Organometallics **1994**, *13*, 5149−5156

NMR Study of the Dynamic Behavior of $[(2\text{-propynylbornyl})Mo_2(CO)_4Cp_2]^+BF_4^-$: Nonfluxional Molybdenum−Cobalt Clusters as the Key to Understanding the Mechanism of the Formation of Metal-Stabilized Cations

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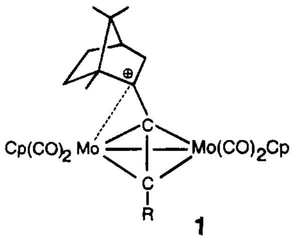
Received June 27, 1994[®]

Treatment of (2-propynylborneol)$Co_2(CO)_6$ with $[(CpMo(CO)_3]^-$ yields (2-propynylborneol)-$CoMo(CO)_5Cp$ as a mixture of diastereomers, **4a** and **4b**, which can be separated and individually protonated. The resulting cations $[(2\text{−propynylbornyl})CoMo(CO)_5Cp]^+$, **5a** and **5b**, are non-fluxional. In contrast, the variable-temperature ^1H and ^{13}C NMR data on $[(2\text{−propynylbornyl})Mo_2(CO)_4Cp_2]^+$, **1**, reveal two different processes with barriers of 13 and 18 kcal mol^{-1}, respectively. These observations, in conjunction with numerous other literature results, are used to show that the diastereomer ratios found for metal-stabilized cationic clusters can be directly correlated to the ionization process itself. It is proposed that, in all cases, elimination of water is anchimerically assisted by the metal and proceeds through an anti-periplanar transition state.

Introduction

The stabilization of carbocations by transition metal centers continues to attract much attention. In particular, propargylium-cobalt clusters, $[Co_2(CO)_6(RC{\equiv}C\text{-}CR'R'')]^+$, have been exploited for synthetic purposes; these aspects have been reviewed by Nicholas.[1] In terms of structural determinations of these cluster-stabilized cations, the greatest success has been achieved with the analogous dimolybdenum complexes, $[Cp_2Mo_2(CO)_4(RC{\equiv}C\text{-}CR'R'')]^+$.[2-10]

Several years ago, the 2-propynylbornyl cluster cations **1** and **2** were prepared, and characterized by NMR spectroscopy.[11] The chiral nature of the terpenoid ligand renders diastereotopic the cobalt centers in **2**.[12] [The absolute configuration of a chiral tetrahedral cluster can be conveniently designated by assigning an ***R*** or ***S*** label to a dummy atom placed at the center of the tetrahedron. The vertex priorities follow the normal Cahn-Ingold-Prelog convention, and the cluster as a whole can then be designated ***R*** or ***S***, as exemplified below.]



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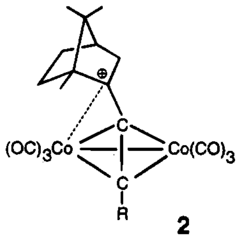

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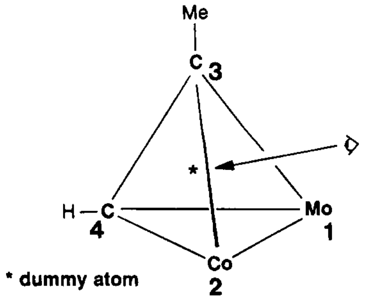

Clu*R*

As shown in Scheme 1, substitution of one of the Co-$(CO)_3$ vertices in the precursor alcohol **3** by an isolobal

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[®] Abstract published in *Advance ACS Abstracts*, November 1, 1994.

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(10) For a ditungsten analogue, see: Froom, S. F. T.; Green, M.; Nagle, K. R.; Williams, D. J. *J. Chem. Soc., Chem. Commun.*, **1987**, 1305.

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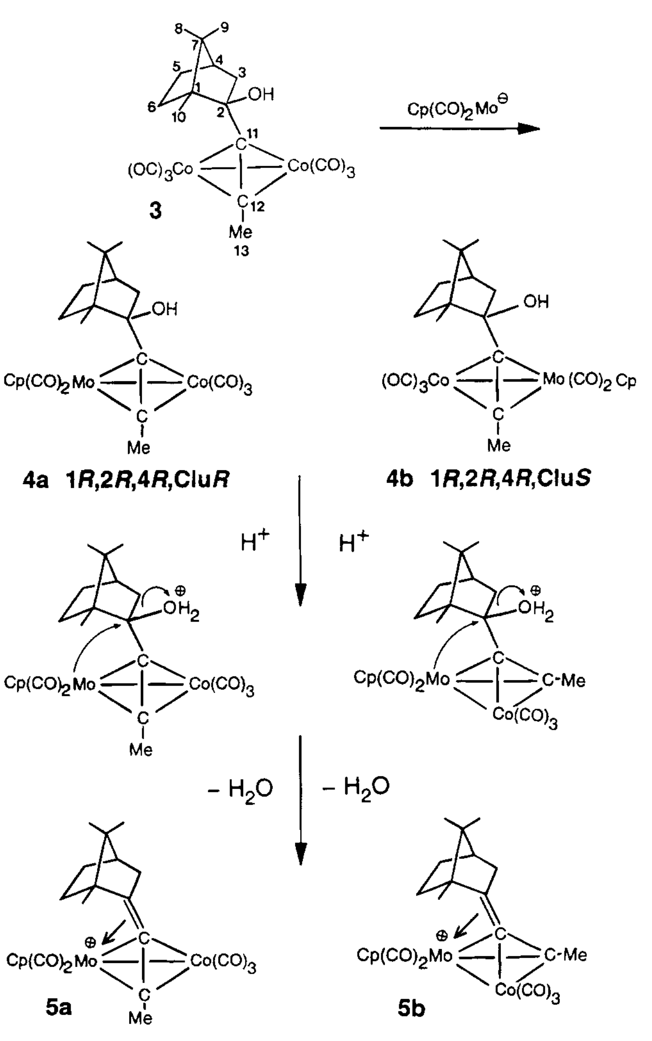
Scheme 1. Syntheses of Mixed-Metal Cationic Clusters

