2-Bornyl cations stabilized by metal clusters: synthetic and X-ray structural and quantum-chemical studies*

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Data on syntheses and structures of 2-bornyl cations stabilized by metal clusters are presented.

Key words: 2-bornyl cations stabilized by metal clusters; X-ray structural study; quantum-chemical calculations.

The structure and rearrangements of carbocationic species have been studied for more than a hundred years.[1] Wagner—Meerwein rearrangements in terpenoid systems are particularly important reactions of this type.[2]

Our investigations have been for the most part devoted to the stabilization of propargyl cations by bimetallic species.[3] Figure 1 presents the simplest of the prepared ions of this type bonded to a dimolybdenum group.

Previously we showed that steroid cations in which the cation center is located in the α-position with respect to the cluster readily undergo a methyl group shift to give the cation with a β-position with respect to the cluster, which results, after elimination, in a mixture of alkenes[4] (Scheme 1).

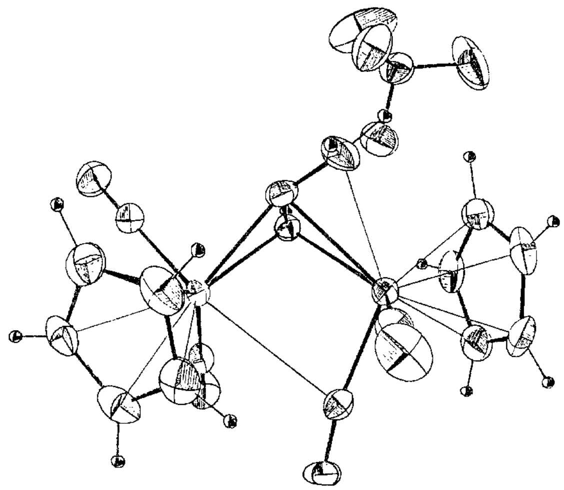
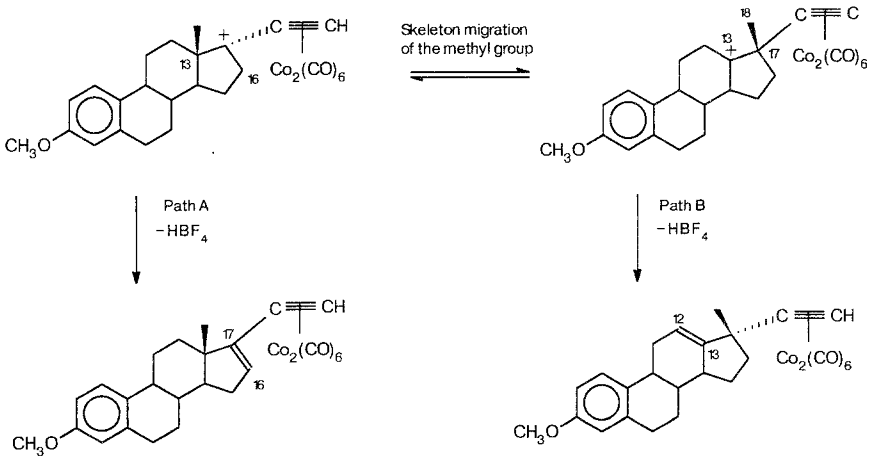


Fig. 1. Molecular structure of the $Mo_2Cp_2(CO)_4(\mu\text{-}HC{-}CCH_2^{+})BF_4^{-}$ complex.

We did not manage to isolate these α- and β-cations, but prepared an isolobal α-cation in which ML_3 is

