

Metal Cluster Stabilized 2-Bornyl Cations: A Synthetic, X-ray Crystallographic, and EHMO Study

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Metal cluster derivatives of the 2-bornyl cation, *viz.* (2-propynylbornyl)(M¹-M²), where M¹ and M² can be (C₅H₅)Mo(CO)₂ or Co(CO)₃, have been synthesized by protonation of suitable precursors. Unlike the uncomplexed 2-alkynylbornyl cations, these metal-stabilized systems do not undergo the Wagner–Meerwein rearrangement to the corresponding 4-alkynylcamphenyl cations. [(2-propynylbornyl)Mo₂(CO)₄(C₅H₅)₂][BF₄], **22**, crystallizes in the orthorhombic space group *P*2₁2₁2₁ with *a* = 8.557(2) Å, *b* = 12.074(3) Å, *c* = 25.888(4) Å, and *V* = 2675(1) Å³ for *Z* = 4. [(2-propynylbornyl)Mo(CO)₂(C₅H₅)–Co(CO)₃][BF₄], **23**, crystallizes in the orthorhombic space group *P*2₁2₁2₁ with *a* = 12.647(2) Å, *b* = 13.874(2) Å, *c* = 14.040(2) Å, and *V* = 2463.6(6) Å³ for *Z* = 4. In both cases, the 2-bornyl cation leans toward a molybdenum atom such that the Mo–C⁺ distance is 2.74 Å for **22** and 2.91 Å for **23**. The preferential stabilization of the cation by the molybdenum vertex rather than by the tricarbonylcobalt fragment is rationalized by means of molecular orbital calculations at the extended Hückel level.

Introduction

The structures and rearrangement behavior of carbocationic species have occupied the attention of organic chemists for more than a century.¹ Of particular significance have been the Wagner–Meerwein rearrangements of terpenoid systems.² Our own studies have focused on the stabilization of acylium ions and alkyl cations by mono-, di-, and trimetallic moieties, such as 1–4.³ It is now recognized on the basis of infrared and NMR spectroscopic data, and also molecular orbital investigations, that in these metal-stabilized cations the positive charge is considerably delocalized onto one or more metal centers. Indeed, a number of these species, *e.g.*, 5 and 6, have been characterized by X-ray crystallography.⁴

Another interesting feature is the use of substituents derived from natural products, such as terpenes or steroids, which not only yield chiral clusters but also render diastereotopic the metal centers.⁵ Within this class of compounds, perhaps the most significant are those which

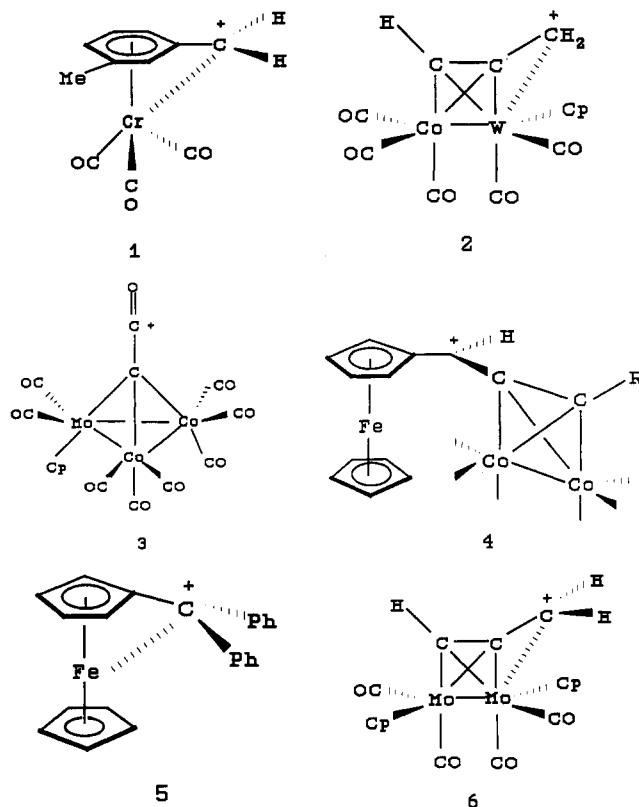


exhibit biological activity. Our own contributions in this area concern the use of hormonal steroids labeled with organometallic probes to assay specific receptor sites.⁶

We here describe the syntheses, X-ray structures, and molecular orbital analyses of molybdenum and cobalt cluster cations derived from *endo*-2-propynylborneol.

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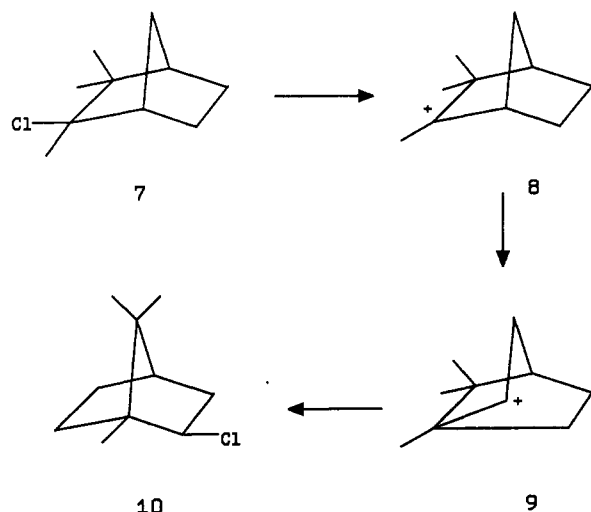
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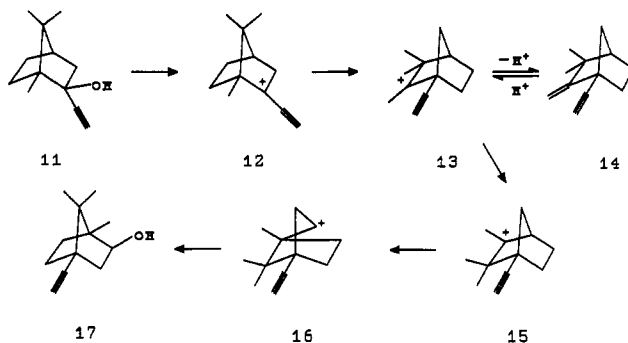
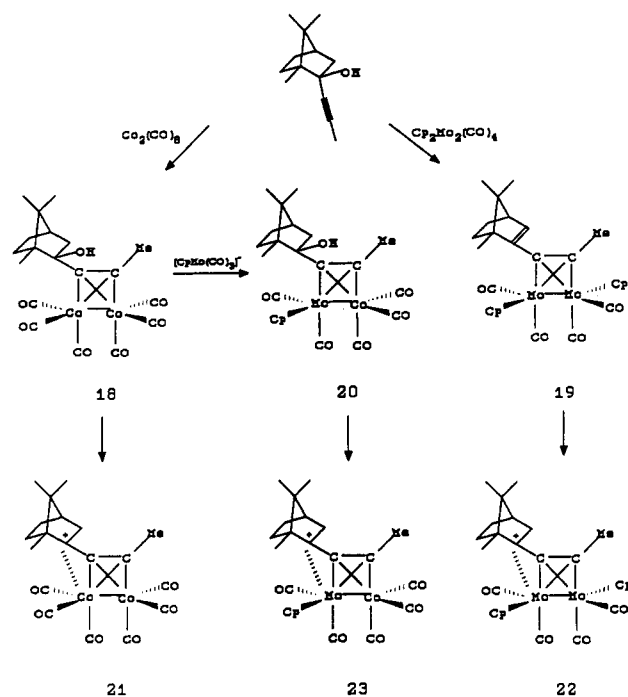
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Scheme I. Wagner–Meerwein Rearrangement of Camphenyl Chloride to Isobornyl Chloride**Results and Discussion**