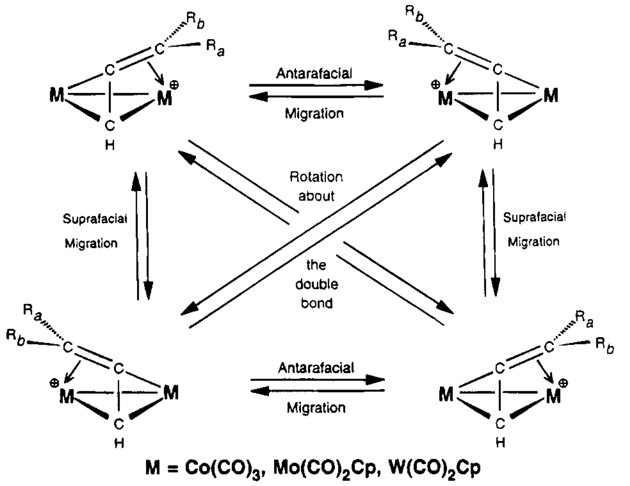


CpMo(CO)$_2$ fragment yields the mixture of diastereomers **4a**,**4b**; subsequent protonation gave the corresponding cations **5a**,**5b**. Very recently, the dimolybdenum complex [(2-propynylbornyl)Cp$_2$Mo$_2$(CO)$_4$]$^+$, **1**, and also one of the mixed cobalt-molybdenum clusters [(2-propynylbornyl)CpMo(CO)$_2$-Co(CO)$_3$]$^+$, **5a**, have been unequivocally characterized by X-ray crystallography.[13] In accord with the earlier spectroscopic data and EHMO calculations,[11] the cationic center was shown to be preferentially stabilized by direct interaction with the molybdenum, rather than the cobalt vertex.

In our original NMR study of the cluster-stabilized 2-bornyl cations,[11] the major focus was the establishment of the structure of the terpenoid moiety since it is known that 2-alkynylbornyl cations undergo facile Wagner-Meerwein skeletal rearrangements.[14] However, it is now evident that incorporation of the alkynyl fragment into an M$_2$C$_2$ tetrahedral cluster allows the bornyl cation to maintain its skeletal integrity.[13]

We here describe a comprehensive variable-temperature ^{1}H and ^{13}C NMR study of the cationic clusters **1**, **5a**, and **5b**, and place these results in the context of the known chemistry of other chiral cations of the type [L$_x$M'-M''L$_y$(RC≡C-CR'R'')]$^+$.

Scheme 2. Fluxional Processes in Cluster Cations



Results and Discussion

Mechanisms of Fluxionality. In recent years, a number of tri- and di-metallic cluster cations have been synthesized and their variable-temperature NMR spectra have been investigated.[15-17] For primary cations, [Cp$_2$Mo$_2$(CO)$_4$(RC≡C-CH$_2$)]$^+$, the low temperature spectra in both the ^{1}H and ^{13}C regimes reveal two different cyclopentadienyl resonances which coalesce upon heating the sample. However, the protons of the methylene group remain distinct even at elevated temperatures.[2,8,17] This behavior has been interpreted in terms of an antarafacial migration of the CH$_2$ moiety from one molybdenum vertex to the other; such a process maintains the *exo* and *endo* character of the methylene protons, as shown in Scheme 2. Indeed, a series of X-ray crystal structures of a variety of cations of the type [Cp$_2$Mo$_2$(CO)$_4$(RC≡C-CR'R'')]$^+$, where the R' and R'' substituents range from H, methyl or ferrocenyl to terpenoid or steroidal groups, has been subjected to a Bürgi-Dunitz analysis[18] which correlates the experimentally determined structures with the EHMO-calculated trajectory for the antarafacial migration mechanism.[19] The NMR-derived barriers found for this process range from ≈ 18 kcal mol^{-1} for primary cations (which require considerable anchimeric assistance from the metal) to ≈ 10 kcal mol^{-1} for tertiary cations which have less need of charge delocalization. Subsequently, a second, higher energy, process which interconverts the *exo* and *endo* environments can be detected, and this

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(14) (a) Kagawa, M. *Chem. Pharm. Bull.* **1959**, *7*, 306. (b) Morris, D. G.; Shepherd, A. G.; Walker, M. F.; Jemison, R. W. *Aust. J. Chem.* **1982**, *35*, 1061.

(15) [Co$_3$(CO)$_9$C-CHR]$^+$ clusters: Edidin, R. T.; Norton, J. R.; Mislow, K. *Organometallics* **1982**, *1*, 561.

(16) [Co$_2$(CO)$_6$(RC≡C-CR'R'')]$^+$ clusters: (a) Padmanabhan, S.; Nicholas, K. M. *J. Organomet. Chem.* **1983**, *268*, C23. (b) Schreiber, S. L.; Klimas, M. T.; Sammakia, S. *J. Am. Chem. Soc.* **1987**, *109*, 5749.

(17) [Cp$_2$Mo$_2$(CO)$_4$(RC≡C-CR'R'')]$^+$ clusters: (a) Sokolov, V. I.; Barinov, I. V.; Reutov, O. A. *Isv. Akad. Nauk SSR, Ser. Khim.* **1982**, 1922. (b) Galakhov, M. V.; Bakhmutov, V. I.; Barinov, I. V.; Reutov, O. A. *J. Organomet. Chem.* **1991**, *421*, 65. (c) Cordier, C.; Gruselle, M.; Jaouen, G.; Bakhmutov, V. I.; Galakhov, M. V.; Troitskaya, L. L.; Sokolov, V. I. *Organometallics* **1991**, *10*, 2303. (d) Galakhov, M. V.; Bakhmutov, V. I.; Barinov, I. V. *Magn. Res. Chem.* **1991**, *29*, 506.

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(19) Girard, L.; Lock, P. E.; El Amouri, H.; McGlinchey, M. J. *J. Organomet. Chem.* **1994**, *478*, 189.