Scheme 1



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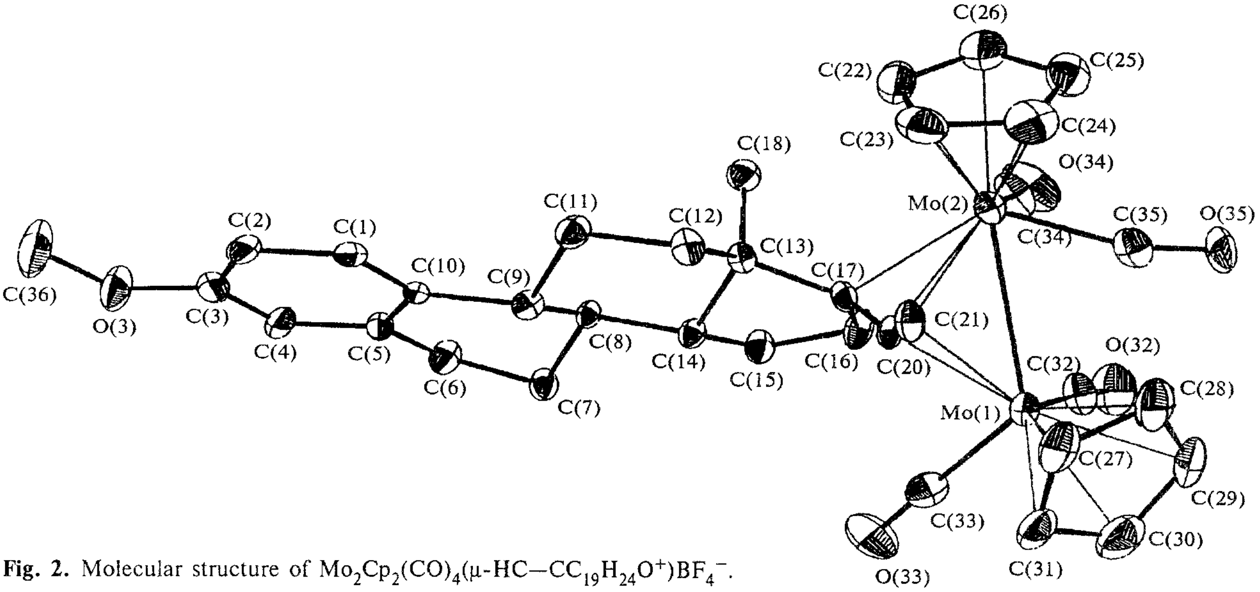


Fig. 2. Molecular structure of $Mo_2Cp_2(CO)_4(\mu\text{-}HC{-}CC_{19}H_{24}O^+)BF_4^-$.

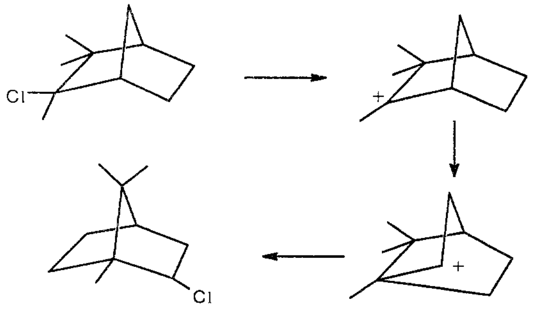
MoCp(CO)$_2$ and determined the structure of this salt (Fig. 2) by X-ray diffraction analysis.

It is of interest that this cation does not isomerize according to any of the possible routes, which is probably due to the fact that the interaction between the carbocation site and molybdenum is stronger than that in the case of cobalt.

These results have stimulated our studies in the field of the chemistry of the complexes of 2-bornyl cations with metal clusters.