Syntheses and Structures of Metal Cluster Complexes of the 2-Bornyl Cation. The many elegant studies of Wagner–Meerwein rearrangements of terpenoid skeletons have greatly enhanced our understanding of the factors contributing to the relative stabilities of carbocations. It has long been known that camphenyl chloride, 7, undergoes self-ionization in nitromethane to yield the tertiary carbocation 8 which rearranges to the secondary cation 9; the final product is isobornyl chloride, 10 (see Scheme I).⁷ Among the factors which must come into play are the unfavorable steric interactions between the chlorine atom and the three methyl substituents in 7. In the final product, isobornyl chloride 10, it is clear that there has been a considerable release of steric strain.

It is, therefore, particularly noteworthy that protonation of 2-ethynylborneol, 11, which is derived from attack of the alkynyl anion on camphor, undergoes Wagner–Meerwein rearrangement in the opposite sense to that exhibited by the camphenyl chloride/isobornyl chloride system.⁸ As shown in Scheme II, the propargyl cation 12 isomerizes to the ethynyl–camphenyl cation 13 which suffers loss of a proton to yield the ethynyl–camphene 14. Subsequent reprotonation (with $\text{CCl}_3\text{CO}_2\text{H}$ at 60 °C for 4 days) initially regenerates 13 which undergoes methyl migration to 15 before Wagner–Meerwein rearrangement to 16 occurs. When 16 is quenched, the final product is found to be 4-ethynylborneol, 17.

It is evident that the ethynyl group destabilizes the neighboring cationic center in 12 sufficiently to cause it to rearrange to the sterically less favored camphenyl cation 13. Subsequently, 13 undergoes a methyl shift in preparation for the second Wagner–Meerwein rearrangement

Scheme II. Wagner–Meerwein Rearrangement of 2-Ethynylborneol to 4-Ethynylborneol**Scheme III. Routes to Metal Cluster Stabilized Cations**

which regains the sterically preferred bornyl skeleton whilst avoiding the electronically unattractive propargyl cation.

We have already reported that coordination of the alkyne linkage in 2-*endo*-propynylborneol to either a $\text{Co}_2(\text{CO})_8$ or a $(\text{C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$ unit yields the tetrahedral clusters 18 and 19, respectively, both of which have been characterized crystallographically.^{3c,9} Moreover, as shown in Scheme III, protonation of 18 or 19 leads to the cationic species 21 or 22, respectively, whose ¹³C NMR spectra reveal that, in contrast to the behavior of the free ligand, the bornyl skeleton has not suffered rearrangement. It is also noteworthy that protonation of the heterometallic cluster 20 produces the mixed metal cationic system 23, the ¹³C NMR spectrum of which indicates that the electron deficiency at C(2) is preferentially alleviated by the molybdenum rather than the cobalt vertex. It has been noted previously that in dicobalt cations of the type $[\text{Co}_2(\text{CO})_6(\text{RC}\equiv\text{C}-\text{CR}_2)]^+$ the ¹³CO resonances appear at approximately δ 194; that is they are shielded relative to their chemical shifts of δ 204–200 in the starting alcohols,

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Table I. Crystallographic Data for [(2-propynylbornyl)Mo₂(CO)₄(C₅H₅)₂][BF₄] (22) and [(2-propynylbornyl)Mo(CO)₂(C₅H₅)Co(CO)₃][BF₄] (23)

	22	23
chemical formula	C ₂₇ H ₂₉ O ₄ Mo ₂ BF ₄	C ₂₃ H ₂₄ O ₅ CoMoBF ₄
fw	696.2	622.1
cryst syst	orthorhombic	orthorhombic
space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
Z	4	4
a, Å	8.557(2)	12.647(2)
b, Å	12.074(3)	13.874(2)
c, Å	25.888(4)	14.040(2)
V, Å ³	2675(1)	2463.6(6)
F(000)	1392	1248
ρ(calcd), g·cm ⁻³	1.73	1.68
μ(Mo Kα), cm ⁻¹	9.73	12.29
diffractometer	CAD4	CAD4
monochromator	graphite	graphite
radiation	Mo Kα (0.710 70)	Mo Kα (0.710 70)
temp, °C	20	20
scan type	ω/2θ	ω/2θ
scan range θ, deg	0.8 + 0.34 tan θ	0.8 + 0.34 tan θ
2θ range, deg	2–46	2–50
no. of reflctn collcd	2137	2453
no. of reflctn used	1457 (I > 3σ(I))	1792 (I > 3σ(I))
R	0.0483	0.0526
R _w ^a	0.0555	0.0590
abs corr	min 0.93, max 1.10	min 0.85, max 1.18
second ext par.	no	no
weighting scheme	unit weights	unit weights
rms (shift/esd) (last ref)	0.23	0.28
no. of ls params	316	293

$$^a R_w = [\sum_i W_i (F_o - F_c)^2 / \sum_i W_i F_o^2]^{1/2}.$$

Co₂(CO)₆(RC≡C—CR₂—OH).^{9,10} Analogously, stabilization of a propargyl cation by a molybdenum or tungsten center brings about a shielding of the molybdenum carbonyl resonances from approximately δ 230–225 (δ 216=212 for W) into the range δ 220–215 (δ 208–200 for W).^{4a,11,12}

As outlined above, the structures of several cationic tetrahedral dimolybdenum clusters have been obtained by X-ray crystallography and so it seemed reasonable to attempt to determine the molecular geometries of the cluster-stabilized terpenoid cations in the solid state. Thus far, it has not proven possible to obtain satisfactory crystals of any complexes of the type [Co₂(CO)₆(RC≡C—CR₂)⁺ and such is also the case for 21. Gratifyingly, however, both the dimolybdenum cation, 22, and also the cobalt–molybdenum analogue 23 yielded single crystals suitable for X-ray diffraction studies. In both cases, this was accomplished by treatment of the neutral clusters 19 or 20 with HBF₄ in ether to yield a brown microcrystalline powder. X-ray quality crystals were grown by slow diffusion of ether into dichloromethane. [(2-propynylbornyl)Mo₂(CO)₄(C₅H₅)₂]⁺[BF₄]⁻, 22, crystallizes in the orthorhombic space group P2₁2₁2₁, and numbers related to the data collection appear in Table I. A view of the molecule is shown in Figure 1 and reveals clearly that the methyl substitution pattern is unchanged from that of the original 2-propynylborneol. That is, no Wagner–Meerwein skeletal rearrangement has occurred.