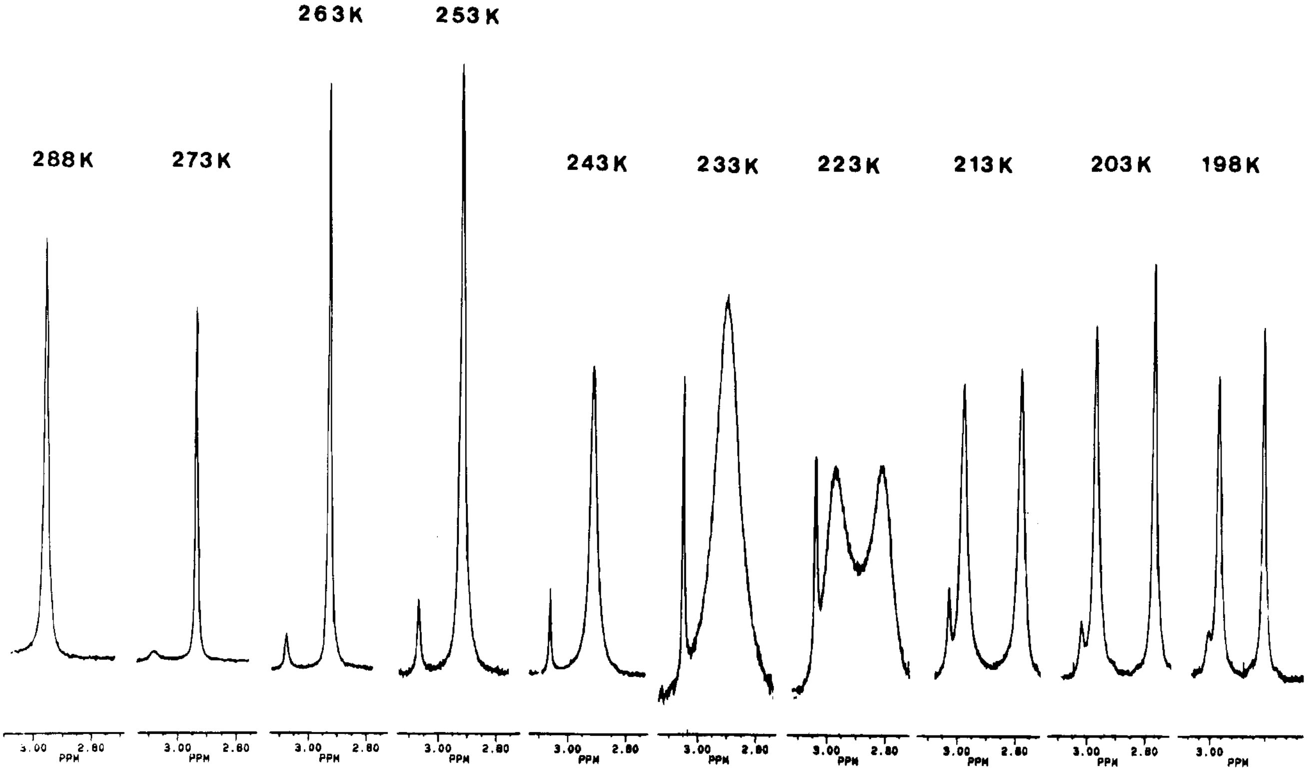
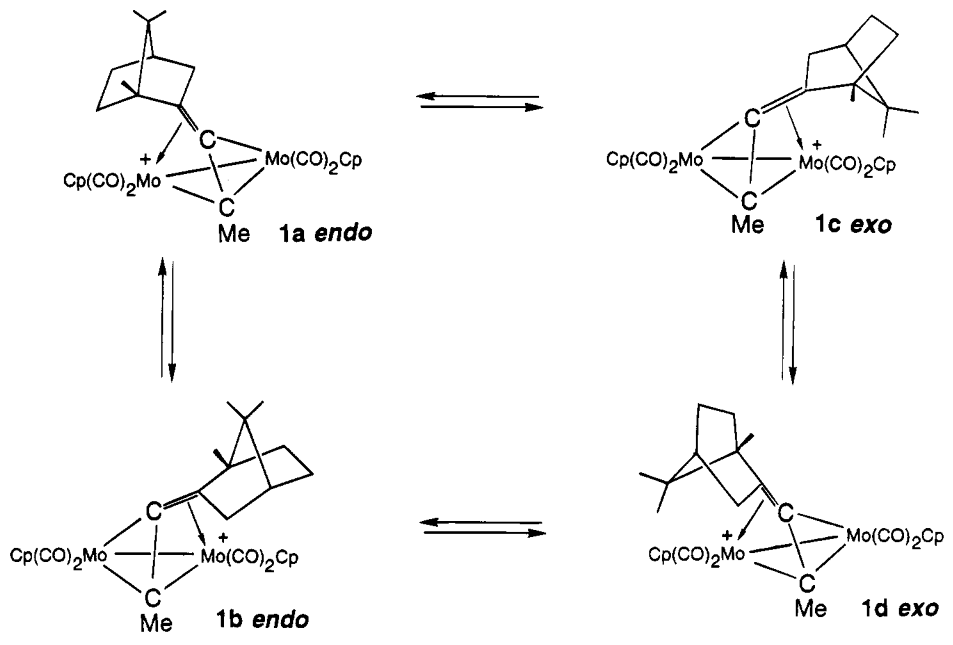


Figure 1. Sections of the variable-temperature 250 MHz ^{1}H NMR spectra of **1**, showing the peaks in the alkynyl-methyl region.

Scheme 3. ***exo* and *endo* Diastereomers of [(2–propynylbornyl)$Mo_2(CO)_4Cp_2$]$^+$, 1.**



must involve rotation about the C—CR_2 bond (see Scheme 2). We note that this latter process is phenomenologically equivalent to a suprafacial shift in which the cation merely slides from one metal vertex to the other.

When the Mo_2C_2 tetrahedral cluster cation bears a chiral substituent, as in **1**, the cationic center can bind to either of the two molybdenum vertices, giving rise to a pair of diastereomers, **1a** and **1b**; moreover, as illustrated in Scheme 3, the metal cluster may be situated on either the *endo* or the *exo* face of bornyl skeleton, thus generating another pair of diastereomers, **1c** and **1d**. Molecular modelling studies on the isomers of **1** reveal the steric problems which can arise when the bridging CMe_2 fragment of the terpenoid group is positioned close to a $(C_5H_5)Mo(CO)_2$ vertex, as in **1d**. [Yet another source of asymmetry arises as the result of the presence of a single semi-bridging carbonyl along with three terminal CO's.[20] The barrier towards interconverting semi-bridging and terminal carbonyls is normally rather low ($\approx$ 8 kcal mol^{-1}) and is probably not a major factor in this particular case.]

