A Synthetic and X-Ray Crystallographic Study of Cobalt and Molybdenum Cluster Complexes of the 2-Fenchyl Cation: Metal-Mediated Wagner−Meerwein Rearrangements

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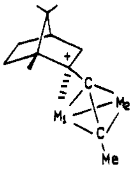
Abstract: Treatment of 2-*exo*-propynylfenchol, **4a**, with dicobalt octacarbonyl gives the sterically crowded (2-*exo*-propynylfenchol)$Co_2(CO)_6$ cluster, **5a**. Upon protonation, **5a** yields the cobalt-stabilized 2-fenchyl cation **6**, which is in equilibrium with its Wagner−Meerwein rearranged 2-bornyl isomer, **9**, bearing the Co_2C_2 tetrahedral cluster moiety at the C(1) bridgehead position. Aqueous quenching of the mixture of cations **6** and **9** yields (2-*endo*-propynylfenchol)$Co_2(CO)_6$, **5b**, together with two alkenes, **7a** and **7b**, derived by deprotonation of the 2-bornyl cation **9**. Replacement of one $Co(CO)_3$ vertex in **7a** by a $(C_5H_5)Mo(CO)_2$ moiety, and subsequent reprotonation, generates the Mo−Co cluster-substituted 2-bornyl cation **19a**, which undergoes Wagner−Meerwein rearrangement to the more sterically demanding *exo*-fenchyl cation **17a**. The isomerization of **19a** to **17a** is rationalized in terms of the enhanced ability of a $(C_5H_5)Mo(CO)_2$ cluster vertex, relative to a $Co(CO)_3$ fragment, to alleviate the electronic deficiency at a cationic center. (2-*endo*-Propynylfenchol)$Co_2(CO)_6$, **5b**, crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 7.408(2) Å, b = 15.750(2) Å, c = 17.591(2) Å, and V = 2052.6(7) Å^3 for Z = 4. [(2−*exo*-Propynylfenchyl)$MoCo(CO)_5(C_5H_5)$][BF_4], **17a**, crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 12.569(2) Å, b = 13.491(6) Å, and c = 14.473(3) Å, and V = 2454(1) Å^3 for Z = 4.

Introduction

The chemistry of tri- and dimetallic tetrahedral clusters bearing terpenoid substituents continues to attract attention.[1] The chiral nature of these molecules renders diastereotopic the metal centers,[2] thus facilitating stereoselective syntheses[3,4] and also providing probes of the molecular dynamics of the systems.[5]

We have recently reported the stabilization of 2-propargylbicyclo[2.2.1]hept-2-ylium systems by organometallic clusters.[6,7] The 2-bornyl cations **1−3** were initially identified spectroscopically, and subsequently the latter two clusters were structurally characterized by X-ray crystallography.[7] In these molecules not only are the 2-alkynylbornyl moieties stabilized against Wagner−Meerwein rearrangement (which is well-established for the free cation),[8] but also it has been demonstrated unequivocally that the electron deficiency at C(2) is preferentially alleviated by interaction with the molybdenum rather than the cobalt vertex.[6,7] The question now arises as to whether such cations will be sufficiently metal-stabilized so as to be able to resist Wagner−Meerwein rearrangement when placed in a situation of considerable steric stress. To probe this question, we have now prepared $Co_2(CO)_6$ complexes of 2-propynylfenchol, **4**, and we here describe their protonation and also the rearrangement behavior of the resulting cations. Moreover, we report the syntheses of several mixed metal (Mo−Co) bornyl and fenchyl clusters, and also the structure of a cation arising from a metal-promoted Wagner−Meerwein skeletal rearrangement.



1: M_1 = M_2 = $Co(CO)_3$

2: M_1 = M_2 = $Mo(CO)_2Cp$

3: M_1 = $Mo(CO)_2Cp$; M_2 = $Co(CO)_3$

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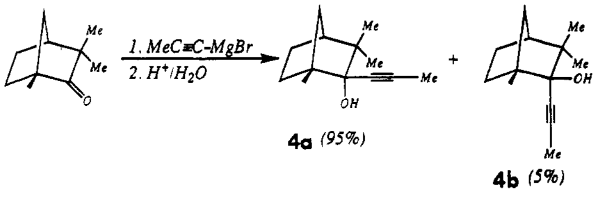
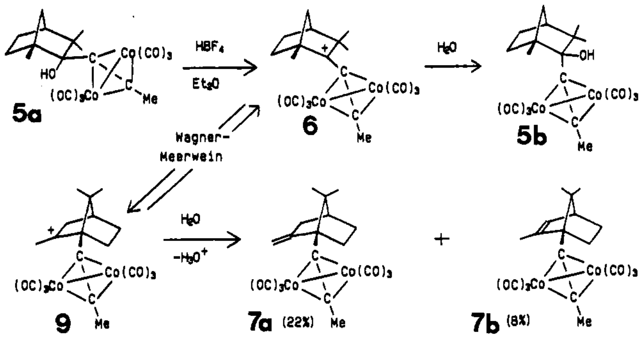
Results and Discussion

$Co_2(CO)_6$ Complexes of the 2-Propynylfenchyl Cation. The reactions of alkynyl anions with ketones have been extensively studied, and the stereochemical features which influence the facial selectivity have been elucidated in some detail.[9] In their pioneering experiments, Cadiot and Chodkiewicz noted that alkynyl anions approached camphor on the *endo* face, presumably to avoid the methyl groups attached to the C(7) bridge.[10] In contrast, it was reported that the analogous reaction with fenchone proceeded via *exo* attack to yield the alcohol **4a**.[11] In our hands, the reaction of a propynyl Grignard reagent with fenchone gave a mixture of **4a** and **4b** in a 95:5 ratio. The stereochemistry of the products was readily established by conventional 2D NMR techniques; these data confirm the original report of Chodkiewicz *et al.*[10] Treatment of this 95:5 mixture of **4a**/**4b** with $Co_2(CO)_8$ yielded the expected cobalt cluster **5a**, but the molecule showed evidence of instability, and it was not possible to obtain NMR spectroscopic data of the quality to which we are accustomed. Nevertheless, when the ethereal solution of **5**, obtained rapidly by flash chromatography, was immediately treated with HBF_4/Et_2O, the $[(2\text{-propynyl-2-fenchyl})Co_2(CO)_6]^+$ cation, **6**, was readily produced. After 30 min, the cation was quenched with water and the red product mixture was separated by column chromatography. The three fractions obtained were further purified by chromatography on silica plates to yield two alkenes, **7a** (22%) and **7b** (8%), traces of two alcohols, **8a** and **8b**, and the (propynylfenchol)$Co_2(CO)_6$ cluster **5b** (23%). The total yield of isolated products was approximately 57%. The cluster **5b** was identified spectroscopically as the epimer of the original complex derived by addition of $Co_2(CO)_8$ to the starting material **4**, and its structure was confirmed by X-ray crystallography (see below). As depicted in Scheme 1, the pair of alkenes **7a** and **7b** were identifiable, on the basis of their NMR spectra, as (1-propynyl-2-methylene-7,7-dimethylbicyclo[2.2.1]heptane)$Co_2(CO)_6$ and (1-propynyl-2,7,7-trimethylbicyclo[2.2.1]-2-heptene)$Co_2(CO)_6$, respectively. The alcohols **8a** and **8b** were obtained in very minor quantities, and their identities remain uncertain at present.

