Anal. Calcd for $C_{48}H_{59}AgO_4W$: C, 58.14; H, 6.00. Found: C, 57.95; H, 6.03. ^{1}H NMR (Py-d_5, 300 K): δ 7.25 (s, 8H, ArH), 5.31 (d, J = 11.6 Hz, 4H, *endo*-CH_2), 4.74 (t, J = 6.8 Hz, 2H, WCC$H_2$$CH_2$$CH_3$),

(14) Floriani, C.; Mange, V. *Inorg. Synth.* **1990**, *28*, 263.

3.35 (d, J = 11.6 Hz, 4H, *exo*-CH_2), 2.0 (m, 2H, $WCCH_2CH_2CH_3$), 1.41 (t, 3H, J = 7.4 Hz, $WCCH_2CH_2CH_3$), 1.19 (s, 36H, Bu^t). ^{13}C NMR (Py-d_5, 300 K): δ 272 ({W*C*(Pr)}{Ag}), 50.0 ($WCCH_2CH_2CH_3$), 27.9 ($WCCH_2CH_2CH_3$), 14.6 ($WCCH_2CH_2CH_3$). The X-ray analysis was performed on the solid recrystallized from pyridine/DME to give [{{*p*-Bu^t-calix[4]$-(O)_4$}W=C(Pr)}$_2${μ-Ag(Py)}$_2$] (**13py**).

Synthesis of 14. $AgNO_3$ (0.50 g, 2.95 mmol) was added to a solution of **4**·2($C_4H_{10}O_2$) (3.03 g, 2.75 mmol) in THF (150 mL) and the mixture stirred overnight. Volatiles were removed in vacuo, and the residue was extracted with Et_2O (100 mL) over 6 h. **14** was collected at room temperature from the Et_2O mother liquors as an orange powder (1.5 g, 53%). Anal. Calcd for $C_{48}H_{61}AgO_4SiW$: C, 56.42; H, 6.01. Found: C, 56.10, H, 6.18. ^1H NMR (Py-d_5, 300 K): δ 7.23 (s, 8H, ArH), 5.07 (d, J = 11.6 Hz, 4H, *endo*-CH_2), 3.31 (d, J = 11.6 Hz, 4H, *exo*-CH_2), 1.16 (s, 36H, Bu^t), 0.56 (s, 9H, $SiMe_3$).

Synthesis of 15. PhCHO (0.18 g, 1.7 mmol) was added to a suspension of **2**·6(C_4H_8O) (2.3 g, 1.7 mmol) in THF (100 mL), and the mixture was stirred for 1 h to give a blue solution. Volatiles were removed in vacuo, toluene was added to the residue, and the solution was filtered. Volatiles were evaporated again, and the residue was washed with pentane to give blue **15**·(C_5H_{12}), which was collected and dried in vacuo (1.3 g, 69%). Anal. Calcd for $C_{125}H_{146}MgO_{11}W_2$: C, 67.74; H, 6.64. Found: C, 67.66; H, 6.48. ^1H NMR (Py-d_5, 300 K): δ 10.67 (s, 2H, PhC(O)*H*), 7.9−6.4 (m, ArH), 5.96 (d, 2H, J = 12.4 Hz, *endo*-CH_2), 5.13 (d, 2H, J = 13.0 Hz, *endo*-CH_2), 4.79 (d, 2H, J = 11.6 Hz, *endo*-CH_2), 4.60 (d, 2H, J = 12.6 Hz, *endo*-CH_2), 4.14 (d, 2H, J = 12.4 Hz, *exo*-CH_2), 3.73 (d, 2H, J = 13.0 Hz, *exo*-CH_2), 3.63 (m, 4H, THF), 3.37 (m, 4H, *exo*-CH_2), 1.59 (m, 4H, THF), 1.54 (s, 18H, Bu^t), 1.45 (s, 18H, Bu^t), 1.2 (m, 6H, pentane), 0.98 (s, 18H, Bu^t), 0.79 (m, 6H, pentane), 0.74 (s, 18H, Bu^t). ^1H NMR (CD_2Cl_2, 300 K): δ 10.2 (s, 2H, PhC(O)*H*), 7.5−6.9 (m, 30H, ArH), 6.49 (m, 2H, ArH), 6.18 (m, 4H, ArH), 5.18 (d, 2H, J = 12.5 Hz, *endo*-CH_2), 4.69 (d, 2H, J = 13.1 Hz, *endo*-CH_2), 4.53 (d, 2H, J = 11.5 Hz, *endo*-CH_2), 3.87 (d, 2H, J = 13.0 Hz, *endo*-CH_2), 3.78 (m, 4H, thf), 3.53 (d, 2H, J = 12.5 Hz, *exo*-CH_2), 3.47 (d, 2H, J = 13.1 Hz, *exo*-CH_2), 3.33 (d, 2H, J = 11.5 Hz, *exo*-CH_2), 2.94 (d, 2H, J = 13.0 Hz, *exo*-CH_2), 2.61 (m, 4H, thf), 1.4 (m, 6H, pentane), 1.35 (s, 18H, Bu^t), 1.33 (s, 18H, Bu^t), 1.25 (s, 18H, Bu^t), 1.17 (s, 18H, Bu^t), 0.90 (m, 6H, pentane). ^{13}C NMR (CD_2Cl_2, 298 K): δ 288 (W=*C*), 79.3 (W=C(Ph)*C*(Ph)(O)H).

Synthesis of 16. Diphenylketene (0.25 g, 1.29 mmol) and **2**·6(C_4H_8O) (1.71 g, 1.25 mmol) were mixed in toluene (80 mL) to give a dark green solution. Volatiles were evaporated, pentane was added to the residue, and green **16**·2(C_7H_8) was collected and dried in vacuo (0.97 g, 64%). Anal. Calcd for $C_{144}H_{150}O_{10}W_2Mg$: C, 71.10; H, 6.22. Found: C, 71.21; H, 6.21. ^1H NMR (Py-d_5, 253 K): δ 7.8−6.4 (m, ArH), 5.45 (d, 4H, J = 13.2 Hz, *endo*-CH_2), 5.26 (d, 4H, J = 11.7 Hz, *endo*-CH_2), 3.57 (d, 4H, J = 13.2 Hz, *exo*-CH_2), 3.26 (d, 4H, J = 11.7 Hz, *exo*-CH_2), 2.11 (s, 6H, tol), 1.40 (s, 18H, Bu^t), 1.39 (s, 18H, Bu^t), 0.69 (s, 36H, Bu^t). Crystals suitable for X-ray analysis were obtained by cooling solutions in toluene/hexane at −25 °C.

Synthesis of 17. 7 (3.0 g, 3.26 mmol) and Bu^tNC (0.26 g, 3.1 mmol) were dissolved in toluene (120 mL). Volatiles were removed in vacuo, and pentane (70 mL) was added to the residue, which was then collected and dried in vacuo to give **17**·(C_5H_{12}) (2.0 g, 60%). Anal. Calcd for $C_{61}H_{79}NO_4W$: C, 68.21; H, 7.41; N, 1.30. Found: C, 67.83, H, 7.59, N, 1.04. ^1H NMR (tol-d_8, 300 K, ppm): δ 8.9 (br d, WC(*H*)Ph), 7.42 (br d, 2H, Ph), 7.17 (m, 2H, Ph), 7.13 (s, 8H, ArH), 6.50 (br d, 1H, Ph), 4.97 (br d, 4H, *endo*-CH_2), 3.29 (d, 4H, *exo*-CH_2), 1.2 (m, 6H, pentane), overlapping with 1.20 (s, 36H, Bu^t), 0.90 (m, 6H, pentane), −0.12 (br d, Bu^tNC). A sharp spectrum was obtained by lowering the temperature. ^1H NMR (tol-d_8, 260 K, ppm): δ 9.04 (s, 1H, WC(*H*)-Ph), 7.46 (m, 2H, Ph), 7.21 (m, 2H, Ph), 7.12 (s, 8H, ArH), 6.48 (m, 1H, Ph), 5.14 (d, 4H, J = 12.7 Hz, *endo*-CH_2), 3.30 (d, 4H, J = 12.7 Hz, *exo*-CH_2), 1.27 (s, 36H, Bu^t), −0.21 (s, 9H, Bu^tNC). By adding an excess of Bu^tNC to the NMR sample, a sharp spectrum (except for coordinated Bu^tNC) was also obtained at room temperature. ^1H NMR (tol-d_8, 298 K, ppm): δ 8.90 (s, 1H, WC(*H*)Ph), 7.45 (m, 2H, Ph), 7.17 (m, 2H, Ph), 7.13 (s, 8H, ArH), 6.46 (m, 1H, Ph), 5.07 (d, 4H, J = 12.7 Hz, *endo*-CH_2), 3.30 (d, 4H, J = 12.7 Hz, *exo*-CH_2), 1.25 (s, 36H, Bu^t), 0.95 (excess Bu^tNC), −0.08 (br d, Bu^tNC). IR (toluene, ν_{max} cm^{-1}): 2194.7 (s), 2132.5 (m). Solutions of **17** evolved to give **18**. The reaction was faster when an excess of Bu^tNC was present.