Variable-Temperature NMR Spectra of Cations

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[20] Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

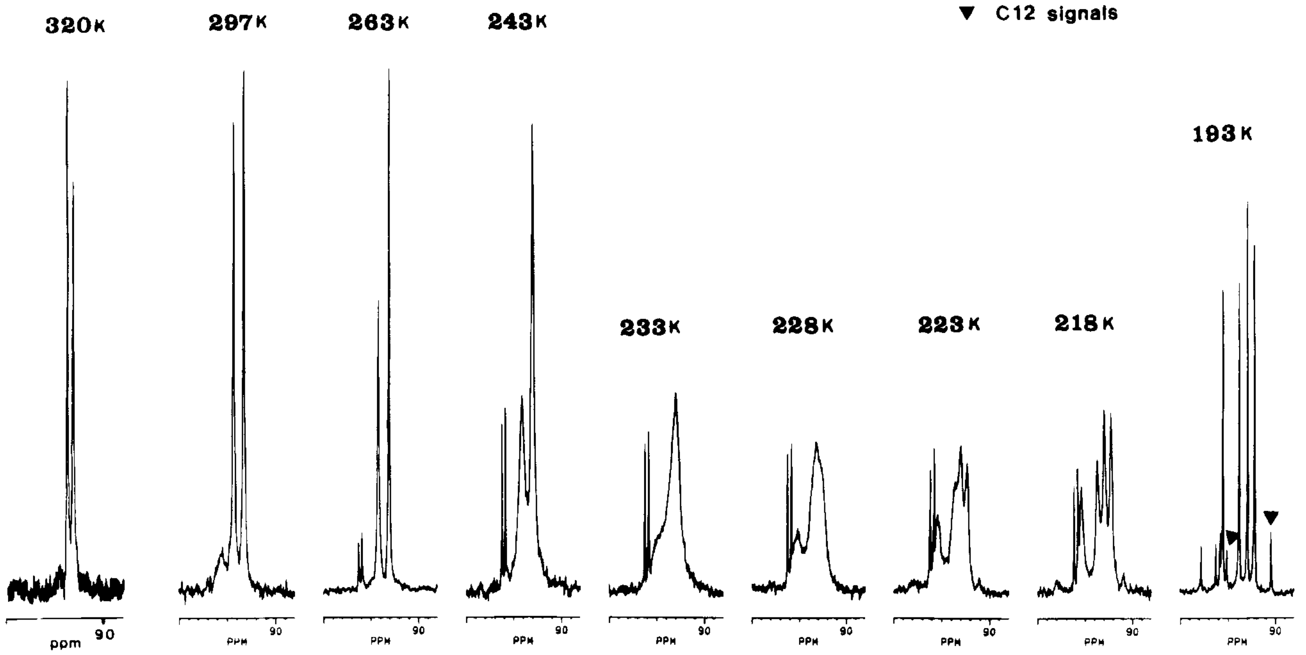

Figure 2. Sections of the variable-temperature 62.9 MHz ^{13}C NMR spectra of **1**, showing the absorptions in the cyclopentadienyl region.

1 and 5. The ^{1}H and ^{13}C NMR spectra of the 2-bornyldimolybdenum cation **1** have been examined over the temperature range 193 K–320 K; assignments were made by the usual 1- and 2-dimensional methods including DEPT, ^{1}H-^{1}H COSY and ^{1}H-^{13}C shift-correlated spectra. The attributions were in accord with those previously reported, and we note in particular our confirmation of the assignments of the C(2), C(11) and C(12) chemical shifts which follow the pattern established for other tertiary carbenium ions adjacent to a $Cp_2Mo_2(CO)_4C_2$ cluster.[17] Evidently, the solid state structure, in which the cationic center is stabilized by direct interaction with a molybdenum vertex, is maintained in solution.

At ambient temperature, the NMR spectrum of **1** reveals, in both the ^{1}H and ^{13}C regimes, two cyclopentadienyl resonances and a single peak for the alkynylmethyl group at C(13). The chiral nature of the terpenoid ligand renders the two Cp rings diastereotopic; moreover, the four metal carbonyl ligands are always non-equivalent.[21] As the temperature is lowered, the ^{1}H singlet for the C(13) methyl group is gradually transformed into two relatively narrow singlets in an approximately 10:90 ratio. Subsequently, as shown in Figure 1, the more intense singlet undergoes further decoalescence to yield ultimately two sharp singlets. This behaviour is paralleled in both the ^{1}H and ^{13}C spectra of **1** in the cyclopentadienyl region; the two singlets observed at room temperature have become two pairs of peaks (10:90) at 263 K. The minor resonances remain unchanged as the temperature is decreased, but the more intense pair of peaks each split into two (see Figure 2). Concomitantly, the four carbonyl resonances observed at room temperature have become eight peaks at 193 K.

These data clearly show the presence of one minor and two major diastereomers at low temperatures; furthermore, the interconversion of the two major diastereomers has a relatively low barrier, while the process which equilibrates them with the minor diastereomer must be considerably higher. These activation

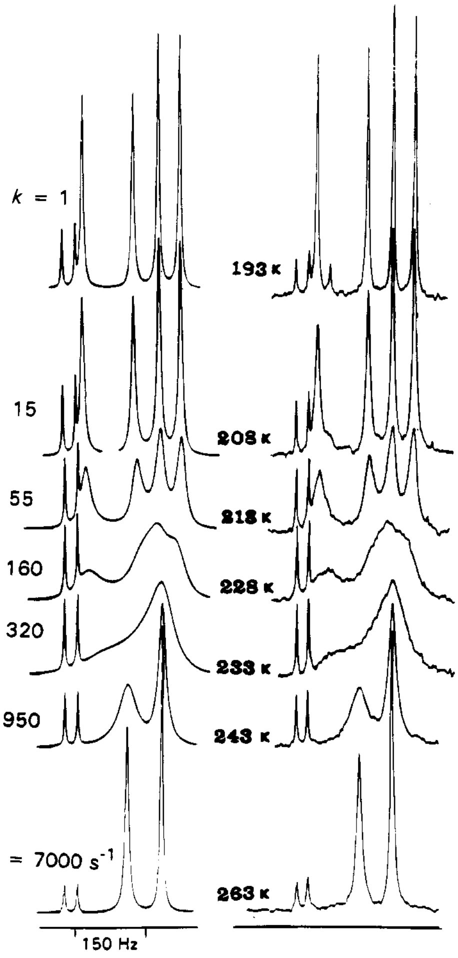

Figure 3. Experimental and simulated 62.9 MHz ^{13}C NMR spectra of **1**, showing the resonances in the cyclopentadienyl region over the temperature range 193–263 K.