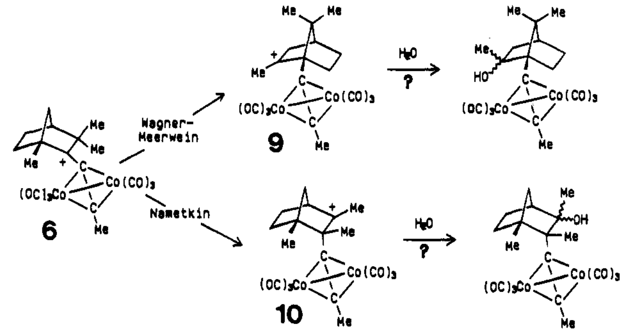


The conversion of the relatively unstable initially formed cluster **5a**, into its epimer **5b**, in which the cluster is now *endo* and the hydroxyl substituent is now *exo*, is readily rationalized in terms of the intermediacy of the cation **6** which is subsequently quenched by attack of water on the *exo* face. In epimer **5b** the sterically very demanding $(MeC{\equiv}C)Co_2(CO)_6$ fragment preferentially adopts a distal position with respect to the methylene bridge. Of course, one must assume that a very small quantity of **5b** is formed directly upon addition of $Co_2(CO)_8$ to **4**, since there is ~5% of the *exo*-alcohol **4b** already present in the original mixture. However, the yields of **5b** after protonation and hydrolysis of **5a** are consistently much too large (20–25%) to have arisen entirely from this source. The alkenes **7a** and **7b** are evidently produced by a Wagner–Meerwein rearrangement (see Scheme 1) to yield the bornyl-type cation **9**, which can eliminate in either of two ways. We have been unable to achieve clean separation of the alcohols **8a** and **8b**, which are obtained in only 4% isolated yield. Their behavior under a variety of chromatographic conditions, and the similarity of their ^{13}C NMR spectra, suggests that they are epimers, and they are probably the *exo*- and *endo*-alcohols derived by quenching the rearranged cation **9**. However, we cannot entirely dismiss the possibility that methyl migration has occurred (*i.e.*, a Nametkin rearrangement[12]) to place the cationic center at C(3); thus, **8a** and **8b** could have arisen by aqueous quenching of the cation **10**, as illustrated in Scheme 2. Certainly, protonation of fenchol itself yields a multitude of such products.[13]

Scheme 1. Protonation of **5a** To Yield the Cation **6** and Its Wagner–Meerwein Rearranged Isomer **9**



Scheme 2. Possible Wagner–Meerwein and Nametkin Rearrangement Products from **6**



At 20 °C, the observed yield of alkenes **7a** + **7b** is approximately 30% while the yield of the alcohol **5b** is ~23%. Interestingly, starting either from **7a** + **7b** or from **5b**, protonation followed by hydrolysis yields the same proportions of final products, indicating facile interconversion of the two isomeric carbenium ions **6** and **9**.

We pause a moment to reflect on the possible structures of the cation **6**; although no cations of the type $[(RC{\equiv}CCR_2)Co_2(CO)_6]^+$ have been crystallographically characterized, there is overwhelming evidence from variable-temperature NMR data[6,14]

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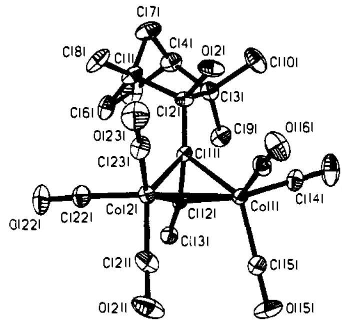
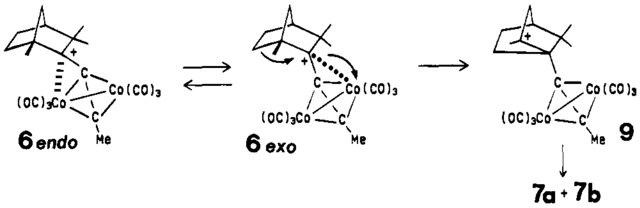


Figure 1. View of **5b** showing the atomic numbering scheme. Salient bond lengths (Å) and angles (deg): C(2)−C(11) = 1.505(9), C(11)−C(12) = 1.320(9), C(11)−Co(1) = 2.009(6), C(12)−Co(1) = 1.979(7), C(11)−Co(2) = 2.007(6), C(12)−Co(2) = 1.968(6), Co(1)−Co(2) = 2.348(1); C(6)−C(1)−C(2) = 109.4(7), C(1)−C(2)−C(11) = 115.9(7), C(3)−C(2)−C(11) = 114.7(6).

Scheme 3. Interconversion of the *endo* and *exo* Isomers of **6**



and also from molecular orbital calculations[15] that these cations adopt a bent geometry such that the cationic carbon interacts directly with a cobalt vertex. Moreover, in a very recent study, isolobal replacement of a $Co(CO)_3^+$ vertex by $Fe(CO)_3$ yielded an X-ray crystal structure of the neutral molecule ($MeC{\equiv}CCH_2)Fe(CO)_3Co(CO)_2PPh_3$ in which the CH_2 group leans toward the $Fe(CO)_3$ unit.[16] Thus, one can readily envisage structures (see Scheme 3) in which the directly bonded cobalt is either *endo* or *exo* with respect to the fenchyl skeleton. It is evident that an aqueous quench of the *endo*-**6** isomer would yield the observed alcohol **5b**. It is also apparent that, to facilitate a Wagner−Meerwein rearrangement leading to the bornyl cation **9**, the favored intermediate would be the *exo*-**6** isomer.