Synthesis of 18. 8 (1.07 g, 1.21 mmol) and Bu^tNC (0.13 g, 1.56 mmol) were dissolved in toluene (80 mL). After 2 days, dark microcrystalline **18**·2(C_7H_8) had formed on the side of the flask and was collected and dried (0.45 g, 37%). The same product was obtained (with a longer reaction time) from the reaction of **7** and Bu^tNC in toluene. In the latter case, *cis*-stilbene (but no *trans*-stilbene) was detected by gas chromatography in the reaction mixture. Anal. Calcd for $C_{112}H_{138}N_2O_8W_2$: C, 66.99; H, 6.93; N, 1.40. Found: C, 66.83; H, 7.02; N, 1.23. ^1H NMR ($CDCl_3$, 298 K, ppm): δ 7.3−7.08 (m, 26H, ArH, tol), 4.90 (d, 4H, J = 12.7 Hz, *endo*-CH_2), 4.63 (d, 4H, J = 12.2 Hz, *endo*-CH_2), 3.42 (d, 4H, *exo*-CH_2), overlapping with 3.33 (d, 4H, *exo*-CH_2), 2.40 (s, 6H, tol), 1.31 (s, 18H, Bu^t), 1.25 (s, 36H, Bu^t), 1.23 (s, 18H, Bu^t), −0.03 (s, 18H, Bu^tNC). IR (Nujol, ν_{max} cm^{-1}): 2202.8 (s). Crystals suitable for X-ray structural determination were obtained by performing the reaction between **7** and excess Bu^tNC in an NMR tube in C_6D_6.

Synthesis of 19. Cp_2FeBPh_4 (1.75 g, 3.46 mmol) and **2**·6(C_4H_8O) (4.39 g, 3.22 mmol) were stirred in Et_2O at 0 °C overnight to give a red suspension. The solid was extracted overnight with its own mother liquors, and then volatiles were removed in vacuo. Pentane (50 mL) was added to the residue, and the resulting solution was allowed to stand overnight, yielding **19**·2(C_5H_{12}) as a microcrystalline red solid, which was collected and dried in vacuo (1.1 g, 33%). Anal. Calcd for $C_{112}H_{138}O_8W_2$: C, 67.94; H, 7.02. Found: C, 67.95; H, 7.29. ^1H NMR (C_6D_6, 298 K, ppm): δ 8.63 (m, 4H, Ph), 7.43 (m, 4H, Ph), 6.94 (s, 18H, ArH, Ph), 4.70 (d, 8H, J = 12.4 Hz, *endo*-CH_2), 3.04 (d, 8H, J = 12.4 Hz, *exo*-CH_2), 1.22 (m, 12H, pentane), 1.02 (s, 72H, Bu^t), 0.88 (m, 12H, pentane). ^{13}C NMR (C_6D_6, 300 K): δ 207 (μ-C_2Ph_2). Crystals suitable for X-ray analysis were grown from hexane/benzene solutions at room temperature.

Synthesis of 20. I_2 (0.51 g, 2.0 mmol) was added to a yellow suspension of **2**·6(C_4H_8O) (2.59 g, 1.90 mmol) in THF (120 mL) and stirred overnight at room temperature. The resulting mixture was filtered, volatiles were evaporated, and toluene (120 mL) was added, and the mixture was stirred overnight. The solution was filtered, volatiles were evaporated in vacuo, and pentane (40 mL) was added. Brown **20**·0.5(C_5H_{12}) was collected and dried in vacuo (1,25 g, 61%). Anal. Calcd for $C_{53.5}H_{63}IO_4W$: C, 59.45; H, 5.87. Found: C, 59.33; H, 5.85. ^1H NMR ($CDCl_3$, 300 K, ppm): δ 7.63 (m, 2H, ArH), 7.56 (m, 2H, ArH), 7.23 (s, 8H, ArH), 6.97 (m, 1H, ArH), 4.64 (d, 4H, J = 12.7 Hz, *endo*-CH_2), 3.29 (d, 4H, J = 12.7 Hz, *exo*-CH_2), 1.18 (s, 39H, Bu^t, pent), 0.86 (m, 3H, C_5H_{12}). ^{13}C NMR ($CDCl_3$, 400 MHz, 300 K, ppm): δ 230.0 (W=*C*(I)Ph, J_{CW} = 212 Hz,). Crystals suitable for X-ray analysis were grown from a solution of toluene/heptane.

X-ray Crystallography for Complexes 2, 4, 7, 9, 13py, 16, and 19. Single crystals suitable for X-ray diffraction were grown from common organic solvents (Table 1). Data for **2**, **4**, and **13py** were collected on a Rigaku AFC6S diffractometer, for **7** and **16** on a Mar345 image plate detector diffractometer, for **9** on a Kuma CCD diffractometer, and for **19** on a Stoe IPDS diffractometer using Mo *K*α radiation. The solutions and refinements were carried out using the programs SHELX76[15] and SHELX93.[16] The details of the X-ray data collection, structure solution, and refinement are given in Supporting Information.[17]

Results

The Alkylation of [*cis*-$(Cl)_2$W{p-Bu^t-calix[4]$-(O)_4$}]. The first attempts to obtain alkyl derivatives of **1** by reaction with 1 or 2 equiv of Li and Mg alkylating agents did not lead to the expected products (see below). On the other hand, when a 3:1 molar ratio was used, alkylidyne derivatives **2**−**4** were readily obtained (Scheme 1). The reaction went well also when β-hydrogens were present, as in the case of **3**. The reaction solvents played an important role both in the selection of the

(15) Sheldrick, G. M. SHELX76. Program for crystal structure determination. University of Cambridge; Cambridge, England, 1976.

(16) Sheldrick, G. M. SHELXL93. Program for crystal structure refinement. University of Göttingen; Göttingen, Germany, 1993.

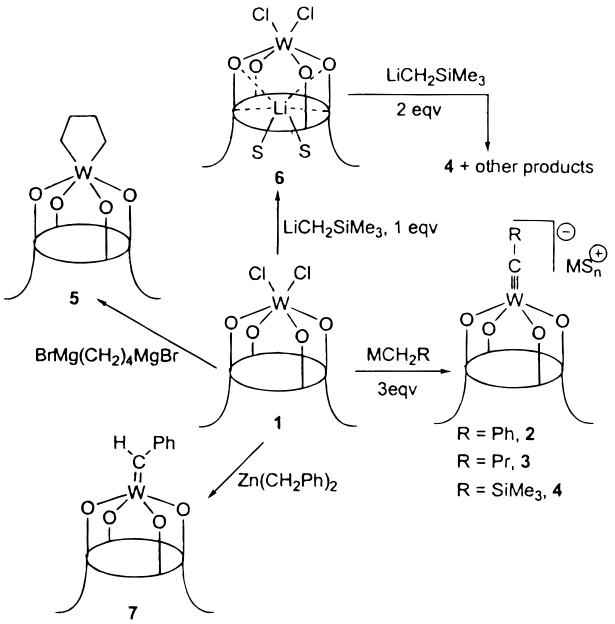
(17) See paragraph at the end of paper regarding Supporting Information.

Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes **2**, **4**, **7**, **9**, **13py**, **16**, and **19**

	2	**4**	**7**	**9**	**13py**	**16**	**19**
formula	$C_{51}H_{57}O_4W\cdot 0.5C_{30}H_{30}MgN_6\cdot 2C_5H_5N$	$C_{60}H_{85}LiO_7SiW\cdot C_4H_8O\cdot C_7H_8$	$C_{51}H_{58}O_4W\cdot 2C_4H_{10}O$	$C_{49}H_{64}O_4SiW$	$C_{106}H_{128}Ag_2N_2O_8W_2\cdot 2C_5H_5N\cdot 2C_4H_{10}O_2$	$C_{130}H_{134}MgO_{10}W_2\cdot 8C_7H_8$	$C_{102}H_{114}O_8W_2\cdot 3C_6H_6\cdot C_5H_{12}$
a, Å	22.038(3)	19.561(4)	12.978(2)	13.042(2)	12.661(2)	21.828(4)	14.867(1)
b, Å	12.415(2)	16.704(3)	18.977(4)	13.503(2)	24.283(3)	23.700(4)	16.100(1)
c, Å	25.171(3)	21.506(4)	21.858(4)	15.708(3)	19.461(3)	31.885(8)	25.700(2)
α, deg	90	90	90	66.42(2)	90	90	74.51(1)
β, deg	98.74(1)	107.06(2)	90	64.83(2)	105.71(2)	106.33(3)	76.74(1)
γ, deg	90	90	90	84.94(2)	90	90	73.97(1)
V, Å^3	6806.9(17)	6718(2)	5883.3(17)	2283.4(9)	5759.7(16)	15829(6)	5616.6(8)
Z	4	4	4	2	2	4	2
formula wt	1325.5	1301.4	1067.1	929.0	2480.1	2985.6	2142.2
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)	$P1$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P1$ (No. 2)
t, °C	22	−130	22	−50	−130	22	22
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.293	1.287	1.317	1.351	1.430	1.253	1.267
μ, cm^{-1}	17.86	18.23	22.37	26.48	24.23	15.43	21.42
transmissn coeff	0.836−1.000	0.730−1.000	0.761−1.000	0.774−1.000	0.695−1.000	0.713−1.000	0.617−1−000
R^a	0.054	0.039	0.046 [0.066]^b	0.076	0.049	0.058	0.042
wR_2	0.148	0.102	0.113 [0.185]^b	0.235	0.126	0.156	0.104
GOF	1.067	1.017	1.060	1.150	1.013	1.061	1.160
N-observed^c	7981	9170	9428	5335	8886	22 233	13 639
N-independent^d	11 982	11 601	11 537	9246	11 883	31 201	15 216
N-refinement^e	10 406	10 699	9428	8353	10 780	22 233	14 809
variables	745	727	589	492	644	1637	1113

^{a} Calculated on the observed reflections. ^{b} Values in brackets refer to the "inverted" structure. ^{c} *N*-observed is the total number of the independent reflections having $I > 2\sigma(I)$. ^{d} *N*-independent is the number of independent reflections. ^{e} *N*-refinement is the number of reflection used in the refinement having $I > 0$ for **2**, **4**, **9**, **13py**, and **19** and $I > 2\sigma(I)$ for **7**, and **16** and corrected for absorption.