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[21] Tondu, S.; Jaouen, G.; D'Agostino, M. F.; Malisza, K. L.; McGlinchey, M. J. *Can. J. Chem.* **1992**, *70*, 1743.

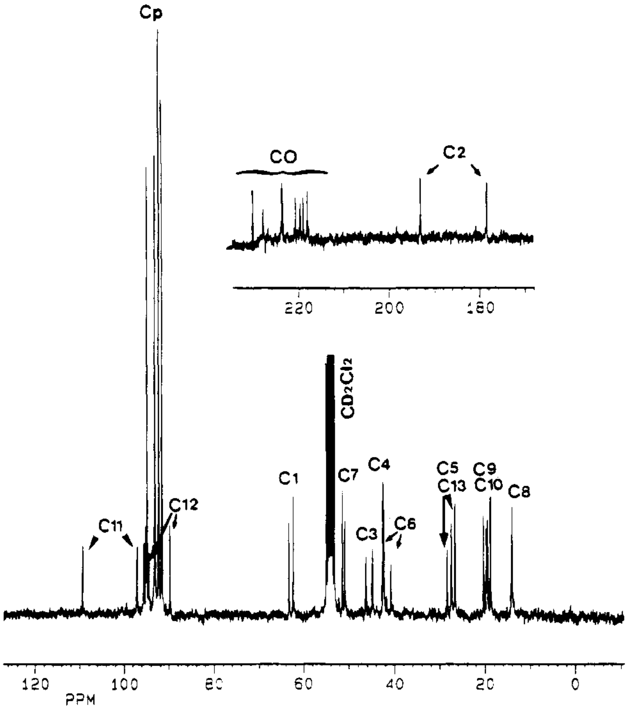
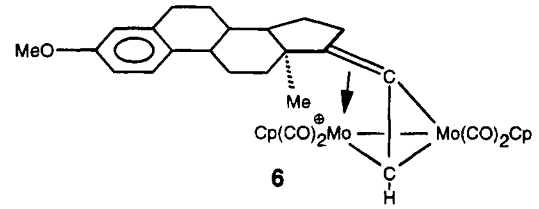


Figure 4. 62.9 MHz ^{13}C NMR spectrum of **1** recorded at 193 K.

energies have been evaluated both by the Gutowsky-Holm peak coalescence method (for the approximately equally populated sites), and also by total lineshape simulations (Figure 3) which yield Arrhenius plots.[22] The estimated barriers are 13.1 ± 0.4 kcal mol^{-1} for the equilibration of the major diasteomers, and ≈18 kcal mol^{-1} for the exchange involving the minor component.

As mentioned previously, one of the diastereomers of $[(2\text{-bornyl})Mo_2(CO)_4Cp_2]^+$ has been characterized by X-ray crystallography as isomer **1a**.[13] Scheme 3 indicates how diastereomers **1a** and **1c** can be readily interconverted via the antarafacial migration process. If the major isomers detected in the variable-temperature NMR spectra are indeed **1a** and **1c**, then one might also expect to see different chemical shifts for the ^{13}C nuclei in the bornyl skeleton. Certainly, if a molybdenum vertex were to bind to the *exo* face of the terpene, as in **1c**, the steric problems engendered by the proximity of the bulky cluster moiety to the bridgehead methyls should markedly change the nature of the $Mo\cdot\cdot C^+$ interaction, relative to the situation in **1a**. Indeed, we see in Figure 4 that, at 193 K, the original room temperature C(2) resonance at δ 181.7 has disappeared, to be replaced by two peaks at δ 178.3 and δ 192.9. Likewise, the metal-complexed alkyne carbons, at C(11) and C(12), are now widely separated, and the remaining bornyl resonances are also doubled; the complete assignments are collected in Table 1.

These considerations lead us to suggest that the minor diastereomer, which is connected to the two major isomers via an 18 kcal mol^{-1} barrier, is probably the *endo* structure **1b**, while the concentration of the remaining diastereomer, **1d**, is so low as to preclude its detection. [We note, however, that one cannot assume that the favored diastereomer is necessarily the least sterically hindered molecule. For example, in the steroidal complex cation, **6**, the crystallographically characterized isomer has the molybdenum bonded to the β-face of the mestranyl skeleton such that the C(13) methyl substituent is *proximal* to the Mo_2C_2 tetrahedron.[9]]



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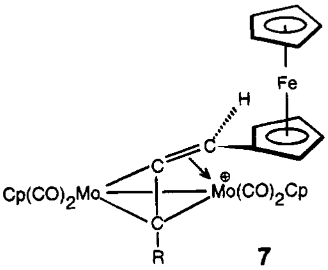
These variable-temperature data for the 2-bornyl-Mo_2 cluster **1** may be contrasted with the behavior of the molybdenum-cobalt clusters **5a** and **5b**. The precursor alcohols **4a** and **4b** have been separated and protonated individually. Each yields a single diastereomer and the structure of **5a** has been determined by X-ray crystallography.[13] The NMR data for **5a**,**5b** are collected in Table 1, and these values are invariant with changing temperature. That is, these mixed-metal clusters are not fluxional on the NMR time scale; in each case, the cationic center remains firmly bonded to molybdenum.

These data help us to construct a hierarchy of organometallic fragments capable of stabilizing carbocationic centers. We have previously shown by NMR and X-ray crystallography that in the cluster $[(C_5H_5)Fe(C_5H_4)\text{-}CH\text{-}(C{\equiv}CR)Mo_2(CO)_4Cp_2]^+$, **7**, it is the molybdenum cluster rather than the ferrocenyl fragment which preferentially stabilizes the electron-deficient center.[8] It is perhaps more realistic to visualize these metal-stabilized carbocations as vinylidene groups coordinated to an M_3 or M_2C triangle.[23-26] We are aware of several other systems, **8** through **12**,[26-30] in which a C=CR′R″ moiety can choose to bind to its preferred metal fragment.