X-Ray Crystal Structure of 5b. The cluster **5b** crystallizes in the orthorhombic space group $P2_12_12_1$, and a view of the molecule appears in Figure 1. The disposition of the three methyl groups indicates that the terpenoid skeleton is of the fenchyl type, with the cluster moiety occupying the 2-*endo* site. It is evident that this epimer, the opposite of that derived by addition of dicobalt octacarbonyl to **4a**, alleviates the steric problems engendered by the proximity of the cluster to the methylene bridge. We have previously reported the X-ray crystal structure of **11**, the bornyl analogue of **5b**, which differs only in the positions of two of the methyl groups.[4] The two structures are remarkably similar, and the only significant difference involves the C(2)−C(3) bond length which is 1.567(6) Å in **11**, but increases to 1.618(6) Å in **5b**. Presumably, this is a reflection of the molecular crowding associated with the neighboring *gem*-dimethyl group at C(3). There is also some twisting about the C(2)−C(3) vector in **5b** so as to prevent eclipsing of the substituents. The dihedral angles O(2)−C(2)−C(3)−C(10) and C(11)−C(2)−C(3)−C(9) are 6° and 11°, respectively. The bond lengths and angles within the tetrahedral Co_2C_2 framework lie in the normal ranges; the crystallographic data are collected in Table 1.

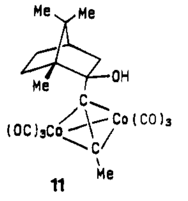


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Table 1. Crystallographic Data for (2-*endo*-Propynylfenchol)-$Co_2(CO)_6$, **5b**, and [(2−*exo*-Propynylfenchyl)$MoCo(CO)_5(C_5H_5)$]-$[BF_4]$, **17a**

	5b	**17a**
chemical formula	$C_{19}H_{20}O_7Co_2$	$C_{23}H_{24}O_5MoCoBF_4$
formula weight	478.2	622.1
crystal system	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
Z	4	4
a, Å	7.408(2)	12.569(2)
b, Å	15.750(2)	13.491(6)
c, Å	17.591(2)	14.473(2)
V, Å³	2052.6(7)	2454(1)
F(000)	976	1248
ϱ(calcd), mg/m³	1.55	1.68
μ (Mo Kα), cm⁻¹	16.48	12.3
diffractometer	CAD4	CAD4
radiation	Mo Kα (λ = 0.710 70 Å)	Mo Kα (λ = 0.710 73 Å)
T, K	293	293
monochromator	graphite	graphite
scan type	$\omega/2\theta$	$\omega/2\theta$
scan range θ, deg	$0.8 + 0.34 \tan\theta$	$0.8 + 0.34 \tan\theta$
2θ range, deg	2−50	2−56
rflns collected	2082	3316
rflns used ($I > 3\sigma(I)$)	1481	2660
R	0.0326	0.0317
R_w[a]	0.0336	0.0309
abs corr (DIFABS)	min 0.90, max 1.11	min 0.92, max 1.06
secondary extinction	75×10^{-6}	no
weighting scheme	unit weights	unit weights
rms (shift/esd) (last ref)	0.07	0.58
ls parameters	254	391

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

The facile interconversion of the two cations **6** and **9** in the fenchyl system contrasts markedly with the behavior of the analogous cobalt-complexed bornyl cation **1** which shows no tendency toward Wagner−Meerwein rearrangement.[6,7] However, it has been previously noted that the [(propargylsteroidal)-$Co_2(CO)_6]^+$ cation, **12**, yields a mixture of elimination products, presumably derived from the rearranged cation **13**, shown in Scheme 4.[17] In contrast, the corresponding [(propargylsteroidal)-$Mo_2(CO)_4Cp_2]^+$ cation, **14**, not only is able to resist cationic rearrangement, but is also sufficiently stable to be amenable to an X-ray crystal structure determination.[17]

The migration of the β-methyl group, from C(13) to C(17), observed in the case of the cobalt cluster cations **12** and **13**, can perhaps be related to the fluxional character of this species. As discussed already for the fenchyl cation **6**, migration of a neighboring group is favored when the stabilizing metal is disposed trans to the incoming moiety, as in *exo*-**6**. Indeed, it is well established that, for a concerted Wagner−Meerwein rearrangement to occur, the leaving and migrating groups should be antiperiplanar.[12] When the carbenium ion center interacts with a molybdenum atom, as in **14**, the electron deficiency at

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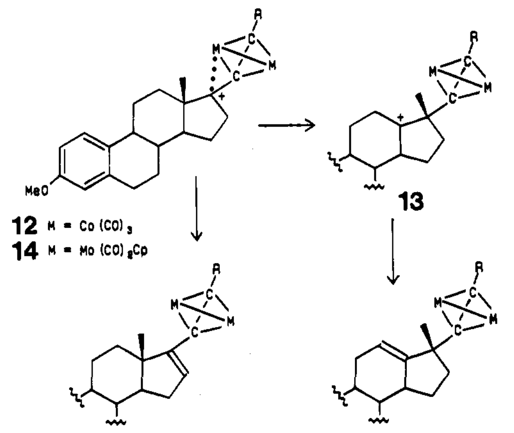
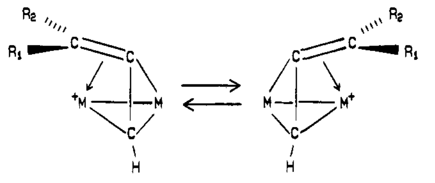
Scheme 4. Methyl Migrations in Metal-Stabilized Steroidal Cations



carbon is alleviated rather efficiently, and the species is relatively stable. However, in the $Co_2(CO)_6$ systems, the carbon center retains some of its cationic character and migration of a neighboring alkyl substituent is still feasible.[17] Nevertheless, the requirement for an antiperiplanar transition state still exists, and so the 1,2-shift of a β-methyl substituent, as in **12** to **13**, should be viable only for the isomer in which a cobalt center is bonded to the α-face of the steroid in **12**. In **14**, the isomer with a β-bonded molybdenum has been crystallographically characterized, but it is known to be in equilibrium with its α-partner.[17] Assuming the same fluxional behavior for the cobalt complex **12**, one can envisage the ready accessibility of the α-isomer which possesses the appropriate geometry for β-methyl migration.