Scheme 1



reaction path (α elimination vs reduction) and in the separation of magnesium and lithium halides. The best results were obtained at low temperature in toluene. The separation of salts was often a problem and not easy to explain: for example, a good yield of **2** was collected from THF, whereas Mg salts stayed in solution. The addition of DME helped the separation of LiCl and reduced the solubility of anionic complexes, probably breaking down dynamic aggregates of these complexes and their countercations.

Recent work by Schrock gave evidence of the possibility of obtaining M≡C functionalities by loss of H_2 from W(IV) primary alkyls.[18] This raises the question of the actual mechanism of the direct generation of alkylidynes described above, especially considering the fact that, using 1 or 2 equiv of MCH_2R (M = Li, Mg; R = Ph, $SiMe_3$, Bu^n), reduced, rather than alkylated, species were obtained. The reaction of **1** with $LiCH_2SiMe_3$ was studied in some detail: the 1:1 reaction in THF led cleanly to the W(V) lithium dichloride derivative **6**, which further reacted with 2 equiv of $LiCH_2SiMe_3$ in toluene to give only minor amounts of **4** (roughly 20−30%, the other main products appeared to be paramagnetic, their spectra being spread over 30 ppm), while the direct reaction of **1** with 3 equiv of $LiCH_2SiMe_3$ was almost quantitative, regardless of the solvent (NMR). When the 3:1 reaction was performed in Et_2O, no H_2 was produced, according to a GC analysis of the gas phase. This suggests that the process leading to alkylation is alternative to the reduction path.[19] Using less reducing alkylating agents in a 2:1 ratio, dialkyls/alkylidenes could be prepared. Reacting **1** with butyl-1,4 di-Grignard in a 1:1 molar ratio, the dialkyl species **5** (best prepared by electron-transfer-catalyzed coupling of ethylene) was obtained, without the formation of any paramagnetic species. The reaction of **1** with $Zn(CH_2Ph)_2$ led to the phenyl alkylidene **7**, first prepared by protonation of the corresponding alkylidyne **2** (see below).

Complexes **2**−**4** were found to be thermally and photochemically very stable. Their NMR spectra in coordinating solvents showed a C_{4v} symmetric calix[4]arene moiety. The alkylidyne carbon gave a signal at 260−300 ppm in ^{13}C NMR spectra. For complex **3**, a J_{CW} of 278 Hz was obtained, in agreement with literature data on alkylidynes.[20] Complexes **2** and **4** were characterized crystallographically. The labeling scheme adopted for the calix[4]arene−W moiety for all complexes is indicated in Chart 1. Selected bond distances and angles are quoted in Table 2 for complexes **2**, **4**, **7**, and **9** and in Table 3 for complexes **13py**, **16**, and **19**. In Table 4, a comparison of

(18) (a) Shih, K.-Y.; Totland, K.; Seidel, S. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 12103. (b) Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N.; Dobbs, D. A.; Shih, K.-Y.; Davis, W. M. *Organometallics* **1997**, *16*, 5195. (c) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9.

(19) Schrock, R. R.; Clark, D. N.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645 and references therein.

(20) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227.

Chart 1

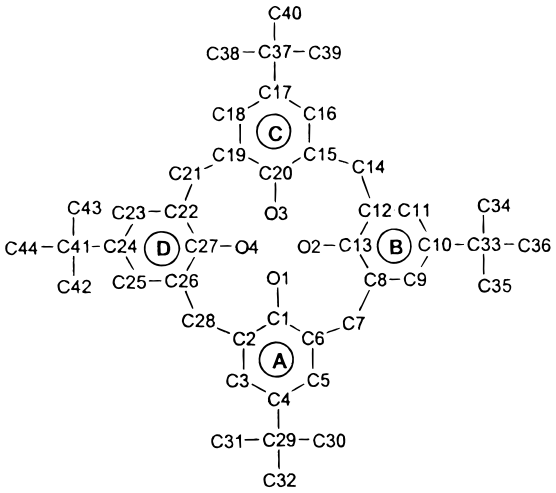


Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **2**, **4**, **7**, and **9**

	2	**4**	**7**	**9**
W(1)−O(1)	2.000(5)	2.026(2)	1.835(5)	1.857(10)
W(1)−O(2)	1.995(5)	1.969(3)	1.995(3)	1.969(7)
W(1)−O(3)	1.959(5)	1.944(3)	1.853(4)	1.864(11)
W(1)−O(4)	1.986(5)	1.963(3)	1.988(4)	1.972(9)
W(1)−C(45)	1.728(7)	1.759(4)	1.913(4)	1.914(10)
C(45)−C(46)	1.445(9)		1.437(6)	1.487(19)
Li−O(1)		1.908(10)		
Si−C(45)		1.835(4)		1.883(16)
W(1)−C(45)-C(46)	173.8(6)		135.2(4)	120.4(9)

relevant conformation parameters within the calix[4]arene−W unit is reported.

The structure of the pyridine solvate of **2** consists of the [{*p*-Bu^t-calix[4]−(O)$_4$}W≡CPh]$^-$ anion (Figure 1, Table 2) and the centrosymmetric cation [Mg(Py)$_6$]$^{2+}$, with two additional molecules of pyridine, one of them hosted in the calix[4]arene cavity. Tungsten exhibits a square-pyramidal coordination involving the four oxygen atoms of calix[4]arene at the base and the C(45) carbon atom of the benzylidyne ligand at the apex. The W−C(45) bond length [1.722(7) Å] has a triple bond character.[2,20] The direction of the W−C(45) bond forms a dihedral angle of 1.9(3)° with the normal to the planar {O$_4$} core. Tungsten is displaced by 0.328(1) Å from this plane toward the C(45) carbon. The W−O bond distances, which are in a fairly narrow range, are slightly longer than those observed in neutral [{*p*-Bu^t-calix[4]−(O)$_4$}W] derivatives containing WCl_2, W=O,[11a] and W(OAr)$_2$[21] functionalities. Calix[4]arene shows a *cone* conformation as is usually found in square-pyramidal five-coordinated metals. The almost symmetrical conformation is indicated by the narrow range of the dihedral angles formed by the plane through the C(7), C(14), C(21), C(28) bridging methylene carbons (*reference plane*) and the aromatic rings [119.5(2)−125.1(2)°]. The *reference plane* is parallel to the {O$_4$} core [dihedral angle 1.3(1)°].

Complex **4** was crystallized from THF/toluene, and its structure is depicted in Figure 2. The calix[4]arene ligand is in a cone conformation with greater distortion than in complex **2** (see Table 4), the {O$_4$} core is essentially planar; W is out of plane by 0.341(1) Å. The greatest difference with respect to the structure of **2** consists of the coordination of the Li$^+$ cation to O(1). As a consequence of the steric bulk of the Li(thf)$_3$ group, the $SiMe_3$ group is bent by 30° with respect to the expected linear geometry. Apparently the geometrical distortion does not affect the triple bond nature of the W−C interaction, as shown by the W−C bond distance [1.720(7) Å]. In addition, the W−O(1) distance is only slightly affected by Li coordination (Table 2).

Reactions with Electrophiles: Generation of Alkylidenes. The electron-rich, anionic alkylidyne species seemed to be particularly good candidates for reactions with electrophiles, summarized in Scheme 2.

The (reversible) protonation of **2**−**4** led cleanly to the corresponding alkylidenes (the trimethylsilyl derivative was not isolated, because of its very high solubility) without any other major change in the coordination sphere of the metal, as is usually the case when monodentate ligands are used. Although the protonation of alkylidynes is known, it is not reversible and occurs with important modifications in the coordination geometry and changes in the nature of the donor atoms around the metal.[22] Many alkylidenes with β-hydrogens are believed to rearrange to olefins; carefully documented examples essentially do not exist, although much evidence points in that direction.[23] We observed that not only **7** but also **8**, which contains

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes **13py**, **16**, and **19**

13py[a]		**16**		**19**	
W(1)−O(1)	1.872(5)	W(1)−O(1)	1.801(5)	W(1)−O(1)	1.848(5)
W(1)−O(2)	2.013(4)	W(1)−O(2)	2.101(4)	W(1)−O(2)	1.997(3)
W(1)−O(3)	1.951(5)	W(1)−O(3)	1.839(4)	W(1)−O(3)	1.838(4)
W(1)−O(4)	1.996(4)	W(1)−O(4)	1.950(4)	W(1)−O(4)	2.004(3)
W(1)−C(45)	1.832(5)	W(1)−C(45)	1.908(6)	W(1)−C(45)	2.089(6)
Ag(1)−N(1)	2.247(6)	Mg(1)−O(2)	2.002(4)	W(1)−C(46)	2.082(6)
Ag(1)−C(45)	2.312(6)	Mg(1)−O(5)	1.891(5)	C(45)−C(46)	1.439(8)
Ag(1)−C(45)′	2.562(6)	O(5)−C(46)	1.297(8)	C(45)−W(1)−C(46)	40.3(2)
C(45)−C(46)	1.492(8)	C(45)−C(46)	1.535(7)	W(1)A−C(45)−W(1)B	105.1(2)
O(1)−W(1)−O(3)	147.3(2)	C(46)−C(47)	1.352(8)	W(1)−C(45)−C(53)	132.1(4)
O(1)−W(1)−O(2)	86.1(2)	W(1)−C(45)−C(48)	122.8(4)	W(1)−C(45)−C(46)	69.6(3)
C(45)−Ag(1)−C(45)′	109.3(2)	W(1)−C(45)−C(46)	119.1(4)	C(46)−C(45)−C(53)	136.0(5)
N(1)−Ag(1)−C(45)′	121.0(2)	C(46)−C(45)−C(48)	117.1(5)	W(1)−C(46)−C(45)	70.1(3)
N(1)−Ag(1)−C(45)	129.6(2)			W(1)A−C(46)−W(1)B	105.6(2)
Ag(1)−C(45)−Ag(1)′	70.7(2)			C(45)−C(46)−C(47)	135.1(5)
W(1)−C(45)−Ag(1)′	94.5(2)			W(1)−C(46)−C(47)	120.5(4)
W(1)−C(45)−Ag(1)	97.6(2)				
Ag(1)′−C(45)−C(46)	108.4(4)				
Ag(1)−C(45)−C(46)	113.3(4)				
W(1)−C(45)−C(46)	146.0(4)				

[a] A prime denotes a transformation of $1-x$, $-y$, and $1-z$.