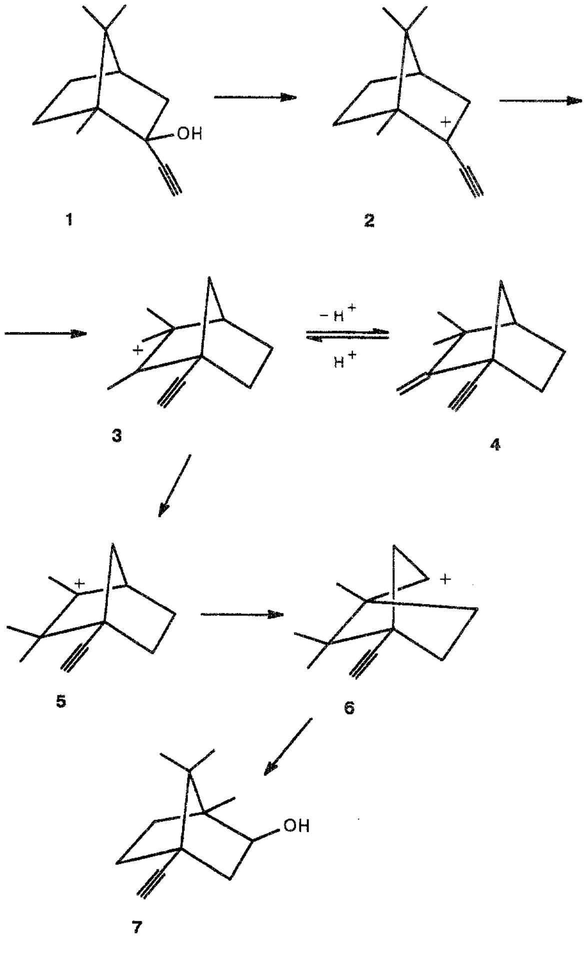
Owing to a variety of elegant studies of Wagner—Meerwein rearrangements of the terpenoid skeleton, we have made a considerable advance in understanding the factors determining the relative stability of carbocations. It has long been known that camphenyl chloride undergoes self-ionization in nitromethane to give a tertiary carbocation which rearranges into a secondary carbocation and isobornyl chloride as the final product.[5] Among the factors affecting the process, one should note the sterically hindered interaction between the chlorine atom and three methyl substituents. The final product, the isobornyl chloride, is obviously characterized by a substantially lower steric strain (Scheme 2).

Scheme 2



Therefore, it should be particularly noted that protonation of 2-ethynylborneol is accompanied by a Wagner—Meerwein rearrangement, which is just the reverse of the rearrangement in the camphenyl chloride/isoborneol chloride system[6] (Scheme 3).

Scheme 3



It is apparent that the ethynyl group destabilizes the neighboring cation site in compound **2** to such a degree that it causes its rearrangement into a less sterically favorable camphenyl cation **3**. Then a methyl shift occurs in compound **3**, which precedes the second Wagner—Meerwein rearrangement. The latter again affords the more sterically favorable bornyl skeleton, and the formation of the propargyl cation, which would be unfavorable in terms of electronic factors, is avoided.