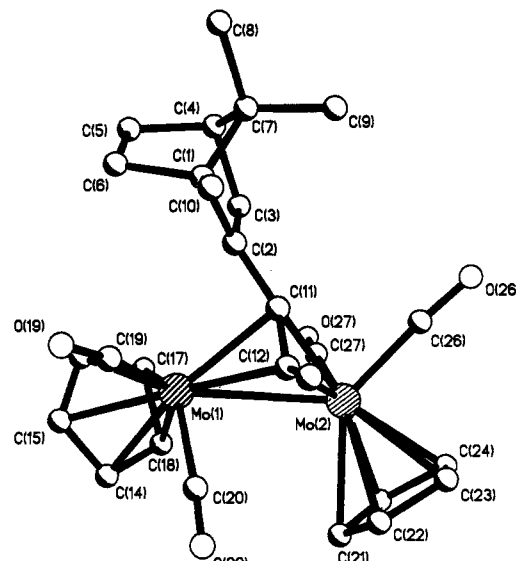


Figure 1. View of the [(2-propynylbornyl)Mo₂(CO)₄(C₅H₅)₂]⁺ cation, 22, showing the atom numbering scheme.

The molybdenum–molybdenum and molybdenum–carbon distances within the tetrahedral cluster 22 are 2.960 (2) and 2.20 Å (average), respectively; these are within the normal range for such molecules.¹³ The fold angles of the cluster, *i.e.* the interplane angles between C(11)–Mo(1) and C(11)–C(12)–Mo(2) and between Mo(1)–Mo(2)–C(11) and Mo(1)–Mo(2)–C(12) are 89 and 48°, respectively; these are similar to those previously reported (90 and 49°) for the neutral precursor 19.^{3c} Again, as is commonly observed in Mo₂C₂ clusters, the cyclopentadienyl substituents are twisted away from the plane defined by the two molybdenum atoms and the center of the C(11)–C(12) bond. In 22 (19) the Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) dihedral angle is 80° (143°). Finally, we note that, although all four carbonyl ligands in 22 deviate significantly from linearity (average Mo–C–O angle of 174.3°), we do not have three clearly terminal ligands and one semibringing carbonyl as is commonly the case in such systems.¹³

The terpenoid skeleton is normal but the alkyne carbon at C(11) is bent 19° in an *exo* fashion out of the plane defined by the C(1)–C(2)–C(3) atoms of the bornyl framework. The most significant result is that the 2-bornyl capping group leans toward Mo(1) such that the C(13)–C(12)–C(11)–C(2) dihedral angle is 64°. A more useful way to view this facet of the structure is to evaluate the extent to which the C(11)–C(2) bond is bent away from the pseudo-3-fold axis of the tetrahedral cluster. The angle C(2)–C(11)–M₂C₂(centroid) is 137°; *i.e.*, the cationic center is bent through 43° away from the “vertical” position. This deformation leaves C(2) within 2.74 Å of Mo(1) and is a clear indication that the molybdenum atom is alleviating the electron deficiency at the α-carbon center. This Mo(1)–C(2) distance in 22 can be compared to the analogous bond lengths in the primary carbocation complex [(C₅H₅)₂Mo₂(CO)₄(HC≡C—CH₂)⁺, 24, 2.44 Å,¹⁴ [(C₅H₄Me)₂Mo₂(CO)₄(HC≡C—CH₂)⁺, 25, 2.47 Å,^{4a} [(C₅H₅)₂W₂(CO)₄–

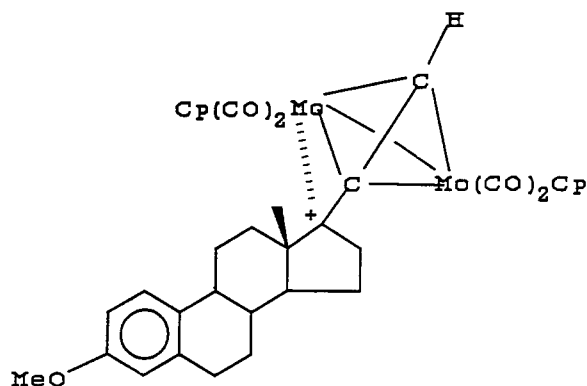
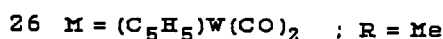
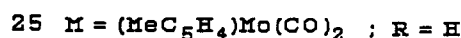
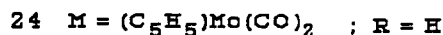
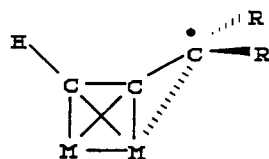
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27

$(HC\equiv C-CMe_2)^+$, 26, 2.84 Å,¹² and $[(C_5H_5)_2Mo_2(CO)_4(HC\equiv C-R)]^+$, 27, 2.74 Å,¹⁵ where R is derived from a steroid.

The mixed metal cluster 20 was prepared from the dicobalt system 18 by isolobal replacement of a $Co(CO)_3$ vertex by a $(C_5H_5)Mo(CO)_2$ moiety. The presence of the chiral bornyl substituent renders diastereotopic the two cobalt atoms in 18, consequently the introduction of a molybdenum vertex gives rise to a mixture of diastereomers. Protonation of this mixture yields two products in an approximately 65/35 ratio as shown by the 1H NMR spectrum which exhibits two cyclopentadienyl resonances, two propynyl methyl peaks, and two sets of three bornyl methyl signals. In principle, this system could give rise to four isomeric cations since both of the diastereomers could yield either a cobalt- or a molybdenum-stabilized cation. Furthermore, one might imagine that the metal which interacts with the electronic-deficient center at C(2) can approach from either the *endo* or the *exo* face of the terpene. However, the bulk of the dimethyl bridge makes the formation of an *exo* isomer rather improbable; indeed, we have seen already in the dimolybdenum cation 22 that the *endo* complex is favored.

Crystals of the cobalt-molybdenum cation 23 were grown from CH_2Cl_2 /ether by diffusion techniques. $[(2\text{-propynylbornyl})Co(CO)_3Mo(CO)_2(C_5H_5)]^+[BF_4]^-$ crystallizes in the orthorhombic space group $P2_12_12_1$, and numbers related to the data collection appear in Table I. A view of the molecule is shown in Figure 2. The remarkable similarity between the cations 22 and 23 is emphasized in Figure 3 in which the two structures are overlapped; this beautifully illustrates the power and utility of the isolobal analogy.¹⁶

The molybdenum-cobalt, molybdenum-carbon, and cobalt-carbon distances within the tetrahedral cluster 23 are 2.677(2), 2.19 (average), and 1.93 Å (average), respec-

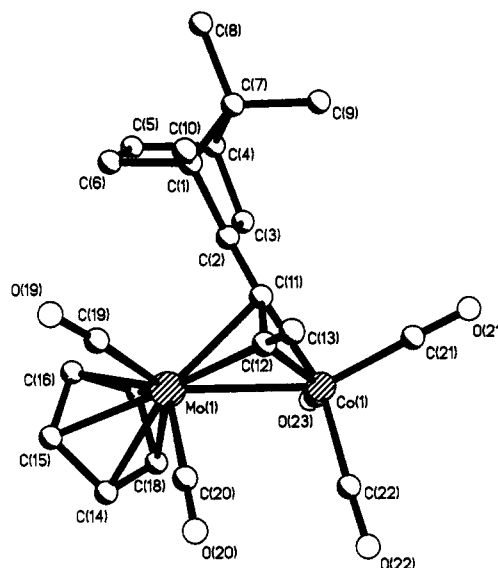


Figure 2. View of the $[(2\text{-propynylbornyl})Mo(CO)_2(C_5H_5)\text{-}Co(CO)_3]^+$ cation, 23, showing the atom numbering scheme.