Table 4. Comparison of Relevant Conformational Parameters within Calix[4]arene for Complexes **2**, **4**, **7**, **9**, **13py**, **16**, and **19**

	2	**4**	**7**	**9**	**13py**	**16**	**19**
			(a) Distance (Å) of Atoms from the O_4 Mean Plane				
O(1)	−0.013(5)	0.021(4)	−0.124(4)	−0.079(7)	−0.143(4)	−0.158(4)	−0.137(5)
O(2)	0.014(5)	−0.021(4)	0.087(3)	0.107(9)	0.130(4)	0.153(4)	0.128(5)
O(3)	−0.014(5)	0.022(4)	−0.117(4)	−0.104(9)	−0.122(4)	−0.152(4)	−0.142(5)
O(4)	0.014(5)	−0.021(4)	0.119(4)	0.080(8)	0.127(4)	0.156(4)	0.127(5)
W	0.331(1)	0.341(1)	0.368(1)	0.384(1)	0.404(1)	0.357(2)	0.454(1)
			(b) Dihedral Angles (deg) between Planar Moieties[a]				
E∧A	124.6(1)	114.8(1)	137.2(1)	136.1(3)	142.4(1)	142.0(2)	130.7(1)
E∧B	122.1(2)	126.6(1)	114.1(1)	126.0(4)	118.5(1)	111.9(1)	116.9(1)
E∧C	125.2(2)	125.3(1)	131.8(1)	128.5(3)	128.2(1)	136.2(2)	137.7(1)
E∧D	119.5(2)	130.9(1)	116.3(1)	120.7(3)	111.8(1)	113.8(2)	117.2(2)
A∧C	110.2(2)	120.0(1)	90.9(2)	95.4(4)	90.6(2)	98.3(2)	91.6(2)
B∧D	118.4(2)	102.4(1)	129.6(2)	113.2(4)	129.7(2)	134.3(2)	126.8(2)
			(c) Contact Distances (Å) between Para Carbon Atoms of Opposite Aromatic Rings				
C(4)···C(17)	8.485(11)	7.953(7)	9.268(8)	9.05(2)	9.346(7)	9.614(9)	9.232(11)
C(10)···C(24)	8.038(10)	8.847(7)	7.411(9)	8.269(17)	7.428(10)	7.208(10)	7.542(8)

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

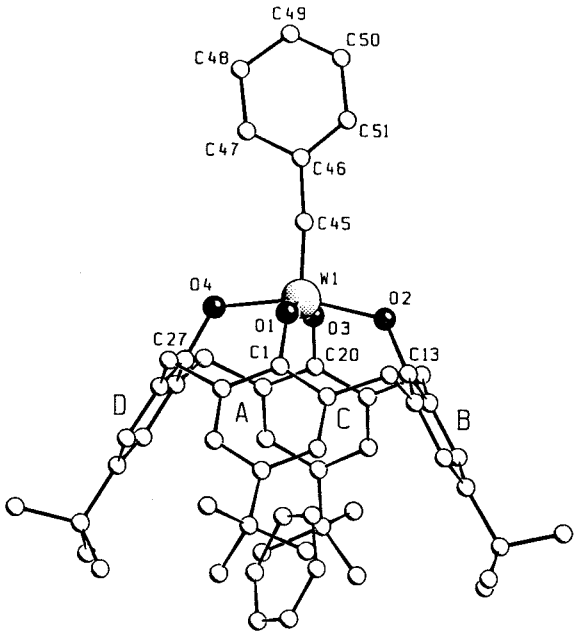


Figure 1. SCHAKAL view of the anion in complex **2**. Disorder affecting the pyridine guest molecule has been omitted for clarity.

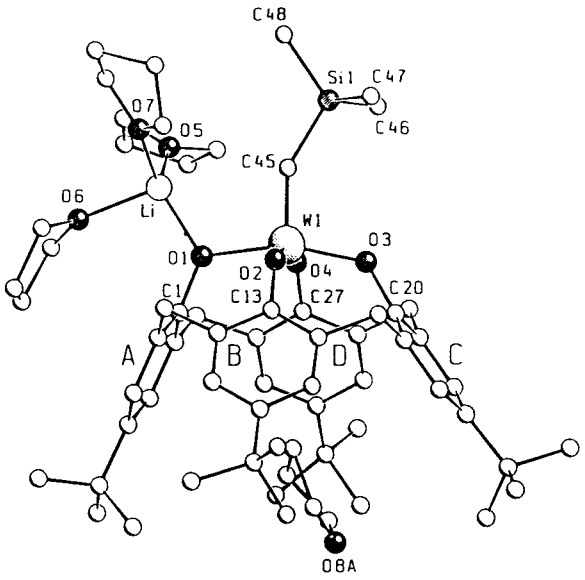


Figure 2. SCHAKAL view of complex **4**. Disorder affecting the butyl groups associated with the C and D rings and the THF guest molecule have been omitted for clarity.

β-hydrogens, were thermally and photochemically highly stable.[18] In the ^{1}H NMR spectra, the calix[4]arene moiety appeared to be of C_{4v} symmetry: like the related η^2-alkene/alkyne species, the carbene ligand must have a very small rotational barrier (see extended Hückel Analysis). The signal of W=C(*H*)R was found at ∼10 ppm. It is of interest to notice that, in the case of **8**, when pyridine was used as solvent, the coupling of the alkylidene H to its carbon as well as to the adjacent CH_2 was lost: we interpret this in terms of a rapid reversible deprotonation of the former by the basic solvent. In the ^{13}C NMR spectrum of **8** in C_6D_6, the carbon bound to tungsten atom gave a signal at 272 ppm, very close to that of the corresponding alkylidyne; the more diagnostic J_{CW} was much lower than for **3**, only 180 Hz.[6,24] The value of J_{CH}, 142 Hz, rules out any agostic coordination of the α hydrogen to W.[6]

Complex **7** was structurally characterized (Figure 3). According to the structural parameters in Tables 2 and 4, the coordination polyhedron is a trigonal elongated bipyramid involving the O(1), O(3), and C(45) atoms in the equatorial plane and the O(2) and O(4) atoms at the axial positions. The W−C(45) bond length [1.913(4) Å], remarkably longer than the corresponding ones in **2** and **4**, is consistent with a metal−carbon double bond.[1,6] W−O bond lengths are alternate, with the mean value of the W−O(1) and W−O(3) distances [1.846(9) Å] significantly shorter than the mean value of the W−O(2) and W−O(4) distances [1.992(3) Å]. The phenylalkylidene ligand is oriented nearly perpendicular to the O_4 core in such a way as to point the H(51) ortho hydrogen atom toward the O(1) oxygen atom, giving rise to a puckered six-membered chelation ring through an intramolecular interaction consistent with a C−H···O hydrogen bond: C(51)···O(1), 3.288(7) Å;

(21) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Chem. Commun.* **1996**, 119.

(22) (a) Reference 2, Chapter 4. (b) Reference 2, Chapter 5. (c) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 6570. (d) Weber, L.; Dembeck, G.; Stammler, H.-G.; Neumann, B.; Schmidtmann, M.; Müller, A. *Organometallics* **1998**, *17*, 5254. (e) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 1124. (f) Doyle, R. A. Angelici, R. J. *Organometallics* **1989**, *8*, 2207. (g) Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 493.

(23) (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.

(24) Köhler, F. H.; Kalder, H. J.; Fischer, E. O. *J. Organomet. Chem.* **1976**, *113*, 11.