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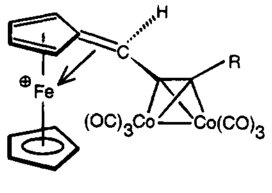

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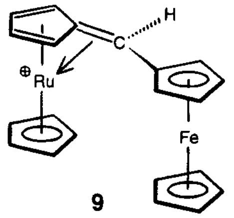
Table 1. ^{1}H and ^{13}C NMR Data for the Clusters 1, 5a, and 5b

	1	1	5a	5a	5b	5b
	^{1}H @ 297 K	^{13}C @ 297 (193 K)	^{1}H @ 297 K	^{13}C @ 297 K	^{1}H @ 297 K	^{13}C @ 297 K
C(1)		63.2 (63.3/62.3)		84.8		84.8
C(2)		*a* (178.3/192.9)		*a*		*a*
CH_2(3)	1.86 (endo) 2.36 (exo)	46.1 (46.1/44.7)	1.95/2.58	46.3	2.05/2.47	48.3
CH(4)	2.06	43.2 (42.4)	2.15	43.9	2.19	45.2
CH_2(5)	1.36 (endo) 2.06 (exo)	27.3 (27.3)	*d*/2.15	27.8	*d*/2.15	27.2
CH_2(6)	1.23 (endo) 2.06 (exo)	41.5 (40.6/42.2)	*d*/2.15	41.3	*d*/2.11	37.6
C(7)		50.9 (50.7/51.3)		64.8		65.7
CH_3(8)	0.86^b T_1 = 1.42 s	13.8 (13.9/14.0)	0.88^b	12.5^b	0.83^b	15.9^b
CH_3(9)	0.98^b T_1 = 1.25 s	19.8 (19.6/20.2)	1.03^b	20.2^b	1.04^b	19.6^b
CH_3(10)	0.87 T_1 = 1.42 s	18.9 (18.7/19.4)	0.93	19.6	1.01	19.3
C(11)		*a* (96.9/109.2)		107.4		*a*
C(12)		*a* (89.6/94.2)		*a*		*a*
CH_3(13)	2.95 T_1 = 1.26 s	27.3 (26.5/28.3)	3.02	24.8	2.95	24.5
C_5H_5's	5.59^c T_1 = 3.43 s 5.63 T_1 = 3.08 s	92.4/93.4/94.8^c (91.4/92.1) (93.0/94.7) (95.0/95.4)	5.76	94.7	5.75	94.7
CO's		219.7 (217.9/218.9) (219.6/220.6) (223.5/223.6) (227.8/230.2)		219.8 (Mo) 214.3 (Mo) 202.3 (Co)		215.5

^{a} Not observed at 297 K. ^{b} Assignments may be reversed. ^{c} Broad signal. ^{d} Obscured by HBF_4-Et_2O peak.



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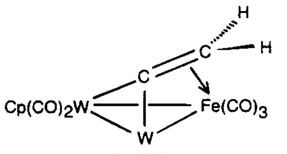

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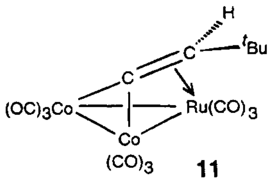

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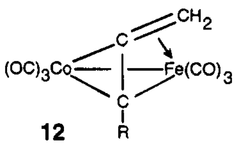

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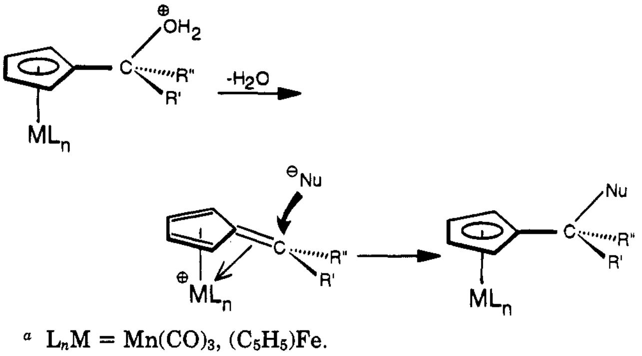
Scheme 4. Mechanism of Nucleophilic Displacement in (Hydroxymethyl)cyclopentadienyl Complexes^a



^{a} L_nM = $Mn(CO)_3$, $(C_5H_5)Fe$.

Thus, in a preliminary fashion, we can begin to arrange metal vertices in order of their ability to stabilize carbocationic centers: molecules **5**, **7**, and **8** tell us that: $Cp_2Mo_2(CO)_4(RC{\equiv}C\text{-})$ > ferrocenyl > $Co_2(CO)_6(RC{\equiv}C\text{-})$. Furthermore, we can see from molecules **9** through **12** that CpRu > CpFe, and that $Ru(CO)_3$ > $Fe(CO)_3$ > $CpW(CO)_2$ > $Co(CO)_3$.

Mechanism of Cation Formation. The stabilization of "benzyl-type" cations in such organometallic complexes as $[(OC)_3Cr(C_6H_5\text{-}CR_2)]^+$,[31] $[(OC)_3Mn(C_5H_4\text{-}CR_2)]^+$,[32] or $(C_5H_5)M(C_5H_4\text{-}CR_2)]^+$,[33] where M = Fe, Ru, Os, has been the topic of numerous theoretical and experimental reports.[34] There is much compelling evidence that protonation of the precursor alcohol, and elimination of water to generate the appropriate cation, is anchimerically assisted by the metal.[35] As depicted in Scheme 4, subsequent nucleophilic attack proceeds with retention of configuration. Indeed, in the case of an optically active ferrocenyl alcohol, the absolute configuration of the carbenium ion, generated under acidic conditions, has been determined and its optical rotation measured.[36] We suggest that these data, together with our own results on cluster cations, allow