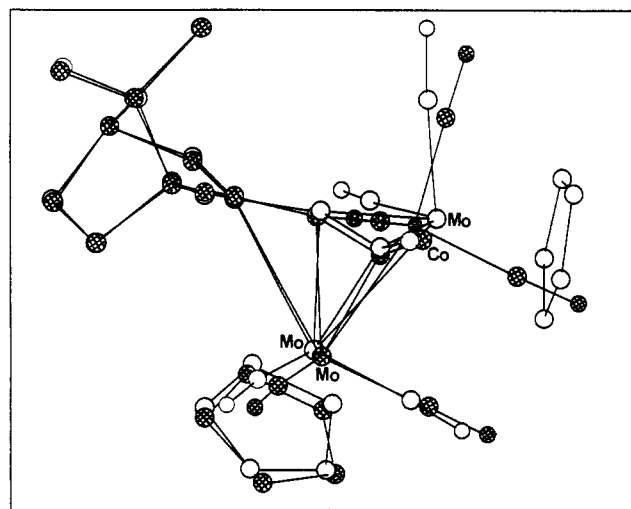


Figure 3. Overlapped view of 22 (open circles) and 23 (cross-hatched circles) showing the closely similar structures.

tively. These values lie within the normal range for Co-Mo tetrahedral clusters.¹⁷ Finally, we note that all three of the cobalt carbonyls as well as the two CO's on Mo(1) are terminally bonded. As was the case for the dimolybdenum cation 22, the alkyne carbon at C(11) is bent out of the plane defined by the C(1)-C(2)-C(3) atoms of the bornyl skeleton; again this deformation is toward the *exo* face but the angle is only 14° rather than 19°. Once again, it is apparent that the 2-bornyl cation leans toward the molybdenum vertex. The C(13)-C(12)-C(11)-C(2) dihedral angle in 23 is 69°; the analogous torsion angle in 22 is 64°. The angle C(2)-C(11)-M₂C₂(centroid) is 142°; *i.e.*, the cationic center is bent through 38° away from the "vertical" position. In 23 the electron-deficient C(2) carbon is a surprisingly long 2.914 Å from Mo(1) and is at the limit of a viable bonding interaction. Nevertheless, this structure does provide the first unequivocal structural evidence that a propargylic cation is preferentially stabilized by a $(C_5H_5)Mo(CO)_2$ vertex rather than by a $Co(CO)_3$ fragment. This corroborates the earlier NMR and

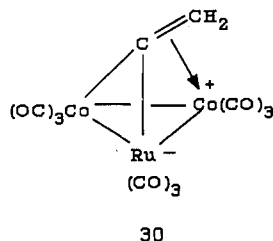
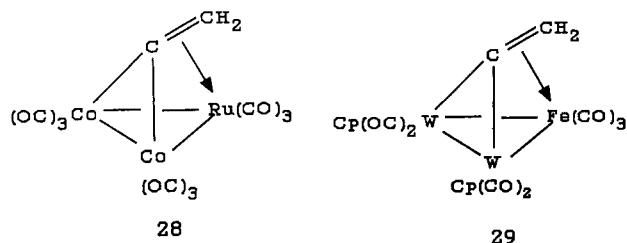
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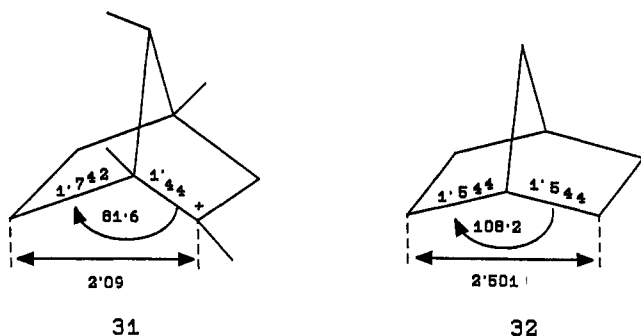
EHMO results which likewise favor cation stabilization by the molybdenum center.^{3c}

We are aware of two published structures which bear on this point. Vahrenkamp noted that in the neutral cluster $\text{Co}_2\text{Ru}(\text{CO})_9\text{C}=\text{CHBu}^t$, **28**, the capping alkylidene



group leans toward the $\text{Ru}(\text{CO})_3$ vertex.¹⁸ However, one cannot merely assume that the heavier transition metal is always the favored site of attachment; Stone has shown that in $(\text{C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4\text{Fe}(\text{CO})_3\text{C}=\text{CH}_2$, **29**, the vinylidene unit bends toward the iron atom.¹⁹ In both **28** and **29** the observed molecular geometry satisfies the 18-electron rule at each metal center, whereas an isomer such as **30** would require a zwitterionic structure. Clearly, any rationale based on the molecular orbital model must account not only for the failure of the metal-complexed 2-bornyl cation to undergo Wagner–Meerwein rearrangement but also for the preferential delocalization of the cationic charge onto molybdenum.

No discussion of a crystallographically characterized 2-bornyl cation would be complete without reference to Laube's seminal work on the unsymmetrically bridged 1,2,4,7-*anti*-tetramethyl-2-norbornyl cation, **31**.²⁰ The



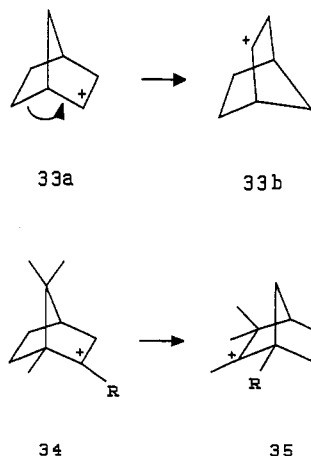
X-ray crystal structure of **31** revealed a marked lengthening of the C(6)–C(1) bond, a shortening of the C(1)–C(2) bond, and a contraction of the C(6)–C(1)–C(2) angle relative to the corresponding values for norbornane, **32** (1.544 Å, 1.544 Å, and 108.2°, respectively). Laube's experimental data are in accord with an unsymmetrically bridged structure,

as suggested by Dewar *et al.* in 1977.²¹ The C(6)–C(1) single bond is weakened by donating electron density to the electron-deficient center at C(2) and is thereby lengthened to 1.742 Å. Concomitantly, the increased electron density in the C(1)–C(2) bond brings about a shortening to 1.44 Å. The bridging interaction between C(6) and C(2) is evident not only in the short distance between these two atoms (2.09 Å) but also in the small C(6)–C(1)–C(2) angle (81.6°).

