copper-zinc reagents **2** also display an interesting chemoselectivity, and the reaction of **2e** with 4-ethyl-4-formylhexanenitrile gives as the sole product the cyano amino alcohol **5i** (entry 9). Substituted reagents like **2f** react regioselectively with aldehydes, giving mostly the "branched" allylated product **5** (branched/linear: 94/6; entry 10).

In conclusion the methylene homologation of vinylic copper compounds by (iodomethyl)zinc iodide allows the preparation of various new allylic zinc and copper reagents which were found to react efficiently with several classes of electrophiles. The extension of this methodology is currently underway in our laboratories.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8818704) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 5a, 127998-28-1; **5b**, 127998-29-2; **5c**, 127998-30-5; **5d**, 127998-31-6; **5e**, 125315-69-7; **5f**, 127998-32-7; **5g**, 127998-33-8; **5h**, 127998-34-9; **5i**, 127998-35-0; **5j** (isomer 1), 127998-36-1; **5j** (isomer 2), 127998-38-3; (*E*)-**6j**, 127998-37-2; (*Z*)-**6j**, 127998-39-4; $H_2C{=}C(Br)CH_2$-*c*-C_6H_{11}, 53608-85-8; $PhSi(Me)_2CH_2C(Br){=}CH_2$, 122244-66-0; $H_2C{=}C(Br)CH_2N(Et)_2$, 13249-59-7; $C_5H_{11}CHO$, 66-25-1; $PhCH{=}NCH_2Ph$, 780-25-6; HCO_2Et, 109-94-4; PhCHO, 100-52-7; $NC(CH_2)_2C(Et)_2CHO$, 2938-69-4; $PhC(Br){=}CH_2$, 98-81-7; $C_6H_{13}CH{=}CHBr$, 1119-88-6; $H_2C{=}C(Br)CH_2Br$, 513-31-5; iodocyclohexane, 626-62-0; 2-(2-bromoethyl)-1,3-dioxane, 33884-43-4; phenyldimethylchlorosilane, 768-33-2; diiodomethane, 75-11-6; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; 2-(4-bromo-4-pentenyl)-1,3-dioxane, 127998-40-7.

Supplementary Material Available: Typical procedure and spectral data for new compounds (6 pages). Ordering information is given on any current masthead page.

Protonation of Alkylidyne(carbaborane)tungsten Complexes: Framework Rearrangement of an Icosahedral Cage at an Unprecedentedly Low Temperature

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Alkylidyne-metal complexes[1] and carbametallaboranes[2] have played important roles in the development of organometallic and metal cluster chemistry, respectively. These two areas of research have converged as a result of the discovery of the salts [X][*closo*-1,2-Me_2-3-(≡CR)-3,3-$(CO)_2$-3,1,2-$WC_2B_9H_9$] (**1**, X = PPh_4, NEt_4, or $N(PPh_3)_2$; R = alkyl or aryl) in which a metal atom is ligated by an alkylidyne group while simultaneously functioning as a vertex of an icosahedral cluster.[3] The reagents **1** display novel chemistry due to the presence of the reactive CR fragment on the periphery of the closo cage. Herein we report protonation studies resulting in migration and hydroboration of the alkylidyne group. This process is accompanied by a framework rearrangement, which occurs at an unprecedentedly low temperature for an icosahedral carbametallaborane structure. Hawthorne and co-workers[4] have previously observed similar polytopal rearrangements of carbametallaborane cages. Thus treatment of [*exo-nido*-4,9-{$(Ph_3P)_2Rh$}-4,9-*μ*-$(H)_2$-7-Me-8-Ph-7,8-$C_2B_9H_8$] with excess PEt_3 affords [*closo*-1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$]. However, this process, itself uncommonly facile, requires heating the reagents in tetrahydrofuran.[4b]