MoCo(CO)$_5$Cp Complexes of the 2-Propynylfenchyl Cation. We have previously shown that isolobal replacement of a $Co(CO)_3$ vertex by $CpMo(CO)_2$, followed by protonation to generate a cation, as in **3**, leads to an $M\cdot\cdot C^+$ interaction only with the molybdenum vertex.[6,7] Moreover, unlike the homodimetallic cations **15**, where antarafacial migration of the CR_2^+ fragment from one metal vertex to the other is well-known,[18] these heterometallic Co–Mo cluster cations are not fluxional.[6]



15 M = $Co(CO)_3$, $Mo(CO)_2Cp$, $W(CO)_2Cp$

Since the clusters **5b** and **7a** were available in reasonable quantities, we chose to study the effect of replacing one $Co(CO)_3$ vertex by a $CpMo(CO)_2$ fragment on the behavior of the resulting cations. Treatment of the alcohol **5b** with the anion $[CpMo(CO)_3]^-$ led to a 70:30 mixture of diastereomers **16a** and **16b**; subsequent protonation yielded the cations **17a** and **17b**, in the same 70:30 ratio. In contrast, replacement of a tricarbonylcobalt vertex by a dicarbonyl(cyclopentadienyl)molybdenum moiety in the alkene complex **7a** proceeded with a high degree of stereoselectivity to give **18a** and **18b** in a 95:5 ratio. Protonation of this mixture with HBF_4/Et_2O at room temperature, and subsequent recrystallization by diffusing ether into a CH_2Cl_2 solution of the product, yielded red-brown X-ray quality crystals. The structure of this product is shown in Figure 2, and it is immediately evident that it is a fenchyl-type cation which has arisen as the consequence of a Wagner–Meerwein rearrangement of the bornyl-type Mo–Co cation **19a** to give **17a**. This reaction sequence is shown in Scheme 5; it corresponds to the reverse of the archetypal rearrangement (see Scheme 6) of camphenyl chloride, **20**, to isobornyl chloride, **21**.[19] In the conversion of **20** to **21**, there is a release of steric strain caused by the unfavorable interactions between the three methyl groups and the chlorine atom in the camphenyl chloride. In the conversion of the Mo–Co cation **19a** to **17a**, the metal-assisted electronic stabilization of the latter must overcome the steric hindrance associated with the fenchyl skeleton.

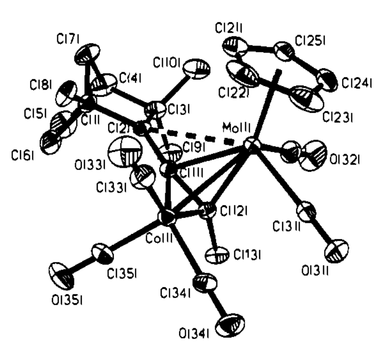


Figure 2. View of **17a** showing the atomic numbering scheme. Salient bond lengths (Å) and angles (deg): C(2)–C(11) = 1.365(6), C(11)–C(12) = 1.377(6), C(11)–Mo(1) = 2.229(4), C(12)–Mo(1) = 2.108(5), C(11)–Co(1) = 1.938(5), C(12)–Co(1) = 1.948(6), Mo(1)–Co(1) = 2.6781(8); C(6)–C(1)–C(2) = 100.6(5), C(1)–C(2)–C(11) = 126.7(5), C(3)–C(2)–C(11) = 126.1(5).

We have commented already that the Wagner–Meerwein rearrangement which interconverts the dicobalt cations **6** and **9** should proceed preferentially through the *exo*-**6** complexed cation. It is therefore not unreasonable to suppose that the reverse process which takes the Mo–Co bornyl-type cation **19a** back to the fenchyl system **17a** should generate the *exo* cation, as indeed it does! Moreover, since the absolute configuration[5] of the $MoCoC_2$ tetrahedral cluster unit is unaffected by the Wagner–Meerwein process, it is now apparent that diastereomer **18a** was the major product of replacement of a $Co(CO)_3$ vertex in **7a** by the $CpMo(CO)_2$ moiety.

X-ray Crystal Structure of 17a. The cluster **17a** crystallizes in the orthorhombic space group $P2_12_12_1$, and a view of the cation appears in Figure 2. The Mo–Co, Mo–C, and Co–C bond distances 2.678, 2.168 (average), and 1.94 Å (average), respectively, are in the normal ranges.[20] The terpenoid skeleton is clearly that of a fenchyl cation and, superficially, resembles the previously reported Mo–Co bornyl cation **3**.[4] However, there are significant differences. Of course, the methyl substitution pattern on the bicyclo[2.2.1]heptyl framework is different, but more importantly, we note that the molybdenum atom in **17a** occupies an *exo* position, rather than the *endo* site adopted in **3**. There are also significantly different $M\cdot\cdot C^+$ distances in **3** and in **17a**. In the bornyl cation **3**, the distance Mo–C(2) is 2.914 Å, and the angle C(2)–C(11)–(M_2C_2 centroid) is 142°; that is, the cationic center is bent through 38° away from the "vertical" position toward the molybdenum. In the fenchyl cluster **17a**, the cation is considerably further from the metal centers: Mo–C(2) = 3.08 Å, Co–C(2) = 3.14 Å. Furthermore,