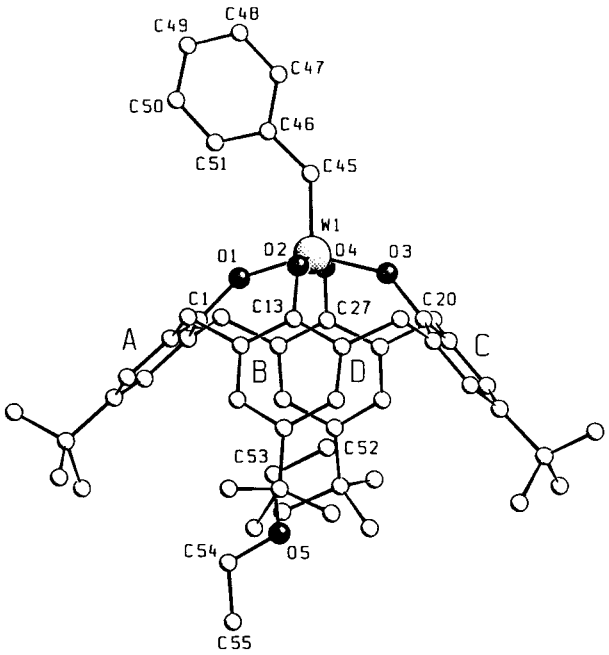
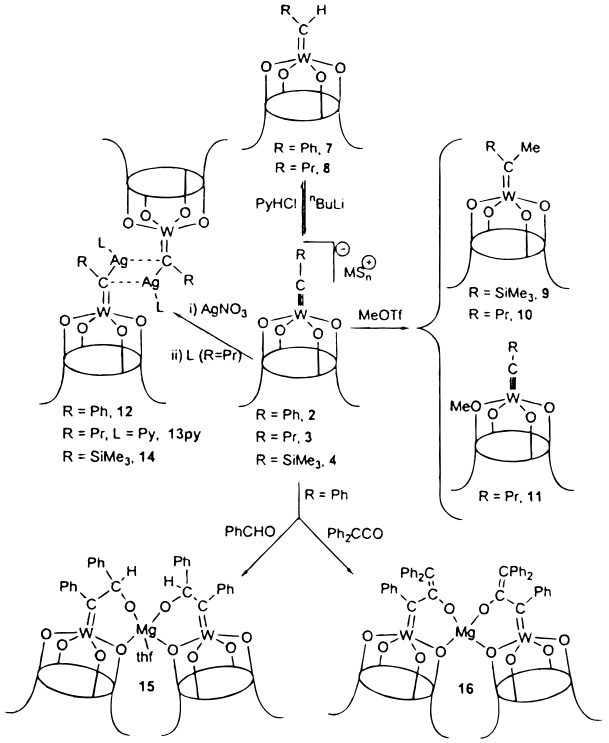


Figure 3. A SCHAKAL view of complex **7**. Disorder affecting the butyl groups associated with the A and B rings has been omitted for clarity.

Scheme 2



H(51)···O(1), 2.59 Å; C(51)−H(51)···O(1), 132.6°. The calix[4]arene unit assumes an elliptical cone section (see Table 4), W protruding out of the O_4 plane by 0.359(1) Å.

The reaction of **4** with MeOTf, known to be a powerful source of Me^+, led to the isolation of the alkylidene **9** (Scheme 2), which was fully characterized, including a crystal structure shown in Figure 4.

The coordination polyhedron is a trigonal elongated bipyramid involving the O(1), O(3), and C(45) atoms in the equatorial plane and the O(2) and O(4) atoms at the axial positions. The main structural features are similar to those observed in **7**: (i) the O_4 core shows significant tetrahedral distortions with tungsten displaced by 0.384(1) Å toward the C(45) atom (Table 4); (ii) the four W−O bond lengths are different, the mean value of the W−O(1) and W−O(3) distances [1.861(11) Å] being significantly shorter than the mean value of the W−O(2) and W−O(4) distances [1.971(8) Å]; (iii) the W−C(45) [1.914(10) Å] bond length is close to that in **7** (Table 2).

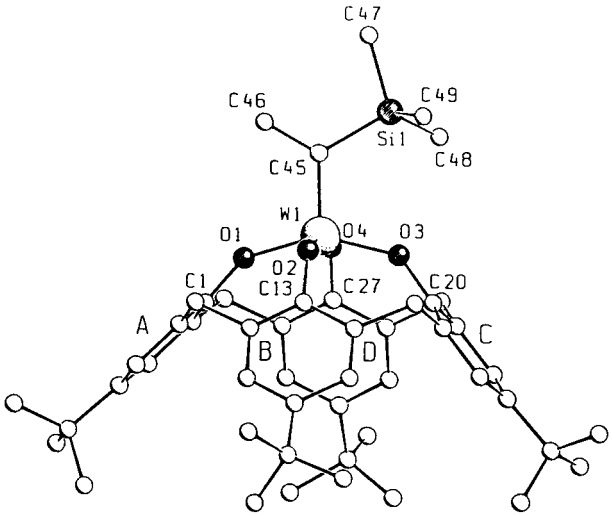


Figure 4. SCHAKAL view of complex **9**. Disorder affecting the butyl groups associated with the B and D rings has been omitted for clarity.

The reaction with MeOTf was not as clean as that with PyHCl: another product of lower symmetry was detected by ^{1}H NMR in the reaction mixture. Performing the same alkylation reaction on **2** or **3** we obtained mixtures of two products, in similar amounts, of apparent C_{4v} and of C_s symmetry (NMR). The regiochemistry of the alkylation with MeOTf seems to depend mainly on the alkylidene: the ratio of the two products was almost the same performing the reaction at room temperature or at −80 °C. The mixture of the two products **10** and **11** obtained in the alkylation of **3** was characterized by NMR methods. **10** is the analogue of **9**. The alkylidene carbon fell at 293 ppm, with a J_{CW} of 177 Hz, while the methyl group gave a signal at 28.4 ppm in ^{13}C NMR and at 5.52 ppm in ^{1}H NMR; the latter exhibited cross-peaks with signals from the Pr residue in a TOCSY (^{1}H−^{1}H) experiment.[25] Complex **11** showed a C_s symmetry, with three signals for the Bu^t (2:1:1) and two pairs of doublets for the bridging methylenes in ^{1}H NMR. The alkylidyne carbon fell at 301.7 ppm, with a J_{CW} of 278 Hz, while the methoxy group gave a signal at 80.7 ppm in ^{13}C NMR and at 5.12 ppm in ^{1}H NMR; the latter did not show any cross-peak with signals from the Pr^n residue in a TOCSY (^{1}H−^{1}H) experiment.[25]

A synthetically useful derivatization of the anionic alkylidynes **2**−**4** would be their metalation, which, in the present case, was performed using the carbophilic Ag^+. A different kind of M≡C metalation reaction leading to dimetallacyclopropenes, rather than to the class of compounds here mentioned, has been reported.[26] Complexes **2**−**4** reacted with $AgNO_3$ to give **12**−**14** (Scheme 2). Elemental analysis first indicated the successful exchange of Li^+ or Mg^{2+} with Ag^+. The ^{1}H NMR of the three species was similar to those of the respective starting materials,

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

(26) (a) Clark, G. R.; Cochrane, C. M.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1980**, *199*, C35. (b) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89.

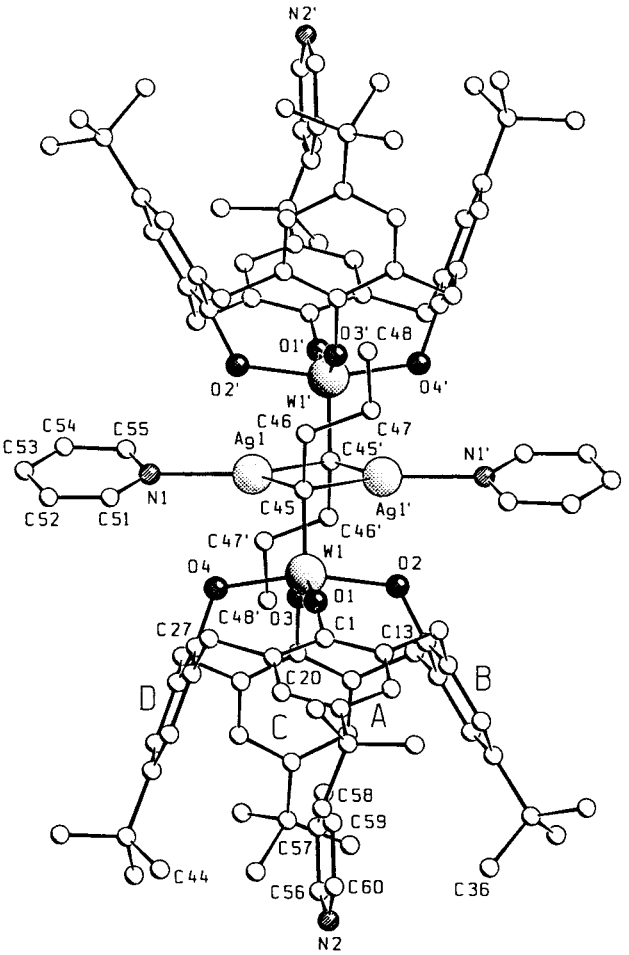


Figure 5. SCHAKAL view of complex **13py**. Disorder affecting the butyl groups associated with the A and C rings has been omitted for clarity. Prime denotes a transformation of $1 - x, -y, 1 - z$.

hence not very informative. Complex **12** was by far the most soluble of the three, so most of the spectroscopic work was done on it.

The ^{13}C NMR spectrum of **12** in noncoordinating solvents showed a broad triplet at 241 ppm, which was attributed to the coupling of the alkylidene carbon with two equivalent (on the NMR time scale) Ag^+ ions (J_{Cag} = 59−60 Hz). As a consequence, in solution the product must be at least a dimer, but most likely a tetramer, given the preference of Ag^+ for linear coordination.[27]

X-ray analysis of the pyridine solvate **13py** showed the latter to be a dimer (Figure 5), where two silver ions bridge two alkylidene fragments and are further coordinated by a pyridine molecule. Planar trigonal coordination has commonly been encountered in Cu^+ and Ag^+ alkyl/aryl species in the presence of N-donors.[27]

Complex **13py** crystallizes as a centrosymmetric dimer, hosting a pyridine molecule in each aromatic cavity. The calix-[4]arene assumes an elliptical cone conformation, W protruding of 0.404(1) Å from the $\{O_4\}$ core (maximum deviation from planarity 0.18 Å) (Table 4). The W−O bond distances fall within the range of values observed for the present compounds (Table 3), the shortest distance [W−O(1), 1.872(5) Å] corresponding to the largest bond angle [W−O(1)−C(1), 162.2(4)°]. The polyhedron coordination could be described as a trigonal

(27) Van Koten, G.; James, S. L.; Jastrzebski, B. H. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 3; Chapter 2.