In contrast, the C(6)–C(2) and C(1)–C(2) bond lengths in the metal clusters **22** and **23** are 1.55 ± 0.02 Å. Moreover, the C(6)–C(1)–C(2) bond angles are 104.0 and 104.8°, respectively. It is clear that the cluster-stabilized systems **22** and **23** are classical cations, and their structures show no tendency toward Wagner–Meerwein rearrangement.

Extended Hückel Molecular Orbital Calculations. Although high level calculations have been carried out on numerous 2-substituted norbornyl cations and related systems,²² we have chosen to use the EHMO approach since it is readily applicable to metal clusters. Of course, calculations at the EHMO level will not provide us with novel insights into the "nonclassical ion problem".²³ However, they do allow comparison of the relative energies of various free and complexed 2-bornyl cations calculated at the same level of approximation.

The simplest model of the Wagner–Meerwein rearrangement of the 2-norbornyl cation, **33a** → **33b**, can be presented in terms of the interactions of three orbitals. As



shown in Figure 4, the HOMO shows the transformation of the C(6)–C(1) σ bond into a C(6)–C(2) σ bond, *via* a structure in which the orbital at the migrating C(6) center is in-phase with the incipient π -bond between C(1) and C(2). The LUMO is primarily a vacant p_z orbital at C(2) which is transformed via a C(1)–C(2) π^* combination into a vacant p_z orbital at C(1). It has been noted that Wagner–Meerwein rearrangements occur readily in 2-norbornyl cationic systems because of favorable orbital overlap between the C(6)–C(1) σ system and the vacant p orbital at C(2).²⁴ One might wonder whether the delocalization of the positive charge at C(2) onto a metal center in **21**–**23**

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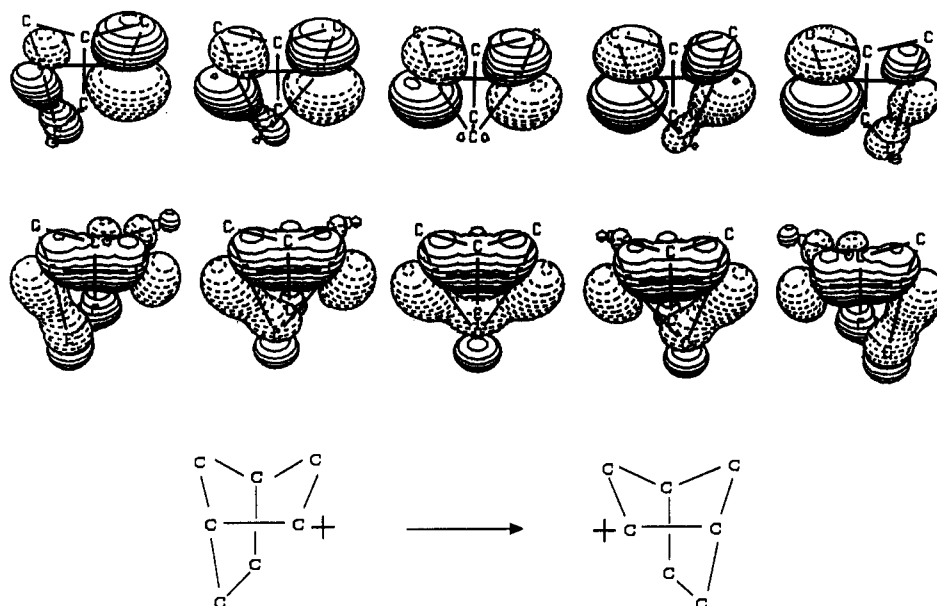


Figure 4. EHMO-calculated transformations of the LUMO (upper series of plots) and HOMO (lower series) during the course of an idealized rearrangement of the 2-norbornyl cation.

might bring about a reorientation of the vacant orbital at C(2) and hence disfavor the migration of C(6) from C(1) to C(2).

The Wagner–Meerwein rearrangement of the 2-substituted bornyl cation **34** yields the 4-substituted camphenyl cation **35**. When R = H, molecular orbital calculations at the extended Hückel level tell us that the rearranged tertiary cation **9** is energetically favored over the secondary cation **8** by 14.1 kcal mol⁻¹. However, we must remind ourselves that these calculations provide comparisons only between the cations and take no account of the very different steric environments of the chlorine atoms in camphenyl chloride, **7**, and isobornyl chloride, **10**. In the ethynyl system, EHMO calculations reveal that the 4-ethynylbornyl cation, **13**, is favored over the 2-ethynyl isomer, **12**, but by only 0.6 kcal mol⁻¹. Not surprisingly, the charge deficiency at C(2) can be at least partially alleviated by interaction with the π manifold of the alkyne. Nevertheless, it has been established experimentally that the transformation **12** \rightarrow **13** proceeds readily in good yield.⁸ The most interesting result is obtained for the case where R = (HC \equiv C–)Co₂(CO)₆. It is found that the initial cation in which the C(2) center can interact with a cobalt atom, as in **21**, is stabilized to the tune of 30.4 kcal mol⁻¹ relative to the isomer with the cluster in the 4-position. The most energetically favorable geometry for the 2-substituted cationic dicobalt cluster is remarkably similar to those found crystallographically for **22** and **23**. Interestingly, the total energy of the system is not strongly dependent on the precise distance from C(2) to the metal center, and bond lengths ranging from 2.8 to 3.1 Å give rise to a deep but rather flat valley. We note that in the two crystallographically characterized cations **22** and **23** the Mo(1)–C(2) distances are 2.74 and 2.91 Å, respectively. These may well be controlled to some extent by steric interactions between the cyclopentadienyl ligand and the methyl group at C(1).

As mentioned above, one might consider whether the delocalization of the cationic charge at C(2) onto molybdenum or cobalt might alter the orientation of the LUMO which is primarily a p_z orbital on C(2). Figure 5 depicts the LUMO's, as calculated by using the EHMO approach,

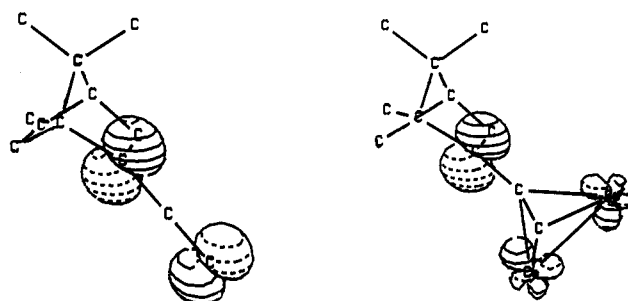
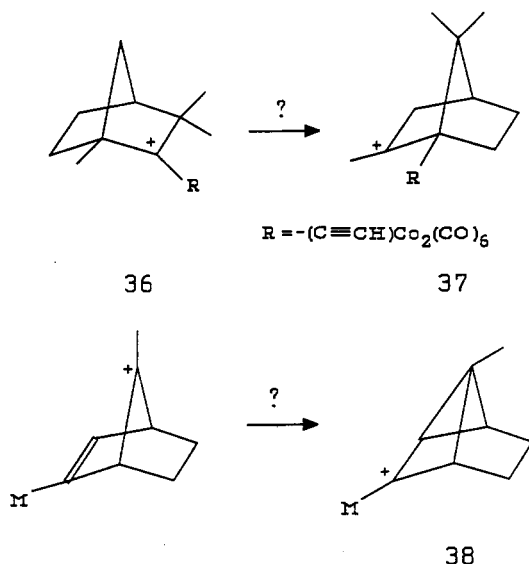