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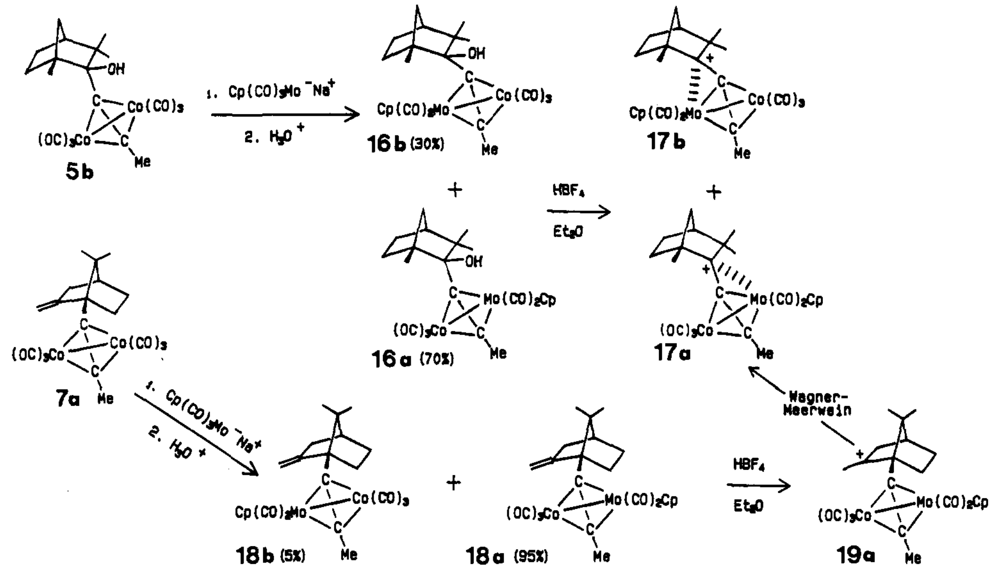
(18) (a) Meyer, A.; McCabe, D. J.; Curtis, M. D. *Organometallics* **1987**, *6*, 1491. (c) Sokolov, V. I.; Barinov, I. V.; Reutov, O. A. *Isz. Akad. Nauk SSR, Ser. Khim.* **1982**, 1922. (d) Reutov, O. A.; Barinov, I. V.; Chertkov, V. A.; Sokolov, V. I. *J. Organomet. Chem.* **1985**, *297*, C25. (e) Froom, S. F. T.; Green, M.; Nagle, K. R.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1305. (f) Galakhov, M. V.; Bakhmutov, V. I.; Barinov, I. V.; Reutov, D. A. *J. Organomet. Chem.* **1981**, *421*, 65.

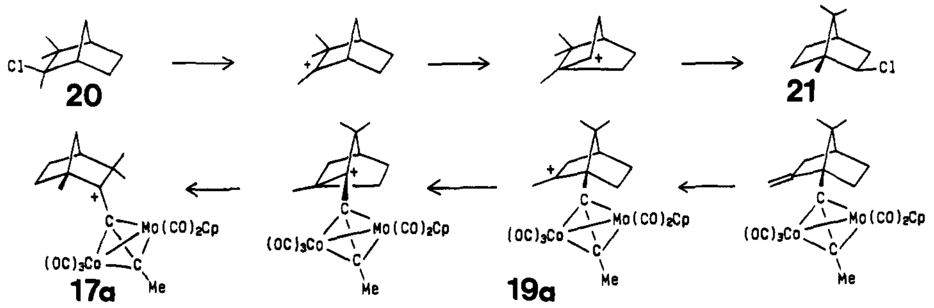
(19) Meerwein, H.; van Emster, K. *Berichte* **1922**, *55*, 2500.

(20) (a) Beurich, H.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 863. (b) Sutin, K. A.; Li, L; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1991**, *10*, 2362 and references therein.

Scheme 5. Products of Protonation of **5b** and of **7a**



Scheme 6. Interconversions among Camphenyl, Bornyl, and Fenchyl Cations



the angle C(2)−C(11)−(M_2C_2-centroid) is now 155°; that is, the cationic carbon is oriented only 25° away from an imaginary vertical line which passes through the capping carbynyl carbon, C(11), and the center of the tetrahedron.

These differing geometries are also reflected in the C(2)−C(11)−Mo(1) angle which has opened up to 116° in **17a**, from only 105° in **3**. We had previously noted that in **2** (**3**) the alkyne capping carbon is bent out of the plane defined by the C(1)−C(2)−C(3) atoms of the bornyl skeleton by 19° (14°); this deformation is toward the *exo* face of the molecule.[4] In **17a**, the corresponding out-of-plane bend is 10° in the *endo* direction. Although these $M\cdot\cdot C^+$ distances of 2.91 Å in **3** and 3.08 Å in **17a** would seem to be too long for direct interactions, we should recall that previously reported EHMO calculations on the [(2-ethynyl-2-bornyl)$Co_2(CO)_6$]$^+$ cation found that $M\cdot\cdot C^+$ distances ranging from 2.8 to 3.1 Å give rise to a steep but rather wide valley.[7]

It is interesting that the structures of the fenchyl-*exo*-Mo−Co cation **17a** and the bornyl-*endo*-Mo−Co cation **3** parallel the behavior of nucleophiles attacking fenchone and camphor, respectively. In fenchone, the sp^2 center accepts electron density from an *exo*-attacking nucleophile while for camphor the nucleophile approaches from the *endo* face. It may be the case that, since the *exo*-stabilized bornyl cation is disfavored by the presence of the $Me_2C(7)$ bridge, the transition state for Wagner−Meerwein migration is less readily accessible. One must emphasize, however, that the bicyclo[2.2.1]hept-2-yl skeleton in each of these metal-stabilized cations is that of a classical cation.[21] These systems are quite different from that reported by Laube for the 1,2,4,7-*anti*-tetramethyl-2-norbornyl cation which is clearly unsymmetrically bridged.[22]

We have recently described how the antarafacial migration of a cation from one metal vertex to the other (as in **15**) can be modeled by examining a series of X-ray crystal structures of cations of the type [$Cp_2Mo_2(CO)_4(RC{\equiv}CCR'R'')$]$^+$, where the R′ and R″ substituents range from H, methyl, or ferrocenyl to terpenoid or steroidal groups.[23] In this Bürgi−Dunitz approach,[24] one can use the crystallographic data to map out a trajectory through which the antarafacial migration can occur. The highest point on such a pathway would place the cation midway between the two metal centers, but no such species have been characterized in the solid state; the cationic center is always seen to be leaning toward one of the metal vertices. It is, therefore, of particular interest to find that, in the Co−Mo cluster **17a**, the crystal structure reveals the most nearly linear orientation yet observed. This structure currently represents the closest approach to the transition state for cation migration from metal to metal.

It is clear that it is not essential to have a direct bond between the electron-deficient center and the metal vertex to generate a metal-stabilized carbocation. Nevertheless, the cluster must be playing a crucial role in the delocalization of the charge. The metal carbonyl infrared stretching vibrations for the precursor

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[21] For references to 2-substituted 2-norbornyl cations bearing conventional organic groups, see: Olah, G. A.; Reddy, V. P.; Rasul, G. K. S. *J. Org. Chem.* **1992**, *57*, 1114 and references cited therein.

[22] Laube, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 560.

[23] Girard, L.; Lock, P. E.; El Amouri, H.; McGlinchey, M. J. *J. Organomet. Chem.* **1994**, *478*, 189.