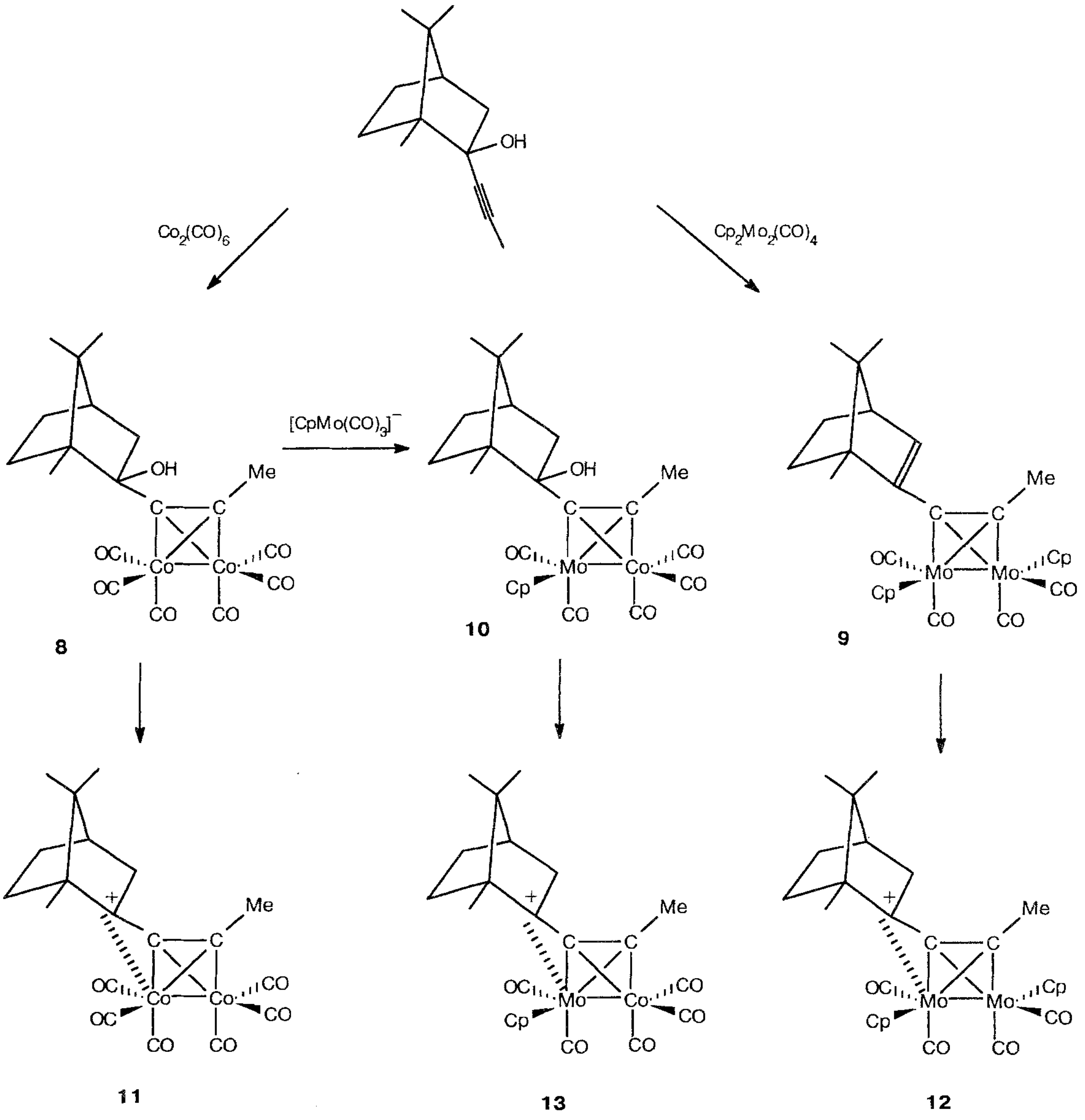
The coordination of the triple bond in 2-*endo*-propynylborneol with $Co_2(CO)_6$ and $Cp_2Mo_2(CO)_4$ complexes results in the formation[7] of tetrahedral clusters **8** and **9**, respectively (Scheme 4).

Protonation of compounds **8** and **9** affords cationic species **11** and **12**, respectively, whose ^{13}C NMR spectra indicate that the bornyl skeleton in these compounds, in contrast to that in free ligands, is not isomerized.

It should be noted as well that protonation of heterometallic cluster **10** gives the mixed metallic cationic complex **13**. For both the dimolybdenum cation **12** and the cobalt-molybdenum analog **13** single crystals suitable for X-ray diffraction analysis have been obtained (Figs. 3, 4).

Dimolybdenum cation **12** has a normal terpenoid skeleton, but the alkyne carbon atom at C(11) is deflected by 19° in the *exo*-direction from the plane in

Scheme 4



which the carbon atoms of the bornyl skeleton, C(1), C(2), and C(3), lie. The distance between C(2) and Mo, equal to 2.74 Å, unambiguously shows that the molybdenum atom balances the deficiency of the electron density at the carbon cation site. The Mo—C$^+$ distance in compound **12** is comparable with analogous bond lengths in other tertiary carbocation complexes. For example, in a steroid cation[4] the distance between Mo and C$^+$ is also 2.74 Å.