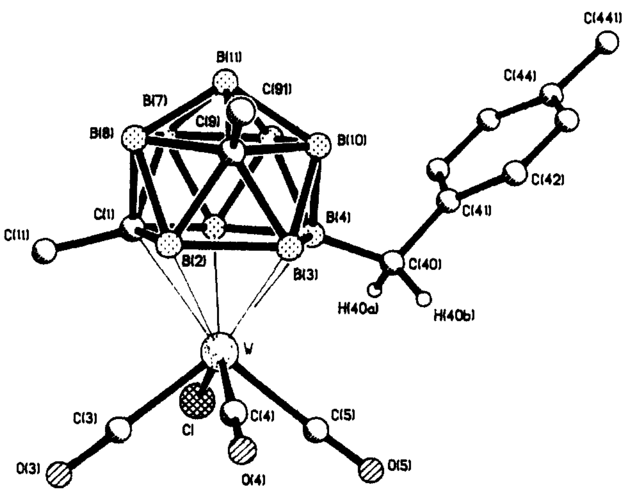
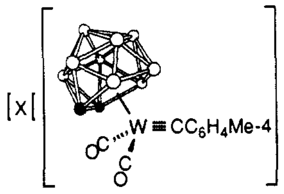
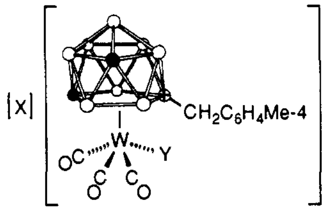


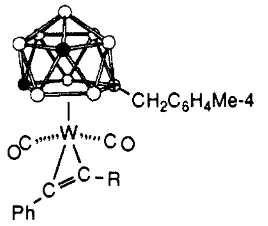
Figure 1. Structure of the anion [*closo*-1,8-Me_2-11-$(CH_2C_6H_4Me\text{-}4)$-2-Cl-2,2,2-$(CO)_3$-2,1,8-$WC_2B_9H_8]^-$ of **2b** showing the crystallographic numbering scheme. Selected distances (Å): W–Cl, 2.549 (2); W–C(1), 2.395 (7); W–B(2), 2.310 (7); W–B(3), 2.320 (7); W–B(4), 2.439 (6); W–B(5), 2.391 (7); B(4)–C(40), 1.62 (1); C(1)–B(2), 1.70 (1); C(1)–B(5), 1.72 (1); C(1)–B(7), 1.73 (1); C(1)–B(8), 1.73 (1); C(9)–B(2), 1.70 (1); C(9)–B(3), 1.72 (1); C(9)–B(8), 1.69 (1); C(9)–B(10), 1.70 (1); C(9)–B(11), 1.72 (1).



	X
1a	PPh_4
1b	NEt_4
1c	$N(PPh_3)_2$



	Y
2a	I
2b	Cl



	R
3a	Me
3b	Ph

● CMe ○ BH ⊕ B

A CH_2Cl_2 (20 mL) solution of **1a** (X = PPh_4, R = C_6H_4Me-4)[3a] (1.00 g, 1.19 mmol) was stirred rapidly at −78 °C and treated dropwise with 1 equiv of HI (57% aqueous solution). Successive IR measurements progressively indicated the course of the reaction, which was complete within 10 min.[5] Warming to ambient temperature and removal of solvent in vacuo to ca. 3 mL, followed

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(5) At ambient temperatures the reaction proceeds to completion before IR measurements can be made by standard techniques.

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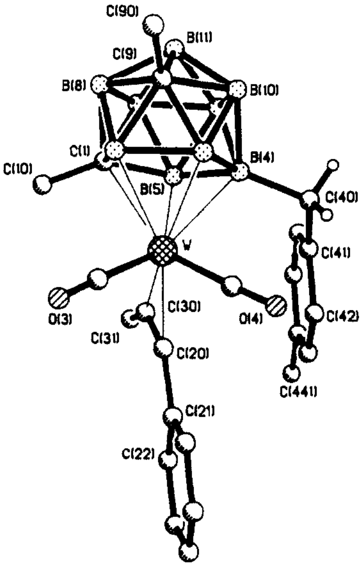

Figure 2. Molecular structure of [*closo*-1,8-Me_2-11-($CH_2C_6H_4Me$-4)-2-(η-MeC_2Ph)-2,2-$(CO)_2$-2,1,8-$WC_2B_9H_8$] (**3a**) showing the crystallographic numbering scheme. Selected distances (Å): W–C(1), 2.411 (4); W–B(2), 2.369 (6); W–B(3), 2.394 (7); W–B(4), 2.359 (5); W–B(5), 2.368 (4); W–C(20), 2.083 (5); W–C(30), 2.047 (5); B(4)–C(40), 1.621 (7); C(20)–C(30), 1.314 (5).