[24] Bürgi, H.-B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153.

alcohols **16a** and **16b** are seen at 2034, 1986, 1965, and 1927 cm^{-1}; the corresponding ν_{CO} values for the cations **17a** and **17b** are 2083, 2047, 2029, and 2017 cm^{-1}. These data are characteristic of considerably decreased back-donation from the metal to the vacant π^* manifold of the CO's, and indicate unequivocally that the metal bears some degree of positive charge. This may be relevant to the fluxional behavior of [$Cp_2Mo_2(CO)_4(RC{\equiv}CCR'R'')]^+$ complexes. In these systems, the barrier to antarafacial migration is much lower for tertiary cations than for primary cations,[18] and the M$\cdot\cdot$C$^+$ distance is also longer in the former cases, yet the molybdenum is still able to stabilize these otherwise short-lived electron-deficient species.

Conclusions

The original goal of this project was to see whether metal clusters were capable of stabilizing cations of the 2-propargylbicyclo[2.2.1]hept-2-ylium series, and also preventing them from undergoing Wagner–Meerwein rearrangements. In the 2-bornyl series, the cluster cations **1–3** are all stable toward skeletal rearrangement and can be readily isolated. In contrast, in the fenchyl clusters, where we have deliberately imposed steric hindrance close to the cationic site, the $Co_2(CO)_6$ complexes find two ways of relieving the steric strain. The first method is to epimerize so as to place the cluster as far away from the other bulky groups as possible; the second route involves Wagner–Meerwein rearrangement and subsequent elimination to yield alkenes. In contrast, incorporation of a $CpMo(CO)_2$ vertex, as in **17a** and **17b**, not only prevents skeletal rearrangement away from the fenchyl structure, but also brings about Wagner–Meerwein rearrangement of bornyl carbocations which are not stabilized by a metal center such that they adopt the fenchyl framework. This again illustrates that the $CpMo(CO)_2$ moiety is much more efficient than the $Co(CO)_3$ vertex at alleviating charge deficiency. We have made some progress toward constructing a hierarchy of such organometallic fragments, and their use in enantioselective synthesis is the subject of current investigation in these laboratories.

Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were purified and dried before use by conventional distillation techniques under argon. ^{1}H and ^{13}C NMR data were recorded on a Bruker AM 200, AM 250, or AM 400 spectrometer using a 5 mm dual frequency ^{1}H/^{13}C probe. ^{1}H–^{1}H COSY and ^{1}H–^{13}C shift-correlated spectra were performed by using standard pulse sequences. Infrared spectra were recorded in CH_2Cl_2 on an FT Bomem Michelson 100 instrument. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The adsorbent used for column and thin layer chromatography was silica gel 60 GF$_{254}$. Elemental analyses were performed by the regional microanalysis service (Université Pierre et Marie Curie).

2-*exo*-Propynylfenchol (4a). Bromomethane (3.6 g, 38 mmol) and Mg (0.72 g, 30 mmol) in ether (30 mL) were used to prepare the Grignard reagent into which propyne was bubbled for 1.5 h at room temperature. Over a 2 h period, (−)-fenchone (3.0 g, 20 mmol) in ether (15 mL) was added dropwise, and the solution was hydrolyzed with acidified water. Extraction and recrystallization yielded 2-propynylfenchol (2 g, 10.4 mmol; 50%), shown by NMR to be 95% of the *exo*-propynyl isomer **4a**. ^{1}H NMR (400 MHz, C_6D_6): δ 2.23 (m, 1H, H-6$_{endo}$), 1.91 (s, 1H, OH), 1.86 (m, 2H, H-7), 1.80 (m, 1H, H-5$_{endo}$), 1.70 (m, 1H, H-4), 1.62 (s, 3H, alkyne-Me), 1.42 (m, 1H, H-5$_{exo}$), 1.37 (s, 3H, Me-10), 1.27 (s, 3H, Me-9), 1.15 (m, 1H, H-6$_{exo}$), 1.07 (s, 3H, Me-8). ^{13}C NMR (100 MHz, C_6D_6): δ 83.3 (alkyne-C, C-12), 82.1 (C-2), 80.6 (alkyne-C, C-11), 53.7 (C-1), 49.1 (C-4), 43.9 (C-3), 41.4 (C-7), 30.4 (Me, C-9), 27.4 (C-6), 26.4 (C-5), 22.0 (Me, C-8), 18.5 (Me, C-10), 3.2 (Me, C-13).

Preparation, Protonation, and Hydrolysis of (2-*exo*-Propynylfenchol)$Co_2(CO)_6$ (5a). 2-*exo*-Propynylfenchol (0.96 g, 5 mmol) in ether (20 mL) was treated with $Co_2(CO)_8$ (1.74 g, 5 mmol), and the progress of the reaction was followed by TLC on a silica plate by using pentane as the eluent. After 2 h, the solution was filtered and chromatographed rapidly on silica gel, and a small aliquot was evaporated to provide an NMR sample. The ^{1}H spectrum in $CDCl_3$ was broad, but it did exhibit a singlet at 2.8 ppm, typical of a methyl group on cobalt-complexed alkyne. Thus, the ethereal solution of **5a** was used directly, and HBF_4–Et_2O (2 mL) was added at room temperature. After 30 min, the mixture was hydrolyzed with water, extracted with ether, dried, and evaporated to give 1.9 g of crude product. This red material was subjected to column chromatography using pentane as eluent, and gave three fractions: the least polar fraction (0.6 g) comprised two alkenes which were separated on silica gel plates to give **7a** and **7b** in a 3:1 ratio; the middle fraction (0.17 g) was a mixture of two alcohols, **8a** and **8b**; the final, and most polar, fraction (0.6 g) was the pure alcohol **5b**.