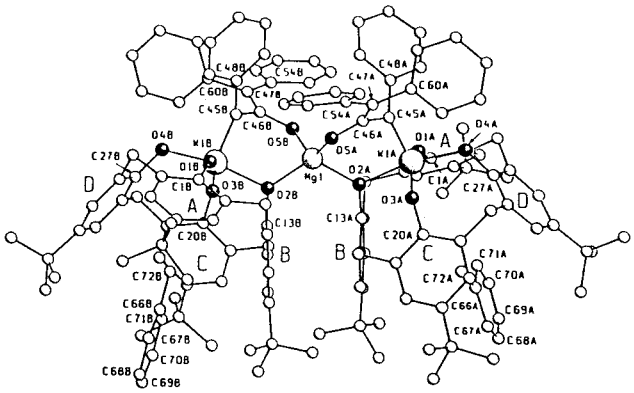


Figure 6. SCHAKAL view of complex **16**. Disorder affecting the butyl groups associated with the C ring (molecule A) and the A and C rings (molecule B) has been omitted for clarity.

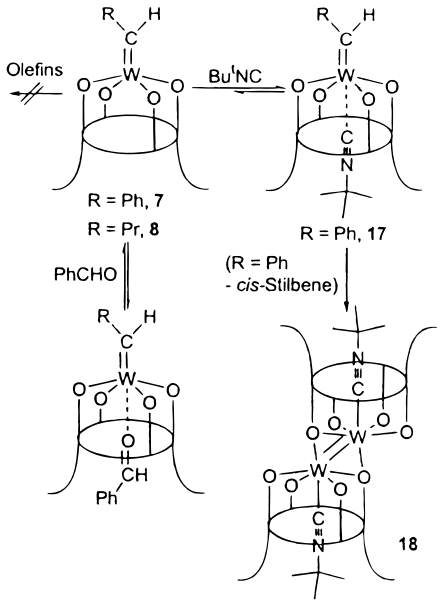
elongated bipyramid involving the O(1), O(3), and C(45) atoms in the equatorial plane and the O(2) and O(4) atoms at the axial positions. The W−C distance is 1.832(5) Å, and the angle W(1)−C(51)−C(52) is 145.83(56)°. These parameters are close to those corresponding to an alkylidene, as expected given the high carbophilicity of Ag^+. The silver cations behave as asymmetric bridges [W−C(45), 2.312(6) Å vs W−C(45′), 2.562(6) Å]. The resulting Ag_2C_2 inner core, which is planar from symmetry requirements, is sandwiched between parallel O_4 cores [dihedral angle $Ag_2C_2 \wedge O_4$, 8.0(1)°]. The silver cation achieves a trigonal coordination through the N1 nitrogen atom from a pyridine molecule.

The mode of Ag^+ coordination, and hence the nature of the complex can be modified by added ligands. The silver derivatives did not seem to retain an aggregated structure in neat pyridine: both **12** and **13** exhibited a singlet at 265−270 ppm in their ^{13}C NMR in Py-d_5. In the case of **12**, J_{CW} was determined: its value, 256 Hz, is typical of alkylidyne species.[20,24] It should be noted that the color changed from red to yellow when **12** was dissolved in pyridine (the parent alkylidyne **2** is yellow, the parent alkylidene **7** brown).

Alkylidynes can also react with neutral electrophiles, such as a carbonylic functionality, provided it is sterically accessible. The reaction between **2** and benzaldehyde (Scheme 2) illustrates the possibility of using anionic alkylidynes as organometallic Grignard reagents. **15** has a rigid structure, as shown by the lack of symmetry in NMR, even in Py-d_5 (where in any case THF is exchanged). The alkylidene carbon falls at 291 ppm; the former carbonyl carbon of the benzaldehyde moiety gives a signal at 79.3 ppm and is bound to the H giving the singlet at 10.2 ppm in ^1H NMR (HSQC).[25] The proposed structure of **15** (Scheme 2) is also supported by the crystal structure of **16**, obtained in an analogous reaction of **2** with diphenylketene. Possibly because of the steric demand of the CPh_2 group, **16** is rather fluxional in solution, and a good ^1H NMR, indicating the C_s symmetry of the complex, could only be obtained at low temperature (253 K).

The structure of **16** consists of two crystallographically independent anions (called A and B) bridged by a magnesium cation (Figure 6). Magnesium is tetrahedrally coordinated to the calix[4]arene O(2) oxygen atoms and the O(5) enolato oxygen atoms from the two anions. The two independent anions have similar geometry. Thereafter the values refer to the anion A. Values for molecule B are given in Supporting Information. The O_4 core is tetrahedrally distorted with tungsten protruding by 0.357(2) Å from the mean plane toward the C(45) atom (Table 4). The trend of bond distances and angles in the

Scheme 3



coordination sphere (Table 3) is similar to that observed in **7** and **9** (Table 2). So the coordination polyhedron around tungsten could be described as an elongated trigonal bipyramid having the O(1), O(3), and C(45) atoms in the equatorial plane and the O(2) and O(4) atoms at the axial positions. The calix[4]arene skeleton assumes a very pronounced elliptical cone section (Table 4). The geometry of the alkylidene ligand [W−C(45), 1.908(6) Å] is consistent with the presence of a localized C(46)−C(47) double bond [1.352(8) Å] and a O(5)−C(46) single bond [1.297(8) Å] (Table 3).

Endo Coordination and Labilization of Alkylidenes. Whereas the negatively charged alkylidynes do not seem to have any affinity for Lewis bases (nor any metathesis activity toward acetylenes), alkylidenes **7** and **8** coordinated suitably shaped bases, such as benzaldehyde and Bu^{t}NC, as outlined in Scheme 3.

Complexes **7** and **8** were inert with linear olefins but formed labile complexes with PhCHO, as shown by a shift and broadening of the PhC*H*O signal, by a (smaller) shift of the alkylidene proton in the ^{1}H NMR, and above all by IR spectra of solutions of PhCHO and **7** or **8** in a 1:1 ratio, where the band of the CO stretching of free PhCHO at 1705.8 cm^{-1} was accompanied by two other bands at 1683.4 and 1660 cm^{-1}, which could be assigned to coordinated PhCHO.[28] Solutions **7**, **8**, and PhCHO were fairly stable at room temperature for 24 h.

It is worth mentioning that complexes of the kind [(RO)$_n$-(X)$_{4-n}$W=CRR′] readily react with aldehydes and, especially for n = 4, also with ketones, esters, and amides to give metathesis products.[29] It is generally accepted that the most acidic site in a five-coordinate W alkylidene complex is the one trans to the multiply bonded ligand.[22a] With monodentate ligands, the adduct can rearrange to place the incoming ligand cis to the alkylidene, making metathesis possible.[7] We might assume that using {*p*-Bu^t-calix[4]arene−(O)$_4$}$^{4-}$ as the supporting ligand, the incoming, potentially reactive, ligand is trapped in the trans position. This might explain the exceptionally low Wittig-type reactivity of our alkylidenes.

The reaction of **7** and Bu^{t}NC was studied in some detail. The addition of a stoichiometric amount of Bu^{t}NC to a solution of **7** led to the isolation of a 1:1 adduct, **17**, whose IR in toluene solution showed, together with a band at 2195 cm^{-1}, corresponding to coordinated Bu^{t}NC, also a smaller band at 2132 cm^{-1}, corresponding to free Bu^{t}NC, proving the reversibility of Bu^{t}NC complexation. In the ^{1}H NMR spectrum of **17** at room temperature, the signals of the substituents of the alkylidene carbon, the Bu^{t}NC, and the *endo*-CH$_2$ were severely broadened. Adding an excess of Bu^{t}NC to the NMR sample, a sharp spectrum (except for the Bu^{t}NC signal) was obtained. The main difference with respect to the one of the free **7** is the chemical shift of the W=C(*H*)Ph, which moved 1.2 ppm to higher fields. At low temperature, without the addition of excess Bu^{t}NC, a similar sharp spectrum was obtained for complex **17**, coordinated Bu^{t}NC giving a sharp singlet at −0.21 ppm, very close to the value observed for the analogous η^2-ethylene complex (−0.11 ppm).[12] The trend of spectroscopic data and the analogy with η^2-olefin complexes led to the conclusion that Bu^{t}NC coordinates the complex in the endo position, trans to the multiply bonded carbon group. Extended Hückel calculations, reported in the following, showed that cis coordination is unlikely.

Solutions of **17** changed slowly at room temperature (the reaction was faster when excess Bu^{t}NC was present) to give the edge-sharing dimer **18** (Scheme 3). In the reaction mixture, *cis*-stilbene (and not the more stable trans isomer) was detected by gas chromatography, proving a bimolecular decomposition path. Complex **18** was also obtained by reacting **8** and Bu^{t}NC.

The bimolecular decomposition of an alkylidene to give an olefin and a reduced metal species was firmly established as early as 1978 by Schrock.[30] What is new here is that the alkylidene in itself is (surprisingly) stable vs this kind of reaction and is labilized ("activated") by the trans ligand.

Complex **18** is diamagnetic in solution and exhibits a C_s ^{1}H NMR spectrum. Bu^{t}NC falls at −0.03 ppm, typical of this ligand when bound to W in the endo position, inside the calix[4]arene cavity. The metal−metal double bond (W−W distance 2.5827(8) Å; W−O2′−W′ acute angle, 79.04(26)°) makes W(IV) a net electron acceptor, as shown by the high value of the C−N stretching in the IR spectrum (2203 cm^{-1}). Complex **18** was best obtained by coordination of Bu^{t}NC to the product of photochemical decomposition of [{*p*-Bu^t-calix[4]−(O)$_4$}-W(η^2-C$_2$H$_4$)], as discussed elsewhere,[11b] together with full crystallographic details.