by chromatography on alumina and eluting the column with CH_2Cl_2, afforded orange [PPh_4][*closo*-1,8-Me_2-11-($CH_2C_6H_4Me$-4)-2-1-2,2,2-$(CO)_3$-2,1,8-$WC_2B_9H_8$] (**2a**) (0.56 g, 50% yield).[6] An analogous chloro compound (**2b**)[7] was obtained from **1b** and 36% aqueous HCl and its structure (Figure 1) established by X-ray diffraction.[8]

The tungsten atom in the anion is ligated on one side by three CO groups and a Cl atom and, on the other side, by the nido-icosahedral fragment in the usual pentahapto manner. However, unlike **1a**,[3b] the CMe groups in **2b** are not adjacent. Moreover, a boron atom in the face of the cage carries a $CH_2C_6H_4Me$-4 substituent. This group evidently arises from protonation of the alkylidyne ligand in the precursor, followed by insertion of the resulting alkylidene fragment into a cage B–H bond.

The salts **2** are likely to be useful reagents in further syntheses. Thus treatment of a CH_2Cl_2 (15 mL) solution of **2a** (200 mg, 0.20 mmol) with MeC≡CPh (100 mg, 0,86 mmol), followed by addition of $AgBF_4$ (40 mg, 0.20 mmol) in small portions, until the reaction was complete (IR), gave a dark mixture. Solvent was removed in vacuo, and the residue was chromatographed in hexane to yield a purple eluate. Reduction in volume to ca. 3 mL and cooling to −20 °C afforded purple crystals of [*closo*-1,8-Me_2-11-($CH_2C_6H_4Me$-4)-2-(η-MeC_2Ph)-2,2-$(CO)_2$-2,1,8-$WC_2B_9H_8$] (**3a**) (0.12 g, 90% yield).[9] Complex **3b** was similarly obtained.[10] The structure of **3a** (Figure 2) was established by X-ray diffraction.[11]

The tungsten atom is coordinated by the 1,8-C_2B_9 cage fragment, as in **2b**, and by two CO groups and the MeC≡CPh molecule. In order for the metal atom to attain a filled 18-electron valence shell, the alkyne must function as a four-electron donor.[12] In agreement, in the $^{13}C\{^1H\}$ NMR spectra of **3a** and **3b** the ligated carbon atoms of the alkyne molecules resonate[9,10] in the expected range (ca. 180–230 ppm) for four electron donor alkynes.[13]

While the mechanism of addition of HCl or HI to the salts **1** and the facile rearrangement of the cage CMe groups has yet to be established, it appears that the anions [*closo*-1,2-Me_2-3-(≡CR)-3,3-$(CO)_2$-3,1,2-$WC_2B_9H_9$]$^-$ have a chemistry more diverse than that of their isolobal analogues [W(≡CR)$(CO)_2$(η^5-C_5H_5)].

Supplementary Material Available: Data for crystal structure analyses and tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and isotropic displacement parameters for **2b** and **3a** (17 pages); listing of observed and calculated structure factors for **2b** and **3a** (38 pages). Ordering information is given on any current masthead page.

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(6) For **2a**: IR (ν(CO) cm^{-1} in CH_2Cl_2) 2007 (vs), 1917 (br, vs); NMR (all in CD_2Cl_2 as $N(PPh_3)_2^+$ salt) ^1H δ 1.54, 1.89 (s × 2, 6 H, CMe), 2.19 (s, 3 H, Me-4), 2.40 (m br, 2 H, $CH_2C_6H_4Me$-4), 6.84, 6.86 ($(AB)_2$, 4 H, C_6H_4, J_{AB} = 9 Hz), 7.45–7.68(m, 30 H, Ph); $^{13}C\{^1H\}$ δ 231.3 (WCO, J_{WC} = 124 Hz), 221.2, 220.8 (WCO, J_{WC} = 65 Hz), 146.1, 131.8, 129.2, 126.9 (C_6H_4), 63.3, 61.9 (*C*Me), 32.9 (C*Me*), 32.1 (q br, BCH_2, J_{BC} ~ 70 Hz), 29.5 (C*Me*), 21.9 ppm (Me-4); $^{11}B\{^1H\}$ (rel $BF_3 \cdot Et_2O$ (external)) δ 4.13 (s, 1 B, BCH_2), −4.20 (m, 3 B), −8.20 (s, 1 B), 10.90 (m, 2 B), −12.91 (s, 1 B), −16.24 ppm (s, 1 B). Satisfactory elemental analyses for all compounds reported herein have been obtained.

