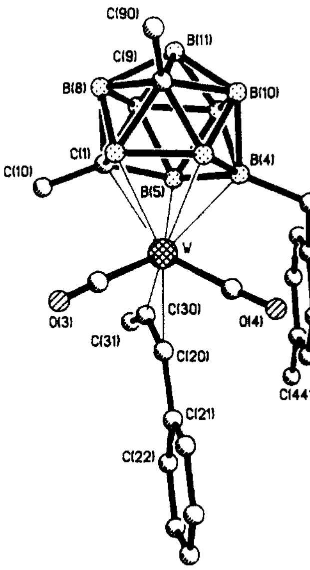

Figure 2. Molecular structure of [*closo*-1,8-Me_2-11-($CH_2C_6H_4$Me-4)-2-(η-MeC_2Ph)-2,2-$(CO)_2$-2,1,8-$WC_2B_9H_8$] (**3a**) showing the crystallographic numbering scheme. Selected distances (Å): W–C(1), 2.411 (4); W–B(2), 2.369 (6); W–B(3), 2.394 (7); W–B(4), 2.359 (5); W–B(5), 2.368 (4); W–C(20), 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-($CH_2C_6H_4$Me-4)-2-I-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 $CH_2C_6H_4$Me-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-($CH_2C_6H_4$Me-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, $CH_2C_6H_4$Me-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 $3° \leq 2\theta \leq 50°$), 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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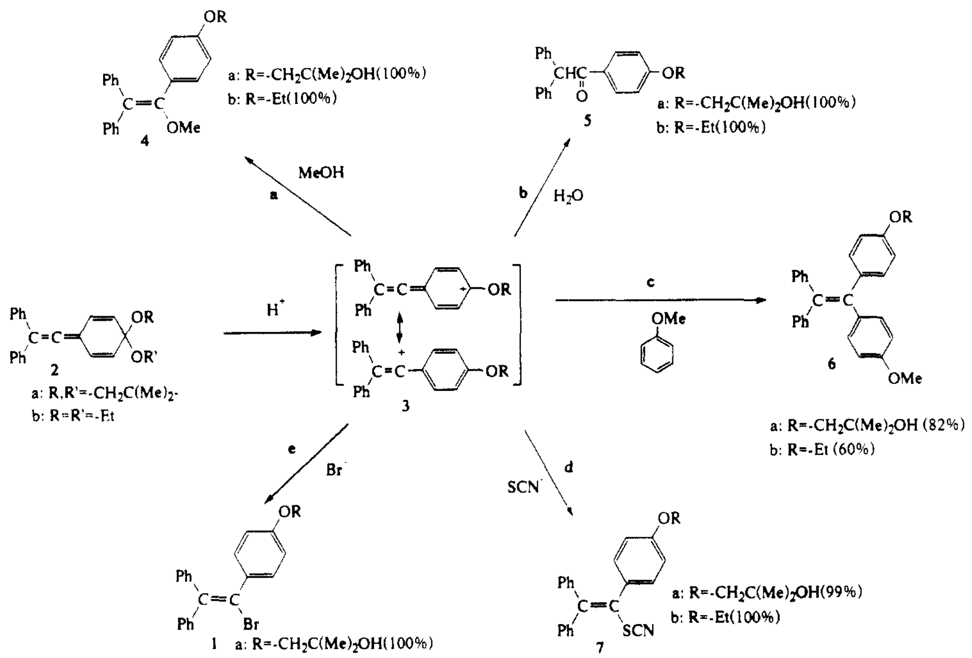
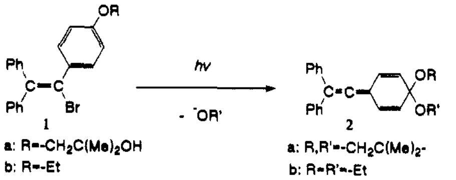
Scheme I



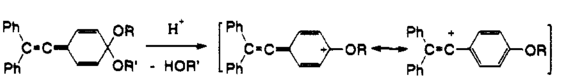
for generation of vinyl cations. Since these methods are applicable to the generation of unstable members of this family, including the parent,[4] α-unsubstituted,[3,5] and bent[3,5,6] vinyl cations, they are expected to have extensive application in mechanistic and synthetic studies.

In the course of our studies on photolysis of arylvinyl halides, we have found that ipso substitution occurs in arylvinyl cations[7] and the intermediate ipso adducts can be isolated by capture of alkoxide ion in the case of alkoxy groups as substituents.[8] Ipso



(1)

substitution in other destabilized benzylic cations has recently been reported.[9] The ipso adducts have a unique structure with acetal and *exo*-vinylidene components as reactive sites. Loss of one of the alkoxy groups from the ipso adduct results in re-formation of an arylvinyl cation, which can also react with nucleophiles.



(2)

Here we report a novel method for the generation of arylvinyl cations under *mild conditions* and the reactions of these cations with several nucleophiles. This method can be used for mechanistic investigations under mild conditions such as low temperature and for synthetic applications.

The ipso adducts **2a**[8a] and **2b**[8b] employed in this work are stable under neutral or moderately basic conditions at room temperature but decompose under acidic conditions. Even small amounts of acid cause the breakdown of the acetal component.

Scheme I shows several examples of reactions via vinyl cations **3**. Treatment of **2a** with CF_3SO_3H (0.5 equiv) in MeOH afforded quantitatively the methyl enol ether **4a** at room temperature (path a), while H_2SO_4 (1 M, 1.0 equiv) in aqueous dioxane yielded aryl ketone **5a** quantitatively (path b). Reaction with anisole in the presence of CF_3SO_3H (0.5 equiv) gave tetraarylethene **6a** in 82% yield (path c). Treatment with NH_4SCN (2.0 equiv) in MeCN gave ethenyl thiocyanate **7a** in 99% yield (path d). Reaction with HBr resulted in quantitative formation of **1a**, the starting material for preparation of **2a** (path e). Similar reactions of **2b** (paths a–d) provided products derived from the vinyl cation **3b**.

Paths a and b show the products derived from the reaction with nucleophilic solvents, which are obtained usually in solvolytic reaction as the sole product.[1] In path c the resulting arylvinyl cations **3** react with aromatics (electrophilic aromatic substitution), with a high para selectivity (para/ortho > 95/5, in the case of anisole).[10] Paths d and e show the reaction with typical nucleophiles, Br^- and SCN^-.

In summary, vinylidenecyclohexadienone acetals **2**, prepared by photolysis of arylvinyl bromides, decompose easily under acidic conditions to provide arylvinyl cations. Their reactions with several nucleophiles afford the corresponding vinyl derivatives in high yields.[11] These highly efficient reactions show that the vinylidenecyclohexadienone acetals **2** serve as good precursors for arylvinyl cations under mild conditions. Further studies on the above subject are now under active investigation.

Registry No. 1, 125481-67-6; **2a**, 125481-68-7; **2b**, 121410-91-1; **4a**, 125481-69-8; **4b**, 121410-92-2; **5a**, 128191-30-0; **5b**, 128191-31-1; **6a**, 128191-32-2; **6b**, 128191-33-3; **7a**, 128191-34-4; **7b**, 128191-35-5.

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(11) The re-formed arylvinyl cations **3** may be captured by the nucleophiles at the ipso position of **3**. Under acidic conditions, however, ipso attack is unlikely to occur because ipso attack on **3** has been observed when a basic alkoxide ion is the nucleophile.[8]