Oxidation of Alkylidynes. The one-electron, outer-sphere oxidation of **2**−**4**, performed with Cp$_2$FeBPh$_4$, gave rise to carbon-centered radical species, [{*p*-Bu^t-calix[4]−(O)$_4$}-W=C·(R)],[31] which, according to the nature of R and reaction conditions, could either abstract a H atom (probably from the solvent) to give the corresponding alkylidenes or couple to give a C−C bonded species. For R = Ph (Scheme 4) the reaction was quite clean, leading to the alkylidene **7** when performed at −15 °C and to complex **19** at 0 °C in Et$_2$O.

The structure of complex **19** contains two crystallographically independent [{*p*-Bu^t-calix[4]−(O)$_4$}W] fragments (A, B) bridged by a μ^2-η^2:η^2-Ph$_2$C$_2$ (Figure 7). The W···W distance [3.317(5) Å] rules out any possible metal−metal interactions. The four W−C distances [mean value, 2.085(2) Å], which are not significantly different, along with the single bond character of

(28) For aldehyde and ketone complexation, see: Cozzi, P. G.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Chem. Ber.* **1996**, *129*, 1361.

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(30) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

(31) (a) McElwee-White, L. *Synlett* **1996**, 806. (b) Main, A. D.; McElwee-White, L. *J. Am. Chem. Soc.* **1997**, *119*, 4554. (c) Schoch, T. K.; Orth, S. D.; Zerner, M. C.; Jørgensen, K. A.; McElwee-White, L. *J. Am. Chem. Soc.* **1995**, *117*, 6475. (d) Torraca, K. E.; Storhoff, D. A.; McElwee-White, L. *J. Organomet. Chem.* **1998**, *554*, 13. (e) Torraca, K. E.; Abboud, K. A.; McElwee-White, L. *Organometallics* **1998**, *17*, 4413.

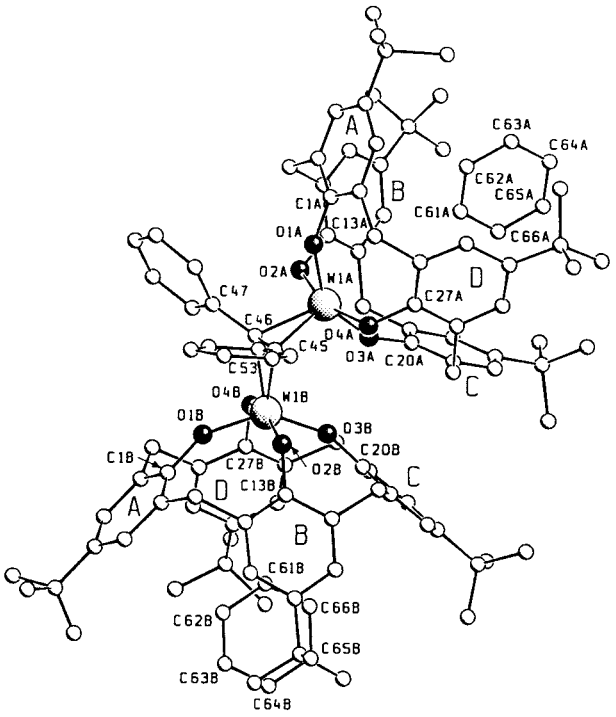
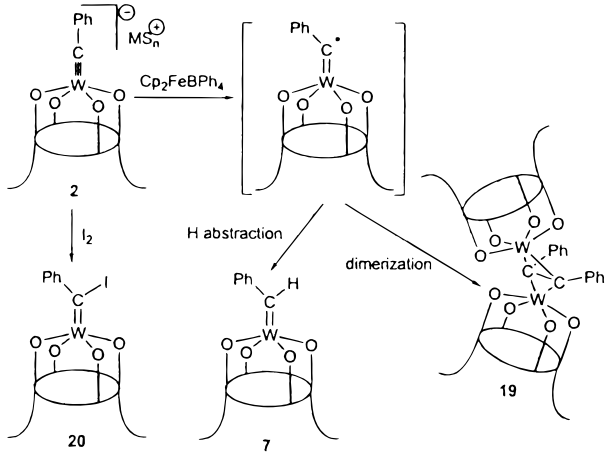


Figure 7. SCHAKAL view of complex **19**. Disorder affecting the butyl groups associated with the A, B, and C rings (molecule A) and the A ring (mol B) has been omitted for clarity.

Scheme 4



C(45)−C(46) [1.439(8) Å] suggest a bismetallacyclopropane structure. The two independent [{*p*-Bu^t-calix[4]−(O)$_4$}W] moieties show a very close geometry. Thereafter, the values refer to the fragment A. Values for molecule B are reported in Supporting Information. The O_4 core is tetrahedrally distorted with tungsten protruding by 0.454(1) Å from the mean plane toward the μ-C_2 bridge. The W, C(45), and C(46) plane is perpendicular to the O_4 mean plane, the dihedral angle between them being 95.2(2)°. The trend of bond distances and angles in the coordination sphere (Table 3) is similar to that observed in **7**, **9**, and **16** (Tables 2 and 3). So the coordination polyhedron could be described as an elongated trigonal bipyramid having the O(1), O(3), and C(45) atoms in the equatorial plane and the O(2) and O(4) atoms at the axial positions, with the calix[4]-arene unit having an elliptical cone conformation (Table 4).

The oxidation of complex **2** (Scheme 4), performed with I_2, led to the clean isolation of halogen-substituted alkylidene **20**,[32] which exhibited a characteristic[1,6] signal in ^{13}C NMR at 230 ppm with a coupling constant to ^{183}W of 212 Hz. The structure sketched in Scheme 4 is supported by a preliminary X-ray analysis.

Discussion

Chemical Considerations. In the basis of the synthetic sequence ending to the anionic W-alkylidynes, we are not able to discriminate between the two major mechanisms, namely, between the reductive alkylation followed by the alkylation of the reduced species with loss of H_2, and a stepwise α-elimination. Although some data are in favor of the latter, both could occur simultaneously. The observed dependency of the alkylation pathway on the nature of the alkylating agent (Zn vs Mg and Li) and on the reaction solvents clearly indicates that both factors can affect more or less the carbanionic nature and by consequence the reducing properties of the reagent. However, regardless of the alkylation pathways, the reactions in Scheme 1 show how the preorganized $[O_4]^{4-}$ ligand preferentially drives the formation of W−C multiple bonds as compared with the simple W−alkyls. This fact is the consequence, as in Schrock's triamidoamine ligands,[18c] of the appropriate set of frontier orbitals at the metal ready to form a σ- and two π-bonds.

However, the $[O_4]^{4-}$ ligand clearly has introduced two novelties in metal−alkylidyne chemistry: (i) the formation of anionic species; (ii) the assistance of the oxygen donor atoms in driving the alkylidyne reactivity. The alkylidyne derivatives **2**−**4** have two potential basic sites which can be engaged in the reaction with protons or, in general, with electrophiles (Scheme 2): the alkylidyne carbon and the oxygens from the calix[4]arene moiety. Protonation occurs selectively on carbon (Scheme 2), while the alkylation, depending on the alkyl substituent, does not discriminate very much and, eventually, both kinds of compound (see complexes **9** and **11** in Scheme 2) can be obtained. We do not know which one of the controlling factors, the charge or the frontier orbital set, is prevailing in either reaction (see below). However, we believe that both protonation and alkylation may involve the assistance of the oxygen. In support of this hypothesis, a significant structural feature of **7** should be emphasized, namely, the interaction of the proton from the alkylidene carbon interacting with one of the calix[4]arene oxygens.

In addition, we should mention that the possibility of interconverting alkylidyne−alkylidene by protonation−deprotonation is due to the very high stability of the macrocyclic structure of the $[O_4]^{4-}$ unit. In all cases so far reported, such a reaction affects the ancillary ligands, with considerable changes in the coordination sphere of the metal.[22]

The extension of the reaction to electrophiles other than H^+ and R^+ may be considered a synthetic methodology to otherwise inaccessible functionalized metal−alkylidenes. In the specific case of the reaction with PhCHO and $Ph_2C{=}C{=}O$, the regiochemistry (see complexes **15** and **16** in Scheme 2) is controlled, among other factors, by the oxophilicity of the countercation Mg^{2+}, which has a particular preference for the alkoxo and enolato ligands. A remarkable access to functionalized alkylidene complexes[22c−f] comes from the oxidation of anionic alkylidynes with I_2 leading to the iodo−alkylidene **20** (Scheme 4).[32] The iodo derivative could undergo substitution reactions with nucleophiles, thus introducing heteroatoms in the alkylidene

(32) For haloalkylidene complexes, see: (a) Reference 19c. (b) Huang, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 3185. (c) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293. (d) Morrison, J. A. *Adv. Organomet. Chem.* **1993**, *35*, 211. (e) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553. (f) Mansuy, D.; Lange, M.; Chottard, J. C.; Bartoli, J. F.; Chevrier, B.; Weiss, R. *Angew. Chem.* **1978**, *90*, 828.

backbone. While the former strategy serves more to introduce functionalities into the β-position, the latter one could be employed to introduce functionalities into the α-position of the alkylidene. [{*p*-Bu^t-calix[4]−(O)$_4$}W−alkylidenes] **7** and **8** display a quite low reactivity, exemplified by the formation of an adduct with benzaldehyde, which does not easily undergo a metathesis reaction. A quite unusual labilization of the W═C double bond can however be achieved in the reaction with Bu^t-NC, leading to the loss of the carbene fragment (see Scheme 3, **17** and **18**). Such a kind of induced and nonspontaneous labilization could be particularly useful if it was necessary to keep the functionality stable in the presence of a substrate and then subsequently to induce its reactivity. The labilization reaction could make it possible to transfer functionalized alkylidenes to appropriate organic substrates.