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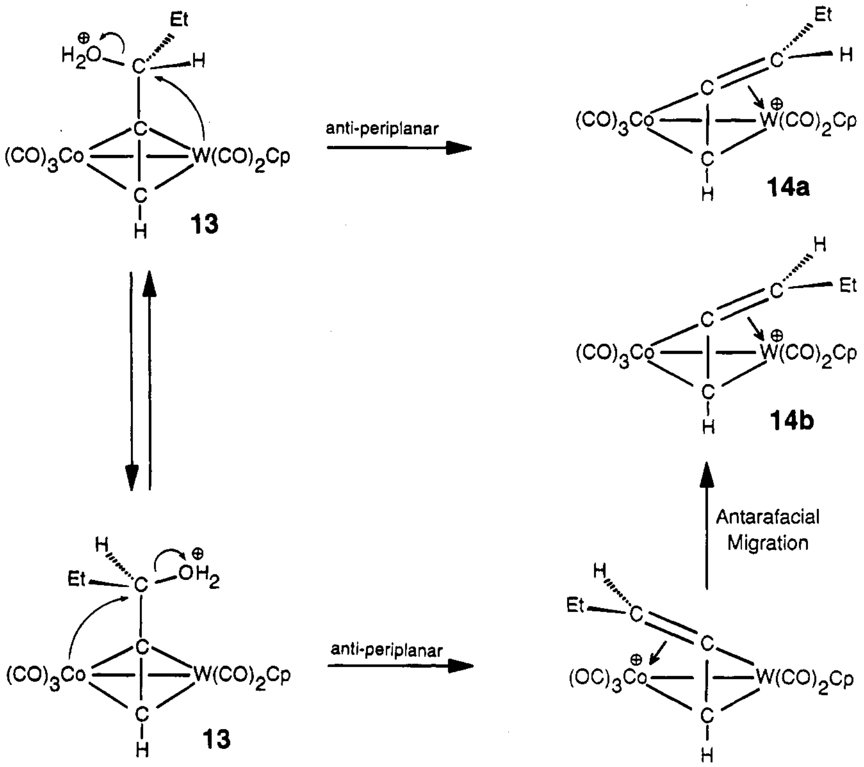
(35) In the recently reported synthesis of the ferrocenyl-stabilized cyclopropyl cation by protonation of the precursor silanol, there is strong evidence to suggest prior coordination of the oxygen to the iron. However, it is likely that after protonation there is rotation about the cyclopentadienyl—C_α bond to allow the departing Me_3SiOH to adopt an anti-periplanar orientation with respect to the incoming metal atom: (a) Prakash, G. K. S.; Buchholz, H.; Reddy, V. P.; de Meijere, A.; Olah, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 1097. (b) Shubina, E. S.; Epstein, L. M.; Timofeeva, T. V.; Struchkov, Yu. T.; Kreindlin, A. Z.; Fadeeva, S. S.; Rybinskaya, M. I. *J. Organomet. Chem.* **1988**, *346*, 59.

Scheme 5. Metal-Assisted Cation Formation in Tungsten–Cobalt Clusters[a]



[a] In each case the process occurs via an antiperiplanar transition state.

the development of a general view of these ionization processes, even when they appear to be diastereoselective rather than stereospecific.

Returning to the case of the cobalt-molybdenum clusters **4a** and **4b**, it is evident that protonation yields in each case a single carbocation and, since the absolute configuration of cation **5a** is known, one can readily deduce the structures of the precursor alcohols (see Scheme 1). Let us now consider the cobalt-tungsten cluster, **13**, which exists as a diastereomeric mixture (65:35). These diastereomers can be separated and individually protonated. As shown in Scheme 5, the ^{13}C NMR spectra of the resulting product, $[(C_5H_5)W(CO)_2Co(CO)_3(HC{\equiv}C\text{-}CHEt)]^+$, reveal that protonation of a single diastereomer of **13** yields two cations, **14a** and **14b**, in an approximate 2:1 ratio.[11] These cations, which are not interconvertible on the NMR time scale, are both stabilized by interaction with the tungsten vertex. They differ merely in the orientation of the ethyl substituent which can be either syn or anti to the alkyne CH group. This result is readily rationalized in that the ratio of diastereomeric cationic products *can be directly correlated to the ionization process itself.* Thus, as depicted in Scheme 5, diastereomer **14a** can be produced directly by elimination of water in a tungsten-assisted process; in contrast, diastereomer **14b** can be produced by cobalt-assisted loss of water, followed by an irreversible antarafacial migration of the cationic center from cobalt to tungsten.

Such reasoning can be applied to the observations reported by Nicholas concerning the phosphine-substituted dicobalt clusters **15**.[37] In this important series ofexperiments, it was shown that protonation of a pure sample of either diastereomer, **15a** or **15b**, yields the same initial mixture of diastereomeric cations such that the **16**-anti isomer predominates; moreover, use of bulky substituents (*i*-Pr, *t*-Bu) leads to exclusive formation of the anti diastereomer. It has been tentatively suggested that these diastereomeric cations might arise through different ionization processes whereby formation of the favored cation, **16**-anti, could proceed by elimination of water either from **15a** through a syn-periplanar transition state, or from **15b** via an anti-periplanar mode.

However, one might suspect that the syn-periplanar transition state is not ideally suited for metal-assisted development of the cationic center. Instead, we hypothesize that one can generate the favored cation via an anti-periplanar transition state, either directly involving the $Co(CO)_2PR_3$ vertex, or indirectly by initial formation of a $Co(CO)_3$-stabilized cation which undergoes irreversible antarafacial rearrangement to the favored **16**-anti isomer. Such a scenario is presented in Scheme 6.

To conclude, one can rationalize the formation of metal-stabilized carbocations by invoking loss of water via an anti-periplanar transition state in which the metal can provide anchimeric assistance to the developing electron-deficient center. In homo-dimetallic clusters, symmetry-allowed antarafacial migration leads to fluxional behavior on the NMR time scale. In those cases where the cluster vertices are different, for example, $(C_5H_5)Mo(CO)_2$ versus $Co(CO)_3$, or $Co(CO)_3$ versus $Co(CO)_2PR_3$, one diastereomer may be markedly favored and only a single isomer is observed. These data lead to an ordering of organometallic fragments in terms of their ability to stabilize carbocations.