Figure 5. LUMO's of the 2-ethynylbornyl cation and of the corresponding Co₂(CO)₆ complex.

in both the 2-ethynyl cation and in its dicobalt complex. In the noncomplexed system the component of this molecular orbital at C(2) has 44% p_z character and 19% p_y character and so is well oriented to accept electron density from the C(6)–C(1) σ bond. However, in the cobalt complex the contributions from p_z and p_y at C(2) are 42% and 10%, respectively, and this has the effect of slightly rotating the LUMO away from the C(6)–C(1) bond. Nevertheless, this minor perturbation is unlikely to be a major factor in determining whether metal-complexed cations, such as **21**, **22**, or **23**, will undergo the Wagner–Meerwein rearrangement which the noncomplexed cation has already been shown to do. The dominant feature appears to be the markedly enhanced stabilization of the 2-bornyl cation when this position bears a metal cluster as the substituent. That is, one can attribute the failure to undergo a Wagner–Meerwein shift to thermodynamic stabilization rather than merely raising the activation energy for the process. Since we are invoking an electronic effect to prevent an otherwise favored rearrangement, one can pose the question whether it is possible to stabilize a cation which is under considerable steric pressure to undergo a Wagner–Meerwein shift. Typically, the cation **36**, derivable from a metal-complexed 2-alkynylfenchol could presumably rearrange to the less hindered isomer **37**, but the reaction may be prevented by the presence of the metal cluster. Moreover, it may be possible to stabilize the tricyclo cation **38** by preferentially locating the positive



charge at the carbon adjacent to the organometallic moiety. These molecules will be the focus of future reports.

Finally, one should present a rationale for the preferential delocalization of the charge onto a $(C_5H_5)Mo(CO)_2$ vertex rather than a $Co(CO)_3$ fragment. Figure 6 depicts the results of a series of EHMO calculations whereby the initially vertical methylene group in $[(C_5H_5)Mo(CO)_2Co(CO)_3HC\equiv C-CH_2]^+$ is allowed to lean down toward either the cobalt or the molybdenum vertex. There is a surprisingly large energy dependence on the orientation of the vertical CH_2^+ fragment relative to the basal triangular plane. It is apparent that bending toward cobalt is energy minimized at $\approx 40^\circ$ after which point steric repulsions bring about a steep increase. The global minimum is found when the methylene moiety is bent through $30-35^\circ$ toward the molybdenum atom. Interestingly, the $Mo-C^+$ interaction is most favorable when the cyclopentadienyl ring is not directly opposite the incoming carbocationic center but rather is oriented almost at right angles to this conformation. Figure 7 shows those occupied molecular orbitals in which interaction of the methylene p orbital with either cobalt or molybdenum is most evident.

These calculations find support in the X-ray crystallographic data for **22** and **23**, not merely in that the cationic center leans through $40 \pm 3^\circ$ so as to interact with molybdenum rather than cobalt, but also in the orientation of the $(C_5H_5)Mo(CO)_2$ unit. Thus, in the dimolybdenum neutral cluster **19**, the $Cp(\text{centroid})-Mo(1)-Mo(2)-Cp(\text{centroid})$ dihedral angle is 143° ,^{3c} after protonation, the analogous torsion angle in **22** is now 80° and the C(2) carbon is positioned *cis* rather than *trans* to the cyclopentadienyl ring.

To conclude, it has been unequivocally demonstrated that the 2-propynylbornyl cation, when complexed to a dimetallic fragment $M\equiv M$, where M can be $(C_5H_5)Mo(CO)_2$ or $Co(CO)_3$, resists the Wagner-Meerwein rearrangement which occurs readily for the free cation. This stabilization arises as the result of a direct interaction of the C(2) center with a metal vertex, preferably a $(C_5H_5)Mo(CO)_2$ fragment. In contrast to the unsymmetrically bridged 1,2,4,7-*anti*-tetramethyl-2-norbornyl cation investigated by Laube, these stabilized cations are best regarded as "classical" systems.

We should, however, finish by commenting on an as yet unexplained observation. While the metal-stabilized

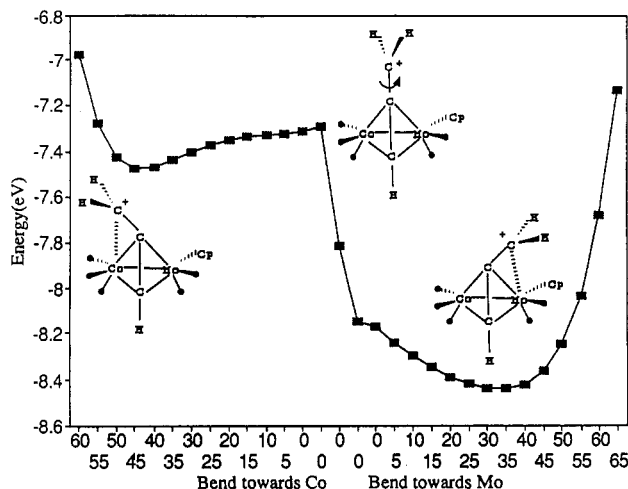


Figure 6. Energy profile depicting the migration of a CH_2^+ group from a cobalt to a molybdenum vertex.

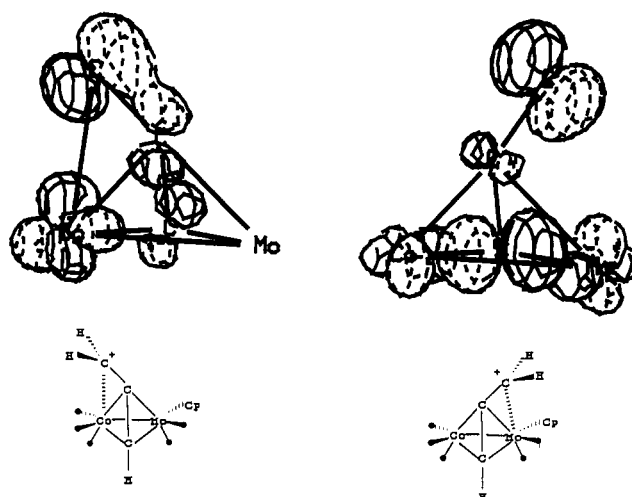
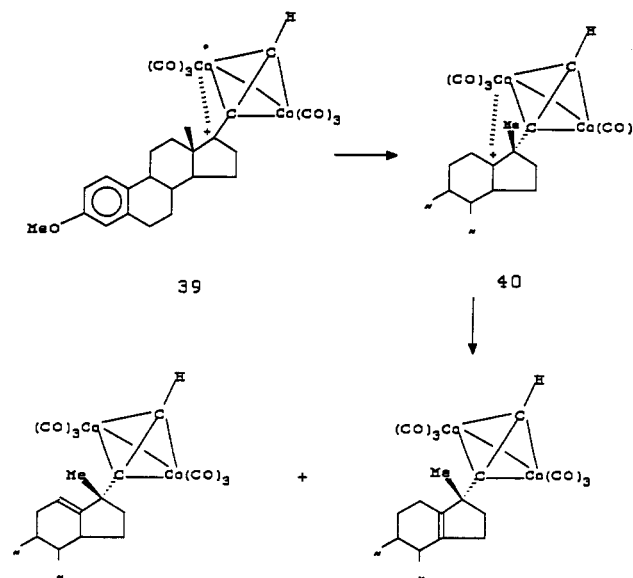


Figure 7. Frontier orbitals depicting the interaction of a CH_2^+ group with either a cobalt or a molybdenum atom.