(7) For **2b**: IR (ν(CO) cm^{-1} in CH_2Cl_2) 2013 (vs), 1916 (br, vs); NMR spectra similar to those of **2a**.

(8) Orange rhombs were obtained by slow diffusion of Et_2O into a THF solution of the complex at 0 °C. Crystal data: triclinic, space group $P\bar{1}$, a = 9.939 (4) Å, b = 11.974 (6) Å, c = 14.108 (6) Å, α = 96.41 (4)°, β = 90.43 (3)°, γ = 99.27 (3)°, Z = 2. An empirical absorption correction was applied to the data (4949 reflections with 3° ≤ 2θ ≤ 50°), which were collected on a Nicolet R3m/V diffractometer at 298 K in the θ–2θ scan mode using Mo Kα X-radiation. The structure was solved (R = 0.036, R_w = 0.036) by heavy-atom (Patterson and difference Fourier) methods and refined by full matrix least squares employing a DEC micro-Vax II computer and using the SHELXTL PLUS system of programs. The hydrogen atoms were constrained (C–H, 0.96 Å; B–H, 1.1 Å) and refined isotropically.

(9) For **3a**: IR (ν(CO) cm^{-1} in hexane) 2037 (vs), 1977 (vs); NMR (all in CD_2Cl_2) ^1H δ 1.776, 1.783 (s × 2, 6 H, CMe(C_2B_9)), 2.19 (s, 3 H, Me-4), 2.68 (s, 3 H, ≡CMe), 6.45, 6.71 ($(AB)_2$, 4 H, C_6H_4, J_{AB} = 8 Hz), 7.54–7.65 (m, 5 H, Ph); $^{13}C\{^1H\}$ δ 217.4, 214.5 (WCO), 207.2, 196.1 (Me*C*$_2$Ph), 142.6–128.5 (C_6H_4 and Ph), 70.9, 70.3 (*C*Me(C_2B_9)), 31.6 (Me), 30.3 (q br, BCH_2, J_{BC} ~ 100 Hz), 29.1, 20.9, 20.2 ppm (Me); $^{11}B\{^1H\}$ δ 11.22 (s, 1 B, BCH_2), −1.20 (s, 2 B), −2.25 (s, 1 B), −5.87 (s, 1 B), −7.82 (s, 1 B), −11.15 (s, 1 B), −12.77 (s, 1 B), −13.72 ppm (s, 1 B).

(10) For **3b**; NMR (all in CD_2Cl_2) ^1H δ 1.62, 1.78 (s, 6 H, CMe), 2.17 (s, 3 H, Me-4), 1.88, 2.22 ((AB), 2 H, CH_2B, J_{AB} = 14 Hz), 6.56, 6.73 ($(AB)_2$, 4 H, C_6H_4, J_{AB} = 8 Hz), 7.19–7.49 (m, 10 H, Ph); $^{13}C\{^1H\}$ δ 216.3, 213.4 (WCO), 203.0 (Ph*C*$_2$Ph, J_{WC} = 35 Hz), 142.4–128.3 (C_6H_4 and Ph), 70.9, 69.1 (*C*Me), 34.6, 32.0 (C*Me*), 30.5 (q br, BCH_2, J_{BC} ~ 80 Hz), 20.9 ppm (Me-4); $^{11}B\{^1H\}$ δ 11.07 (s, 1 B, BCH_2), −1.20 to −13.05 ppm (vbr, 8 B).

(11) Purple prisms of **3a** were grown from hexane at −20 °C. Crystal data: triclinic, space group $P\bar{1}$, a = 8.092 (2) Å, b = 11.019 (3) Å, c = 16.055 (5) Å, α = 73.89 (2)°, β = 75.40 (2)°, γ = 84.61 (2)°, Z = 2. Data collection and structure solution were as for **2b**; for 4694 reflections, R = 0.023 and R_w = 0.025.

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Vinylidenecyclohexadienone Acetals as Precursors of Arylvinyl Cations

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Although there have been many studies of vinyl cations in solvolytic reactions, there have been some restrictions on their generation because of the strong C–X bond of the precursors, for example, vinyl halides, which generally require both a high reaction temperature and a polar protic solvent for the cleavage of the C–X bond.[1] The use of triflates has solved much of the problem of the vinyl halides and has allowed the extensive development of the vinyl cation chemistry.[1,2] Relatively new methods, including photolysis[3] and nuclear decay,[4] have also been found to be useful

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