The remarkable similarity between 2-bornyl cations stabilized by dimolybdenum and molybdenum-cobalt moieties is readily illustrated in Fig. 5, where these two structures are superimposed on one another. This clearly demonstrates the applicability and validity of the isolobal analogy.[8]

As in the case of the dimolybdenum cation, the alkyne carbon atom C(11) in the mixed molybdenum-cobalt cation (see Fig. 4) is deflected from the plane in which the C(1)—C(2)—C(3) bornyl skeleton atoms lie. This deflection is also *exo*-directed, but the angle is only 14° instead of 19°. The electron-deficient C(2) atom and the molybdenum atom in this cation are surprisingly far apart: the distance between them is 2.914 Å, which is about the limit of noticeable binding interactions. Nevertheless, this structure is the first unequivocal structural confirmation of the fact that the propargyl cation is stabilized by the CpMo(CO)$_2$ vertex, rather than by the Co(CO)$_3$ fragment. This is in agreement with the data obtained previously by NMR spectroscopy and quantum-chemical calculations by the extended Hückel method (EHMO)[7a] (Fig. 6).

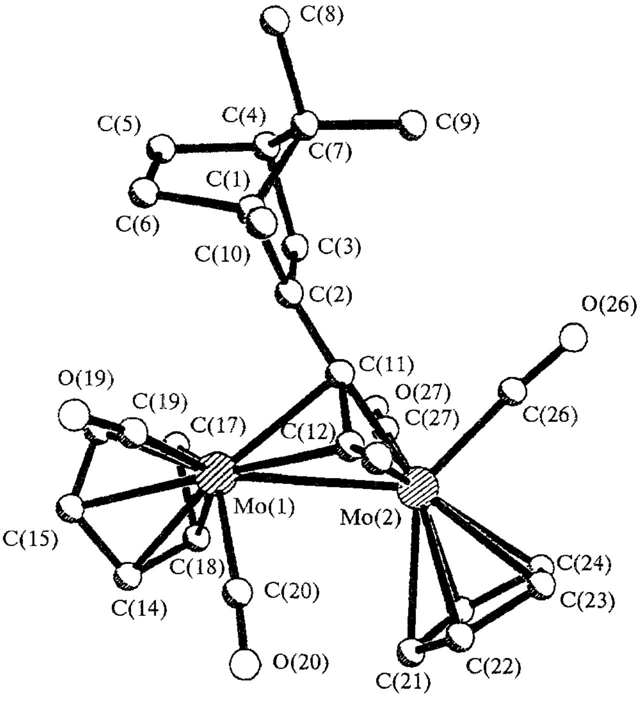


Fig. 3. Molecular structure of the Mo$_2$Cp$_2$(CO)$_4$(μ-2-propynylborneol$^+$)BF$_4^-$ complex.

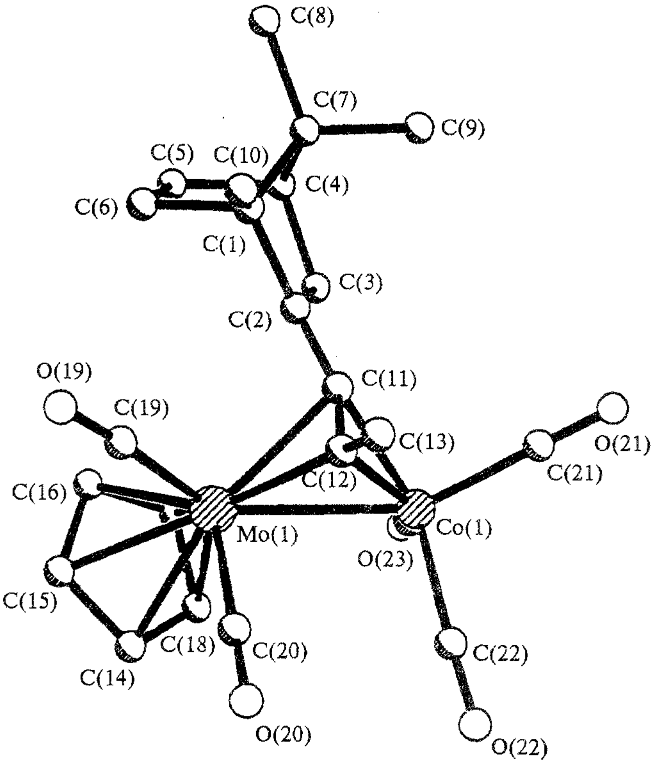


Fig. 4. Molecular structure of the MoCp(CO)$_2$(μ-propynylborneol$^+$)BF$_4^-$ complex.