2-bornyl cations **21**, **22**, or **23** do not exhibit a Wagner-Meerwein rearrangement, the steroidal cation **39** (in which



the carbocationic center is α to the cluster) readily undergoes a methyl shift to yield **40**, which subsequently suffers elimination to a mixture of alkenes.¹⁵ It may be

Table II. Atomic Coordinates for [(2-propynylbornyl)Mo₂(CO)₄(C₅H₅)₂][BF₄] (22)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq), Å ²	<i>U</i> (iso), Å ²
Mo(1)	0.9729(2)	0.4286(1)	0.39842(6)	0.0301	
Mo(2)	0.7018(2)	0.3679(1)	0.33333(6)	0.0283	
O(19)	1.260(2)	0.586(1)	0.3849(7)	0.0732	
O(20)	1.166(2)	0.300(2)	0.3175(6)	0.0544	
O(26)	0.455(2)	0.520(1)	0.2830(6)	0.0755	
O(27)	0.491(2)	0.365(1)	0.4323(5)	0.0563	
C(1)	0.859(2)	0.729(1)	0.3870(6)	0.0214	
C(2)	0.784(2)	0.611(1)	0.3918(6)	0.0227	
C(3)	0.653(2)	0.624(2)	0.4303(7)	0.0306	
C(4)	0.659(2)	0.747(1)	0.4436(7)	0.0313	
C(5)	0.798(3)	0.761(2)	0.4788(7)	0.0398	
C(6)	0.937(2)	0.748(2)	0.4410(7)	0.0347	
C(7)	0.710(2)	0.797(1)	0.3912(6)	0.0331	
C(8)	0.742(3)	0.924(2)	0.395(1)	0.0501	
C(9)	0.596(3)	0.785(2)	0.3468(8)	0.0496	
C(10)	0.963(2)	0.751(1)	0.3415(6)	0.0324	
C(11)	0.794(2)	0.529(1)	0.3540(6)	0.0204	
C(12)	0.887(2)	0.481(1)	0.3197(6)	0.0218	
C(13)	0.971(3)	0.515(2)	0.2714(7)	0.0298	
C(14)	1.061(5)	0.289(3)	0.450(1)	0.0729	
C(15)	1.113(3)	0.385(4)	0.470(1)	0.0606	
C(16)	0.994(3)	0.444(2)	0.4878(7)	0.0580	
C(17)	0.854(3)	0.389(2)	0.4791(7)	0.0439	
C(18)	0.895(5)	0.289(3)	0.455(1)	0.0625	
C(19)	1.145(3)	0.532(2)	0.3906(9)	0.0596	
C(20)	1.089(2)	0.343(2)	0.3470(7)	0.0383	
C(21)	0.796(3)	0.186(2)	0.3203(7)	0.0467	
C(22)	0.815(3)	0.243(2)	0.2761(8)	0.0375	
C(23)	0.674(3)	0.277(2)	0.2565(7)	0.0470	
C(24)	0.557(3)	0.240(2)	0.290(1)	0.0455	
C(25)	0.633(2)	0.181(1)	0.3315(9)	0.0399	
C(26)	0.552(2)	0.467(2)	0.3027(8)	0.0380	
C(27)	0.573(2)	0.375(2)	0.3976(7)	0.0347	
B(1)	0.255(2)	0.976(1)	0.8829(7)		0.19(2)
F(1)	0.171(2)	0.886(2)	0.8969(7)		0.151(4)
F(2)	0.236(2)	1.058(2)	0.9170(7)		0.151(4)
F(3)	0.404(2)	0.946(2)	0.8788(7)		0.151(4)
F(4)	0.215(2)	1.013(2)	0.8356(7)		0.151(4)

the case that the β-cation 40 can receive anchimeric assistance from a cobalt vertex; clearly, this system merits further investigation.

Experimental Section

All reactions were carried out under an inert atmosphere using standard Schlenk techniques. The syntheses of the clusters [2-propynylborneol]Co₂(CO)₆, 18, [2-propynylbornene]Mo₂(CO)₄(C₅H₅)₂, 19, and [2-propynylborneol]Co(CO)₃Mo(CO)₂(C₅H₅), 20, have been described elsewhere.^{3c,9}

Protonation of (2-endo-propynylborneol)[Co₂(CO)₆], 18. A sample of (2-endo-propynylborneol)[Co₂(CO)₆], 18 (0.20 g, 0.4 mmol) was dissolved in CD₂Cl₂ (1 mL), and the solution was filtered into a 5-mm NMR tube and cooled in a dry ice/acetone bath. Under an atmosphere of N₂ in a glovebag, 4–5 drops of HBF₄–Et₂O were added to the solution. The tube was then transferred to the NMR spectrometer (AM 500) where the probe temperature had already been cooled to –40 °C. After allowing the temperature of the NMR sample to stabilize at –40 °C, the spectra of the cation 21 were recorded. ¹³C NMR (125 MHz, CD₂Cl₂, –40 °C): δ 194.4, 192.2 (carbonyls); 180.3 (C-2), 103.9, 102.9 (alkyne quaternary C's); 64.5 (C-1); 52.1 (C-7); 44.5 (C-3); 43.7 (C-4); 39.8 (C-6); 27.5 (C-5); 21.4 (alkyne CH₃); 20.3, 19.3 (C-8 and C-9); 13.2 (C-10). ¹H NMR (500 MHz, CD₂Cl₂, –40 °C): δ 2.86 (s, 3H, alkyne CH₃); 2.57 (m, 1H, H-3_{exo}); 2.19 (m, 1H, H-4); 2.12 (m, 1H, H-5_{exo}); 2.10 (m, 1H, H-6_{exo}); 2.01 (m, 1H, H-3_{endo}); 1.57 (m, 1H, H-5_{endo}); 1.36 (m, 1H, H-6_{endo}); 1.03 (s, 3H), 0.94 (s, 3H) (H-8 and H-9); 0.85 (s, 3H, H-10).