7a was obtained as a brown oil. ^{1}H NMR (250 MHz, C_6D_6): δ 4.95 (d, J = 2.5 Hz, 1H, H-10), 4.85 (d, J = 2.5 Hz, 1H, H-10), 2.4 (s, 3H, alkyne-Me), 2.34 (d, J = 17.5 Hz, of sext, J = 2.5 Hz, 1H, H-3$_{exo}$), 2.01 (d, J = 8.9 Hz, of t, J = 4.2 Hz, 1H, H-5$_{endo}$), 1.83 (d, J = 17.5 Hz, of t, J = 2.5 Hz, 1H, H-3$_{endo}$), 1.64 (m, 1H, H-5$_{exo}$), 1.49 (t, J = 4.3 Hz, 1H, H-4), 1.04 (m, 2H, H-6$_{endo}$, H-6$_{exo}$), 1.00 (s, 3H, Me), 0.87 (s, 3H, Me). ^{13}C NMR (62.9 MHz, C_6D_6): δ 201.0 (Co-CO's), 156.2 (C-2), 106.4 (C-10), 95.7 (C-12, C-11), 58.6 (C-7), 52.3 (C-1), 47.1 (C-4), 39.6 (CH_2), 37.1 (CH_2), 28.4 (CH_2), 22.2 (Me), 20.7 (Me), 20.6 (Me). IR (CH_2Cl_2): ν_{CO} 2083, 2042, 2014 cm^{-1}. $[\alpha]_D$ = +267.1 (c 0.0487, heptane). Anal. Calcd for $C_{19}H_{18}O_6Co_2$ (**7a/7b**): C, 49.57; H, 3.91. Found: C, 49.65; H, 4.14.

7b was obtained as a brown oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.73 (m, 1H, H-3), 2.87 (s, 3H, alkyne-Me), 2.31 (t, J = 2.5 Hz, 1H, H-4), 2.0 (m, 2H), 1.83 (d, J = 1.8 Hz, 3H, Me-10), 1.40 (m, 2H) 0.99 (s, 6H, Me-8, Me-9). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 201.1 (Co-CO's), 145.0 (C-2), 130.1 (C-3), 95.0 (C-12, C-11), 61.3 (C-7), 52.5 (C-4), 46.2 (C-1), 32.0, 26.2 (2 × CH_2), 22.4 (Me), 21.7 (Me), 20.6 (Me), 16.0 (Me). IR (CH_2Cl_2): ν_{CO} 2083, 2042, 2014 cm^{-1}. $[\alpha]_D$ = +82.2 (c 0.0365, heptane).

8a and **8b** were obtained as an approximately 50:50 mixture as a brown oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.81 (s, 3H, alkyne-Me), 2.57–2.32 (m, 1H), 1.98–1.80 (m, 3H), 1.75–1.49 (m, 2H), 1.62 and 1.53 (s, 3H, Me), 1.22 (s, 3H, Me), 1.21–1.14 (m, 1H), 1.09 (s, 3H, Me). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 199.7 (Co-CO's), 106.1, 103.1, 97.0, 92.8, 59.1, 58.7, 53.5, 53.4, 47.0, 46.9, 46.8, 46.7, 34.8, 34.7, 27.0, 24.8, 24.4, 23.6, 21.9, 21.8, 21.7. IR, (CH_2Cl_2): ν_{CO} at 2085, 2045, 2015 cm^{-1}. Anal. Calcd for $C_{19}H_{20}O_7Co_2$: C, 47.70; H, 4.18. Found: C, 48.51; H, 4.10.

5b was obtained as X-ray quality red-brown crystals from pentane after one week at −25 °C. ^{1}H NMR (250 MHz, C_6D_6): δ 2.34 (s, 3H, alkyne-Me), 2.12 (m, 1H, H-7), 1.61 (m, 1H, H-6$_{endo}$), 1.48 (m, 1H, H-4), 1.23 (m, 2H, H-5$_{exo}$, H-5$_{endo}$), 1.23 (s, 3H, Me-10), 1.11 (m, 1H, H-6$_{exo}$), 1.08 (s, 3H, Me-8 or Me-9), 1.02 (m, 1H, H-7), 0.88 (s, 3H, Me-8 or Me-9); ^{13}C NMR (62.9 MHz, C_6D_6): δ 200.0 (Co-CO's), 100.0 and 94.7 (C-12, C-11), 84.7 (C-2), 55.8 (C-1), 50.1 (C-3), 48.7 (C-4), 43.5 (C-7), 29.9 (C-4), 25.5 and 25.4 (Me-8, Me-9), 23.4 (Me-13), 18.3 (Me-10). IR (CH_2Cl_2): ν_{CO} 2085, 2044, 2019 cm^{-1}. $[\alpha]_D = -446.1$ (*c* 0.1076, heptane). Anal. Calcd for $C_{19}H_{20}O_7Co_2$: C, 47.70; H, 4.18. Found: C, 47.84; H, 4.30.

(1-Propynyl-2-methylene-7,7-dimethylbicyclo[2.2.1]heptane)-CoMoCp(CO)$_5$ (18a, 18b). Under an atmosphere of argon, $[(CpMo(CO)_3]_2$ (2.2 g, 4.1 mmol) in dry THF (10 mL) was treated with sodium amalgam (Hg, 2 g; Na, 20 mg, 0.87 mmol), and the initially red solution became yellow-green as anion formation progressed. After filtration, the anion was added to a solution of **7a** (0.18 g, 0.39 mmol) in dry THF (10 mL), and the mixture stirred at reflux. The reaction was monitored by TLC on silica gel using pentane as eluent. After 1 h, the reaction mixture was allowed to cool to room temperature, the solvent was removed, and the residue was extracted in pentane. The product was chromatographed on silica plates using pentane as eluent to yield a diastereomeric mixture of **18a** and **18b** (95:5) (0.11 g, 0.21 mmol; 52%) as a red-brown oil. ^1H NMR (200 MHz, CD_2Cl_2): δ 5.47 (s, 5H, Cp), 5.00 (m, 1H, H-10), 4.72 (m, 1H, H-10), 2.93 (s, 3H, alkyne-Me), 2.58 (m, 1H, H-3), 2.2−1.2 (m, 6H), 1.04 (s, 3H, Me), 0.87 (s, 3H, Me). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 226.3 and 225.6 (Mo-CO's), 205.0 (Co-CO's), 157.0 (C-2), 104.7 (C-10), 90.9 (Cp), 60.0 (C-7), 53.3 (C-1), 46.6 (C-4), 39.1 (CH_2), 37.4 (CH_2), 27.2 (CH_2), 23.4 (Me), 21.8 (Me), 19.7 (Me). IR (CH_2Cl_2): ν_{CO} 2038, 1985, 1969, 1924 cm^{-1}. Anal. Calcd for $C_{23}H_{23}O_5CoMo$: C, 51.68; H, 4.31. Found: C, 53.5; H, 4.93.