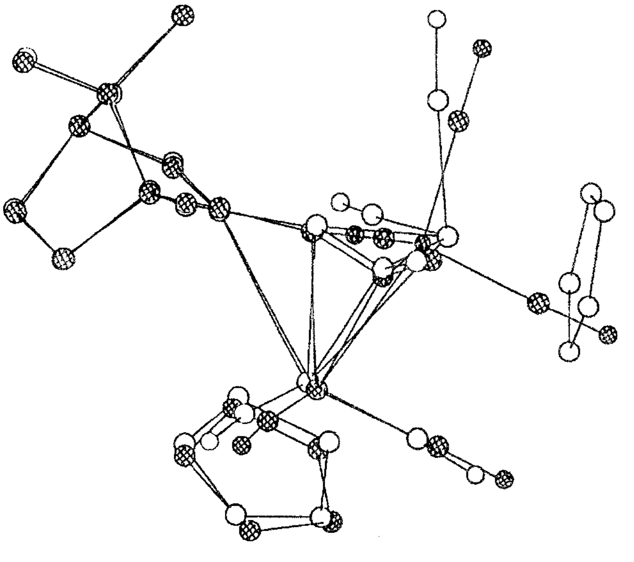


Fig. 5. Structures of cations **12** and **13** superimposed on one another.

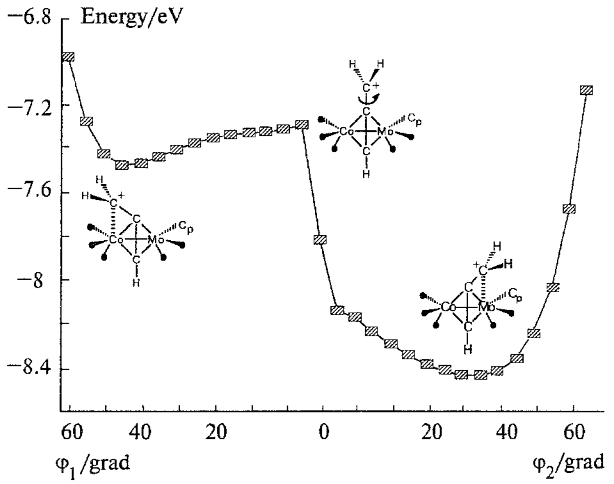


Fig. 6. EHMO calculated energy of stabilization of the C^+ carbocation site in the mixed molybdenum-cobalt cluster (φ_1 is the rotation angle with respect to the Co atom, φ_2 is that with respect to Mo).

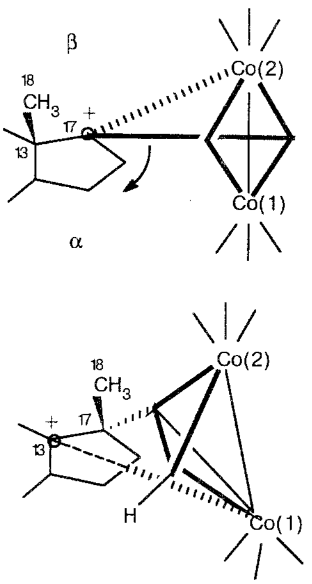


Fig. 7. The skeleton migration of the $C(18)H_3$ group in the steroid cation with assistance from the $Co(CO)_3$ vertex.

The EHMO calculations indicate that the 2-bornyl cations bound in the complexes do not isomerize due to the stabilization of the charge by the metal, which overrides other effects.

In conclusion, we should comment on an observation which has so far not been explained. Although the 2-bornyl cations stabilized by metals do not undergo Wagner—Meerwein rearrangement, the steroid cation (see Scheme 1) in which the carbocation occupies the α-position with respect to the dicobalt cluster readily undergoes a methyl shift. This may be due to the anchimeric assistance received by the β-cation from the cobalt vertex. Such systems surely deserve detailed investigation (Fig. 7).

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