Protonation of [2-prop-1-ynyl-2-bornene][(C₅H₅)₂Mo₂(CO)₄], 19. A sample of [2-prop-1-ynyl-2-bornene][(C₅H₅)₂Mo₂(CO)₄], 19 (0.30 g, 0.5 mmol) was dissolved in CD₂Cl₂ (1 mL), and the solution was filtered into a 5-mm NMR tube and cooled

Table III. Atomic Coordinates for [(2-propynylbornyl)Mo(CO)₂(C₅H₅)Co(CO)₃][BF₄] (23)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq), Å ²	<i>U</i> (iso), Å ²
Mo(1)	0.01389(8)	0.50668(9)	0.64586(8)	0.0388	
Co(1)	–0.0867(2)	0.6273(1)	0.5278(1)	0.0429	
O(19)	–0.046(1)	0.3040(9)	0.721(1)	0.0918	
O(20)	–0.146(1)	0.573(1)	0.804(1)	0.0945	
O(21)	–0.233(1)	0.654(1)	0.372(1)	0.0893	
O(22)	–0.180(1)	0.7624(9)	0.664(1)	0.0809	
O(23)	0.104(1)	0.728(1)	0.455(1)	0.0741	
C(1)	–0.012(1)	0.3264(9)	0.4338(9)	0.0370	
C(2)	0.001(1)	0.4345(9)	0.4512(9)	0.0400	
C(3)	0.079(1)	0.470(1)	0.3764(9)	0.0436	
C(4)	0.106(1)	0.379(1)	0.3242(9)	0.0441	
C(5)	0.176(1)	0.317(1)	0.386(1)	0.0512	
C(6)	0.097(1)	0.282(1)	0.466(1)	0.0476	
C(7)	–0.001(1)	0.323(1)	0.3261(9)	0.0433	
C(8)	0.003(2)	0.220(1)	0.287(1)	0.0730	
C(9)	–0.092(1)	0.377(1)	0.275(1)	0.0617	
C(10)	–0.104(1)	0.278(1)	0.480(1)	0.0573	
C(11)	–0.0641(9)	0.494(1)	0.5018(8)	0.0339	
C(12)	–0.135(1)	0.503(1)	0.5760(8)	0.0393	
C(13)	–0.246(1)	0.468(1)	0.595(1)	0.0524	
C(14)	0.126(2)	0.579(1)	0.754(2)	0.0715	
C(15)	0.152(1)	0.482(1)	0.750(1)	0.0556	
C(16)	0.191(1)	0.463(1)	0.655(2)	0.0638	
C(17)	0.186(1)	0.552(2)	0.607(1)	0.0522	
C(18)	0.151(1)	0.621(1)	0.667(1)	0.0637	
C(19)	–0.025(1)	0.377(1)	0.690(1)	0.0555	
C(20)	–0.085(2)	0.552(2)	0.747(1)	0.0664	
C(21)	–0.179(1)	0.643(1)	0.430(1)	0.0609	
C(22)	–0.142(1)	0.713(1)	0.614(1)	0.0515	
C(23)	0.027(1)	0.690(1)	0.484(1)	0.0525	
B(1)	0.553(1)	0.034(1)	–0.003(1)		0.11(1)
F(1)	0.633(1)	–0.021(1)	0.035(1)		0.141(5)
F(2)	0.592(1)	0.111(1)	–0.052(1)		0.202(8)
F(3)	0.488(1)	0.071(1)	0.065(1)		0.166(6)
F(4)	0.503(2)	–0.016(2)	–0.075(1)		0.246(9)

in a dry ice/acetone bath. Under an atmosphere of N₂ in a glovebag, 4–5 drops of HBF₄–Et₂O were added to the solution. The tube was then transferred to the NMR spectrometer (AM 500) where the probe temperature had already been cooled to 0 °C. After allowing the temperature of the NMR sample to warm up slowly and stabilize at 0 °C, the spectra of the cation 22 were recorded. ¹³C NMR (125 MHz, CD₂Cl₂, 0 °C): δ 227.1, 226.5, 223.0, 220.0 (carbonyls); 181.7 (C-2), 94.0, 92.8 (CH's of cyclopentadienyls); 63.3 (C-1); 51.4 (C-7); 46.0 (C-3); 43.3 (C-4); 41.9 (C-6); 27.6 (C-5); 27.4 (alkyne CH₃); 20.2, 19.3 (C-8 and C-9); 14.2 (C-10). ¹H NMR (500 MHz, CD₂Cl₂, 0 °C): δ 5.60 (s, 5H), 5.56 (s, 5H) (H's of cyclopentadienyl rings); 2.89 (s, 3H, alkyne CH₃); 2.29 (m, 1H), 1.81 (m, 1H) (H-3_{exo} and H-3_{endo}); 2.03 (m, 1H), 1.23 (m, 1H) (H-6_{exo} and H-6_{endo}); 2.00 (m, 1H, H-4); 1.98 (m, 1H), 1.36 (m, 1H) (H-5_{exo} and H-5_{endo}); 0.92 (s, 3H), 0.80 (s, 3H) (H-8 and H-9); 0.82 (s, 3H, H-10).

The ¹H and ¹³C NMR spectra of 22 and 23 were consistent with the data previously reported.^{3c}

Crystal Data for 22 and 23. X-ray quality crystals of the carbenium ions 22 and 23 were derived from 19 and 20, respectively. Typically, to a solution of 19 (0.15 g) dissolved in ether (3 mL) was added HBF₄/ether (0.5 mL) in a dropwise manner. The resulting dark brown precipitate was washed several times with ether and dried in vacuo. Single crystals of 22 and 23 suitable for X-ray crystallography were grown by slow diffusion of ether into a dichloromethane solution of the cation.

Intensity data were collected at room temperature on a Nonius CAD-4 diffractometer using Mo Kα radiation. The accurate cell dimensions and orientation matrix were obtained from least-squares refinements of the setting angles of 25 well-defined reflections. No decay in the intensities of two standard reflections was observed during the course of the data collection. Complete crystal collection parameters are listed in the supplementary material. The usual corrections for Lorentz and polarization

effects were applied. An empirical absorption correction (DI-FABS)²⁵ was applied.

Computations were performed by using CRYSTALS²⁶ adapted for a Microvax II computer. Scattering factors and corrections were from ref 27. In both cases, the structures were solved by standard Patterson-Fourier techniques and refined by least squares with anisotropic thermal parameters for all non-hydrogen atoms (except for those of the tetrafluoroborate ion). As is often necessary with tetrafluoroborate anions, restraints were applied to B-F bond lengths (1.38 ± 0.02 Å) and to F-B-F angles ($109 \pm 0.2^\circ$). Hydrogen atoms were introduced as fixed contributors in theoretical positions, with $U_{120} = 1.2U_{180}$ for the related carbon atom, and their coordinates were recalculated after each refinement cycle. Atomic coordinates for cations **22** and **23** appear in Tables II and III, while anisotropic thermal parameters and interatomic distances and angles, appear as supplementary material.

Molecular orbital calculations were performed via the

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extended Hückel method using weighted H_{ij} 's;²⁸ orbital drawings were obtained by use of the program CACAO.²⁹ Orbital parameters were taken from ref 3c.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and CNRS (France) for financial support. The program CACAO Version 2.2 was kindly provided by Dr. Carlo Mealli, CNR, Florence, Italy. We also thank Dr. David G. Morris (University of Glasgow) for valuable discussions concerning the rearrangement behavior of terpenoid cations.

Supplementary Material Available: Tables listing bond distances and angles and thermal parameters (7 pages). Ordering information is given on any current masthead page.

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