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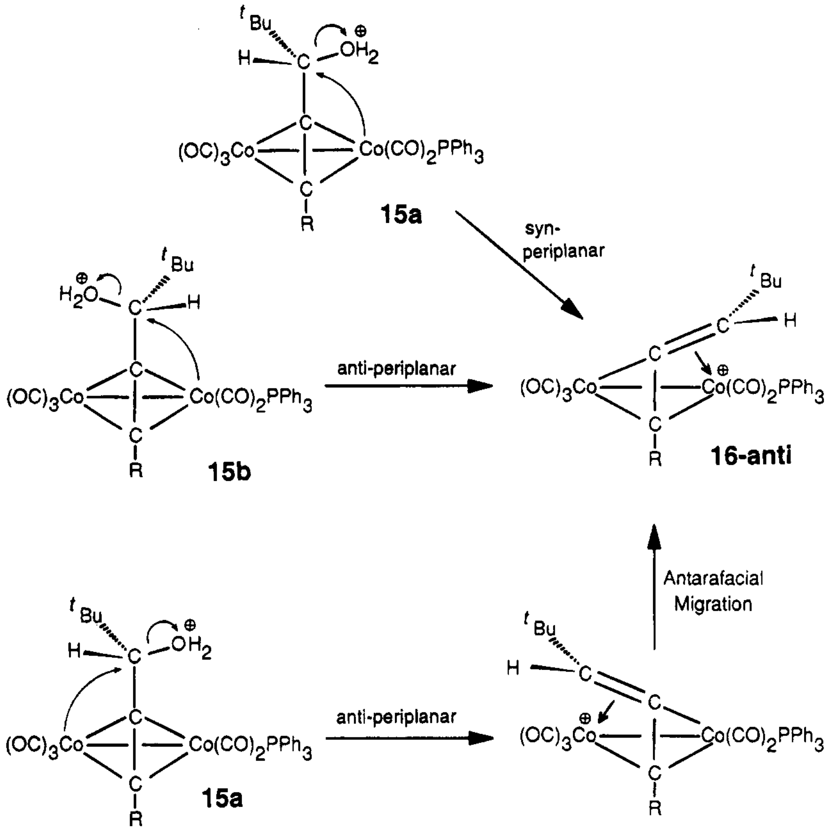
Scheme 6. Proposed Mechanisms To Generate a Single Diastereomer of 16 by Invoking both Syn- and Anti-Periplanar Transition States at the Co(CO)$_2$PR$_3$ Vertex (Upper Part) or by Invoking Only Anti-Periplanar Transition States (Lower Part)



Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The syntheses of the clusters (2-propynylborneol)Co$_2$(CO)$_6$, **3**, and (2-propynylbornene)Mo$_2$(CO)$_4$(C$_5$H$_5$)$_2$, and also of the [(2−propynylbornyl)-Mo$_2$(CO)$_4$(C$_5$H$_5$)$_2$]$^+$ cation, **1**, have been described elsewhere.[11-13] ^{1}H and ^{13}C NMR data were recorded on a Bruker AM 250 spectrometer using a 5 mm dual frequency ^{1}H/^{13}C probe. Typical proton spectra were obtained at 250.133 MHz in 32 scans in 32*K* data points over a 2.5 kHz spectral width, and using a 1 s relaxation delay. Typical ^{13}C spectra were obtained at 62.896 MHz in 600 scans in 64*K* data points over a 15.2 kHz spectral width, and using a 1 s relaxation delay. DEPT and COSY spectra were recorded by using standard sequences; ^{1}H-^{13}C shift-correlated data were acquired using a standard sequence, incorporating the BIRD pulse during the evolution period for ^{1}H-^{1}H decoupling in F1. Spectral simulation of variable-temperature ^{13}C data was carried out on a 50 MHz 486 IBM-compatible PC by using the program EXCHANGE, kindly provided by Professor R. E. D. McClung (University of Alberta, Edmonton).

Preparation and Separation of (2-propynylborneol)-CoMo(CO)$_5$Cp (4a,b). Under an atmosphere of argon, [(Cp-Mo(CO)$_3$]$_2$ (1.200 g, 2.45 mmol) in dry THF (10 mL) was treated with sodium amalgam and the initially red solution became yellow-green as anion formation progressed. After filtration, the anion was added to a solution of (2-propynylborneol)Co$_2$(CO)$_6$, **3**, (0.477 g, 1 mmol) in dry THF (10 mL), and the mixture stirred at reflux. The reaction was monitored by TLC on Kieselgel (eluent: pentane/ether 1/4). After cooling the reaction mixture to room temperature, the solvent was removed, the residue extracted in pentane, and the product was chromatographed on silica plates (eluent: pentane/ether 2/1). The more polar isomer, **4a**, (0.13 g) and the less polar product, **4b**, (0.13 g) were thus obtained as pure diastereomers. **4a**: ^{1}H NMR (250 MHz, CD$_2$Cl$_2$) δ 5.51 (s, 5H, Cp-H's); 2.85 (s, 3H, alkyne-CH$_3$); 2.15 (d of t, 1H); 1.83 - 1.28 (m, 7H); 1.12 (s, 3H, CH$_3$); 0.90 (s, 3H, CH$_3$); 0.85 (s, 3H, CH$_3$). ^{13}C NMR (62.9 MHz, CD$_2$Cl$_2$): δ 229.2, 226.5 (Mo-CO's); 91.1 (Cp-C's); 88.7, 85.5, 56.1, 50.8, 45.3, 30.3, 27.7, 22.6; 22.0 (CH$_3$-10); 21.8 and 11.4 (CH$_3$'s-8,9). **4b**: ^{1}H NMR (250 MHz, CD$_2$Cl$_2$) δ 5.49 (s, 5H, Cp-H's); 2.90 (s, 3H, alkyne-CH$_3$); 2.17 d of t, 1H); 1.83−1.28 (m, 7H); 1.13 (s, 3H, CH$_3$); 0.87 (s, 3H, CH$_3$); 0.85 (s, 3H, CH$_3$). ^{13}C NMR (62.9 MHz, CD$_2$Cl$_2$): δ 227.2 (Mo-CO's); 90.9 (Cp-C's); 55.3, 51.5, 45.8, 30.4, 27.8, 22.4 (CH$_3$-10), 21.9 and 12.0 (CH$_3$'s-8,9).

Protonation of 1, 4a, and 4b. Following the technique described previously,[13] the alcohol precursors were separately dissolved in CD$_2$Cl$_2$ (1 mL), filtered into a 5 mm NMR tube and cooled in a dry ice/acetone bath. Under an atmosphere of argon, 4−5 drops of HBF$_4$-Et$_2$O were added to the solution which became deep red. The tube was then transferred to the NMR spectrometer (AM 250) where the probe had already been cooled. The ^{1}H and ^{13}C data are collected in Table 1.

Acknowledgment. We thank the C.N.R.S. (France) and N.S.E.R.C. (Canada) for financial support.

OM940505W