(2-*endo*-Propynylfenchol)CoMoCp(CO)$_5$ (16a, 16b). Analogously to the synthesis of **18a** and **18b**, **5a** (0.29 g, 0.61 mmol) was treated with the anion $[CpMo(CO)_3]^-$ to yield, after chromatography, a mixture of diastereomers **16a** and **16b** (70:30) (0.18 g, 0.32 mmol; 53%) as a red-brown solid; these isomers were not separated. **Data for 16a.** ^1H NMR (200 MHz, CD_2Cl_2): δ 5.53 (s, 5H, Cp), 2.99 (s, 3H, alkyne-Me), 2.1−1.0 (m, 2H), 1.85 (s, 1H, OH), 1.72−1.00 (m, 5H), 1.12 (s, 3H, Me), 1.09 (s, 3H, Me), 1.02 (s, 3H, Me). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 90.9 (Cp), 87.2 (C-2), 56.2 (C-1), 50.5 (C-3), 48.7 (C-4), 43.3 (C-7), 29.4 and 24.5 (CH_2-5, CH_2-6), 25.8 and 25.4 (Me-8, Me-9), 23.2 (C-13), 18.5 (C-10). **Data for 16b.** ^1H NMR (200 MHz, CD_2Cl_2): δ 5.49 (s, 5H, Cp), 2.99 (s, 3H, alkyne-Me), 2.1−1.0 (m, 2H), 1.72−1.00 (m, 5H), 1.68 (s, 1H, OH), 1.22 (s, 3H, Me), 1.00 (s, 3H, Me), 0.98 (s, 3H, Me). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 90.7 (Cp), 87.0 (C-2), 56.9 (C-1), 50.5 (C-3), 48.4 (C-4), 43.5 (C-7), 29.4 and 24.5 (CH_2-5, CH_2-6), 25.8 and 25.4 (Me-8, Me-9), 23.2 (C-13), 18.5 (C-10). IR (CH_2Cl_2): ν_{CO} at 2034, 1986, 1956, 1927, 1895 cm^{-1}. Anal. Calcd for $C_{23}H_{25}O_6CoMo$: C, 50.00; H, 4.53. Found: C, 50.89; H, 4.73.

(1,3,3-Trimethyl-2-propynylbicyclo[2.2.1]hept-2-ylium)-CoMoCp(CO)$_5$·BF$_4$ (17a). To a stirred solution of **18a** (0.045 g, 0.084 mmol) in ether (10 mL) was added 5 drops of HBF_4-Et_2O at room temperature. An ether-insoluble red oil was obtained which, after stirring for 30 min, was washed five times with ether to give **17a** (39 mg, 0.063 mmol; 75%). Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of ether into a CH_2Cl_2 solution of **17a**. ^1H NMR (200 MHz, CD_2Cl_2): δ 5.91 (s, 5H, Cp), 3.05 (s, 3H, alkyne-Me), 2.14 (m, 1H, H-4), 2.06 (dm, 1H, H-6), 1.95 (m, 1H, H-5), 1.78 (m, 2H, H-7), 1.62 (dm, 1H, H-6), 1.32 (m, 1H, H-5), 1.28 (s, 3H, Me), 1.25 (s, 3H, Me), 1.11 (s, 3H, Me). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 231.8, 220.5 and 215.9 (Mo-CO's), 201.0 (Co-CO's), 113.5 and 99.2 (C-12, C-11), 94.8 (Cp), 63.6 and 57.0 (C-1, C-3), 50.5 (C-4), 46.0 (C-6), 41.6 (C-5), 35.2 (Me), 27.8 (alkyne-Me), 25.4 (Me), 25.0 (C-7), 19.9 (Me). IR (CH_2Cl_2): ν_{CO} 2083, 2047, 2034, 2020, 1988 cm^{-1}. Anal. Calcd for $C_{23}H_{24}O_5CoMoBF_4$: C, 44.37; H, 3.86. Found: C, 44.43; H, 3.75.

(1,3,3-Trimethyl-2-propynylbicyclo[2.2.1]hept-2-ylium)-CoMoCp(CO)$_5$·BF$_4$ (17a, 17b). As for **17a**, the 70:30 diastereomeric mixture of **16a** and **16b** (0.12 g, 0.22 mmol) was treated with HBF_4-Et_2O; subsequent slow diffusion of ether into CH_2Cl_2 yielded the crystals of a mixture of cations **17a** and **17b** (0.11 g, 0.18 mmol; 83%), which were not separated. **Data for 17a.** ^1H and ^{13}C NMR as above. **Data for 17b.** ^1H NMR (200 MHz, CD_2Cl_2): δ 5.91 (s, 5H, Cp), 3.01 (s, 3H, alkyne-Me), 2.20−1.30 (m, 7H), 1.41 (s, 3H, Me), 1.25 (s, 3H, Me), 1.17 (s, 3H, Me). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 113.5 and 99.2 (C-12, C-11), 94.5 (Cp), 65.4 and 57.0 (C-1, C-3), 50.0 (C-4), 45.2 (C-6), 41.9 (C-5), 36.2 (Me), 28.8 (Me), 27.5 (alkyne-Me), 26.3 (C-7), 19.9 (Me). IR (CH_2Cl_2): ν_{CO} 2083, 2047, 2029, 2017, 2001 cm^{-1}. Anal. Calcd for $C_{23}H_{24}O_5CoMoBF_4$: C, 44.37; H, 3.86. Found: C, 44.39; H, 3.88.

X-ray Crystal Structure Determinations for 5b and 17a. Suitable crystals of **5b** and of **17a** were obtained by slow diffusion of ether into a dichloromethane solution. Accurate cell dimensions and orientation matrices were obtained by least-squares refinement of 25 accurately centered reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. No significant variations were observed in the two check reflections during data collection. Complete crystallographic data and collection parameters are collected in Table 1. The data were corrected for Lorentz and polarization effects; an empirical absorption correction (DIFABS)[25] was applied. Computations were performed by using CRYSTALS[26] modified locally for a Microvax II computer. Scattering factors and corrections for anomalous absorption were taken from ref 27. The structure was solved by direct methods (SHELXS)[28] and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. For **17a**, hydrogen atoms were introduced in calculated positions in the last refinement, and only an overall isotropic thermal parameter was refined. For **5b**, hydrogen atoms were located on a difference Fourier map and their coordinates refined with an isotropic thermal parameter. Final atomic coordinates for **5b** and for **17a** appear in Tables S1 and S6, respectively, of the supporting information.

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Supporting Information Available: Tables of crystallographic data, atomic positional and thermal parameters, bond lengths, and bond angles for **5b** and **17a** (11 pages); tables of observed and calculated structure factors for **5b** and **17a** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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