A reaction that is strictly related to the anionic nature of the reported alkylidynes is the one-electron oxidation, leading to the free-radical species shown in Scheme 4. The free radical can be intercepted by the solvent via an hydrogen transfer or dimerizes to **19**. The latter event is particularly interesting since it suggests, in the case of success of the reverse reaction, the synthesis of alkylidynes and alkylidenes from acetylenes, and, better, the access to metal−carbido derivatives.

Extended Hückel Analysis. Extended Hückel calculations[33] were performed to elucidate the electronic structure of the [{*p*-Bu^t-calix[4]−(O)$_4$}W−alkylidynes], their reaction pathway with protons and electrophiles, and some aspects of their redox chemistry. The calix[4]arene ligands have been slightly simplified by replacing the Bu^t groups and the methylene bridges by hydrogens and symmetrizing to a C_{4v} or C_{2v} local symmetry. This simplified model retains the main features of the whole ligand; in particular, the geometrical constraints on the O_4 set of donors atoms is maintained by fixing the geometry of the four phenoxo groups to the experimental X-ray structural parameters.

The electronic structure of the alkylidyne compounds **2**−**4** and the alkylidene compounds **7** and **8** has been analyzed using as model complexes [(calix)W≡CMe)]$^-$ and [(calix)W═C(H)-Me)], respectively.[34]

The frontier orbitals of the [W(calix)] fragment consist of four low-lying metal d orbitals, as shown on the left in Figure 8. For a symmetrical C_{4v} geometry, the lowest energy metal orbital is a $1a_1(d_{z^2})$, with the degenerate $1e(d_{xz},d_{yz})$ ∼0.5 eV above. Due to the π-interactions with the oxygen atoms, the $1a_2(d_{xy})$ orbital lies 1.0 eV higher in energy. The $d_{x^2-y^2}$, pointing more closely toward the oxygen ligands, are pushed high in energy.

Figure 8 illustrates the expected bonding interactions of the [W(calix)] fragment with the CMe moiety,[34a] i.e., between the $1a_1(d_{z^2})$ and the σ-donor $1a_1$ of CMe and between the two metal degenerate orbitals of the 1e set (d_{xz}, d_{yz}) and those of the π-acceptor 1e set (p_x, p_y).

These electron-rich anionic alkylidynes easily undergo reactions with electrophiles. The regiochemistry of the electrophilic attack may be determined by both charge and frontier orbital factors, and charge effects are expected to be important for these anionic alkylidyne species, especially when hard electrophiles such as H^+ or Me^+ are considered.[35] The results of the Mulliken

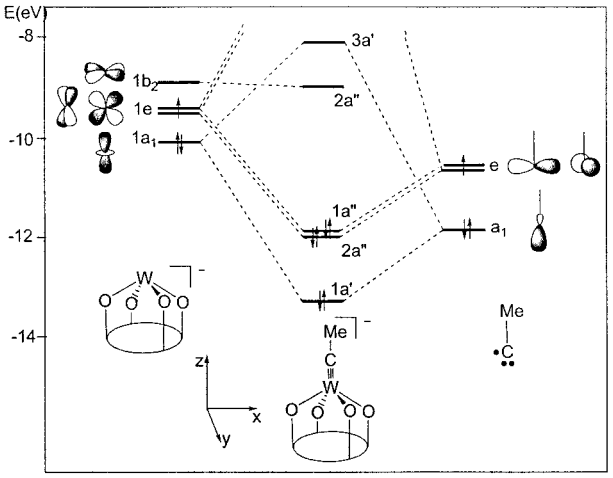


Figure 8. Molecular orbital interaction diagram for [(calix)W≡CMe]$^-$.

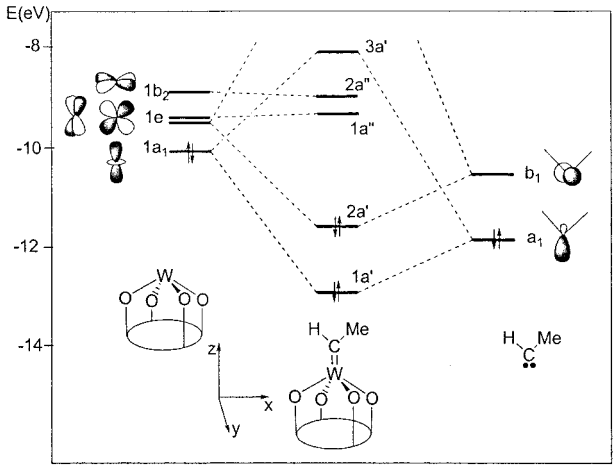


Figure 9. Molecular orbital interaction diagram for [(calix)W═C(H)-Me].

population analysis on [(calix)W≡CMe]$^-$ show that the oxygen atoms and the alkylidyne carbon have by far the highest negative charges with almost equal values (−0.99 and −0.97) so that the incoming electrophiles are expected to attack both oxygen and carbon. This hypothesis agrees well with the regiochemisty experimentally observed for Me^+ attack, as the reaction of **2**−**4** with MeOTf leads to a mixture of both alkylidenes (resulting from C-attack) and O-methylated alkylidynes (resulting from O-attack). The protonation of **2**−**4** with PyHCl leads exclusively to alkylidenes, but this result could be due to the high mobility of the proton which may migrate easily from the oxygen to the carbon atom giving the most stable products. On the other hand, when a soft electrophile such as Ag^+ is considered, frontier orbital factors are expected to prevail,[35] so that the regiochemistry is determined by the high-lying HOMO, which has a W−C π-character, more localized on the carbon atom. The regiochemisty observed for the reaction of **2**−**4** with $AgNO_3$ in fact leads to the silver−alkylidene species **12**−**14**.

Figure 9 illustrates the bonding interactions in the [(calix)-W═C(H)Me] alkylidene.[34b] At variance with the alkylidyne, the π-interaction with the C(H)Me moiety engages only one of the two d_π orbitals, d_{yz}, which is no longer available to the π-donation from the calix[4]arene oxygens, thus W−O bonds are single in the *yz* plane (perpendicular to the alkylidene unit). On the other hand, the π-donation from the oxygens in the *xz* plane to the d_{xz} metal orbital confers to W−O bonds in the latter plane double bond character, thus explaining the strong C_{2v}

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(34) For analogous MO calculations on M═C and M≡C bonds, see: (a) Reference 2, Chapter 3. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; VCH: Weinheim, Germany, 1988; Chapter 4; pp 113−149.

(35) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*, Wiley: London, U.K.; 1976.

distortion of the [W(calix)] unit observed in the X-ray structure of **7** and **9**.

It is also worth noting that, in the [W(calix)] fragment, the presence of two orthogonal d_π orbitals, equally available for interaction with the π-system of the C(H)Me organic fragment, suggests a small activation barrier for the alkylidene rotation around the *z*-axis. Extended Hückel calculations with the organic fragment rotated by 45° with respect to the *xz* plane gave an estimated energy barrier of 3 kcal mol^{-1}. The expected free rotation of the alkylidene is supported by the ^{1}H NMR of **7** and **8**, indicating an apparent C_{4v} symmetry of the calix[4]arene moiety.

The coordination of the H−N≡C trans to the alkylidene unit leads to a strong destabilization of the d_{z^2} orbital (interacting with the carbon lone pair of CNH) and a significant stabilization of the two d_{xz} d_{yz} orbitals (due to their interactions with the empty π*-orbitals of CNH). Both effects lead to a higher energy mismatch between these metal orbitals and the interacting counterparts on the alkylidene unit and thus to a labilization of the metal−alkylidene bonding.

We finally considered the one-electron oxidation of the alkylidyne **2** and the corresponding C−C coupled species **19**. The orbital diagram of the methyl alkylidyne reported in Figure 8 shows that the HOMO is the doubly degenerate 1e orbital, describing the tungsten−carbon π-bonding, which is mainly localized on the carbon atom. The one-electron oxidation of these alkylidynes species leads therefore to carbon-centered radicals, in agreement with the experimentally observed coupling to the C−C bonded compound **19**.

Conclusions

The calix[4]arene macrocyclic tetraanion provides a unique chemical environment for tungsten involved in organometallic chemistry. We should emphasize the consequences on the chemical reactivity of the metal center. The metal frontier orbitals in such an environment are particularly appropriate for stabilizing M−C multiple bonds and, particularly, the alkylidyne functionality.[18c] Due to the tetraanionic nature and the macrocyclic stability of the ancillary ligand, some unique chemistry has been developed on the anionic alkylidynes: (i) the interconversion to the corresponding alkylidenes obtained via the reversible protonation−deprotonation reaction. Such a reaction may have the assistance of the basic oxygens of the coordination environment, as with the heterogeneous catalysts; (ii) the introduction of a variety of functional groups at the alkylidene carbon via the reaction with electrophiles, which is a novel synthetic methodology for obtaining unprecedented alkylidenes containing functional groups; (iii) the metalation leading to the formation of dimetallic alkylidenes; (iv) the one-electron oxidation leading to the oxidative coupling of the alkylidyne functionalities to the corresponding bridging acetylenes.

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Supporting Information Available: Details of the X-ray data collection, structure solution, and refinement; ORTEP or SCHAKAL drawings, tables giving crystal data, fractional atomic coordinates, anisotropic and isotropic thermal parameters, bond lengths, and bond angles for complexes **2**, **4**, **7**, **9**, **13py**, **16**, and **19** (PDF). Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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