Ring Opening of a Cobalt-Stabilized Bornyl Cation: Mechanistic Study of the Alkyne−Dicobalt/Carbynyl−Tricobalt Cluster Transformation

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Received September 4, 2002

Upon protonation with HBF_4, [2-*endo*-((allyldimethylsilyl)ethynyl)borneol]$Co_2(CO)_6$ (**2**) suffers elimination of water or propene, to yield [2-((allyldimethylsilyl)ethynyl)born-2-ene]-$Co_2(CO)_6$ (**11**) and [2-*endo*-((dimethylfluorosilyl)ethynyl)borneol]$Co_2(CO)_6$ (**12**), respectively, and, surprisingly, the tricobalt complex (2-norbornylidene)$CHCCo_3(CO)_9$ (**13**). In contrast, protonation of the terminal alkyne (2-*endo*-ethynylborneol)$Co_2(CO)_6$ (**19**), an anticipated precursor to **13**, led instead to (2-ethynyl-2-bornene)$Co_2(CO)_6$ (**21**) and the ring-opened species (2-ethynyl-4-isopropyl-1-methylcyclohexa-1,3-diene)$Co_2(CO)_6$ (**22**). However, conversion of **19** to **13** was achievable upon prolonged heating at reflux in acetone, thereby also affording the corresponding alcohol [2-(2-hydroxybornyl)]$CH_2CCo_3(CO)_9$ (**20**). A mechanistic rationale is offered for the formation of $RCH_2CCo_3(CO)_9$ clusters upon protonation of alkyne complexes of the type $(RC{\equiv}CH)Co_2(CO)_6$.

Introduction

We have recently shown that an allyl transfer from silicon to a metal-stabilized carbocation occurs readily with concomitant formation of a thermodynamically favored Si−F bond.[1] This migration is thought to proceed via a β-silyl cation, **1**, in a seven-membered ring, as shown in Scheme 1. Related studies by Green[2] and by Schreiber[3] are in accord with this proposal.

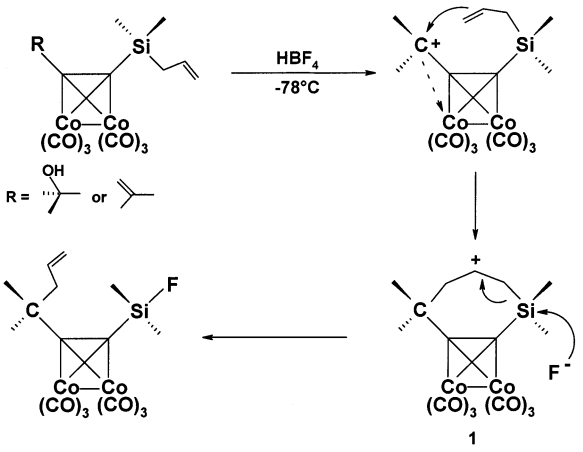
Our original goal was to investigate the stereochemical requirements for this general reaction by incorporating the allylalkynylsilane within a rigid terpenoid skeleton. In particular, we were intrigued by the potential migration of an allyl group from an endo site to the exo face of a bornyl system (i.e., **2** → **3**), and vice versa (i.e., **4** → **5**) for the fenchyl analogue, as depicted in Scheme 2.

We here describe the syntheses of these terpene derivatives and the complex nature of their behavior upon treatment with tetrafluoroboric acid.

Results and Discussion

We have previously reported the syntheses of the 2-*endo*-propynylborneol and 2-*exo*-propynylfenchol hexacarbonyldicobalt derivatives **6a** and **8a**, respectively. Protonation of the bornyl cluster **6a,** at −78 °C, yields a cobalt-stabilized 2-bornyl cation, **7a**, which has been identified by NMR spectroscopy.[4] More compellingly, replacement of a tricarbonylcobalt moiety by an isolobal (cyclopentadienyl)dicarbonylmolybdenum vertex, as in **6b**, affords the corresponding molybdenum-stabilized cation **7b**, which has been characterized by X-ray crystallography.[5] Conversely, the analogous fenchyl−dicobalt cluster cation **9a** immediately undergoes a Wagner−Meerwein rearrangement to **10**, while the corresponding fenchyl−molybdenum cation **9b** is considerably more stable and has been structurally characterized (Scheme 3).[6]

Scheme 1. Allyl Transfer via a Seven-Membered-Ring Intermediate



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† McMaster University.
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(1) Ruffolo, R.; Brook, M. A.; McGlinchey, M. J. *Organometallics* **1998**, *17*, 4992.
(2) (a) Green, J. R. *J. Chem. Soc., Chem. Commun.* **1998**, 1751. (b) Patel, M. M.; Green, J. R. *J. Chem. Soc., Chem. Commun.* **1999**, 509. (c) Lu, Y.; Green, J. R. *Synlett* **2001**, 243. (d) Green, J. R. *Synlett* **2001**, 353. (e) Green, J. R. *Curr. Org. Chem.* **2001**, *5*, 809.
(3) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128.
(4) D'Agostino, M. F.; Frampton, C. S.; McGlinchey, M. J. *J. Organomet. Chem.* **1990**, *394*, 145.
(5) Gruselle, M.; El Hafa, H.; Nikolski, M.; Jaouen, G.; Vaissermann, J.; Li, L.; McGlinchey, M. J. *Organometallics* **1993**, *12*, 4917.
(6) Kondratenko, M.; El Hafa, H.; Gruselle, M.; Vaissermann, J.; Jaouen, G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6907.

10.1021/om020727r CCC: $25.00
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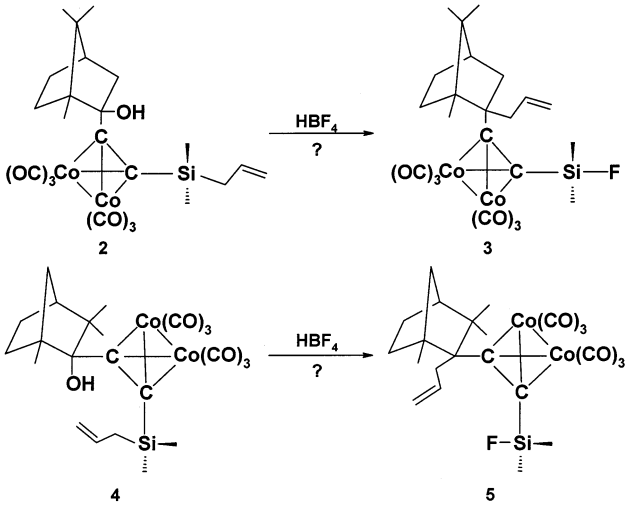
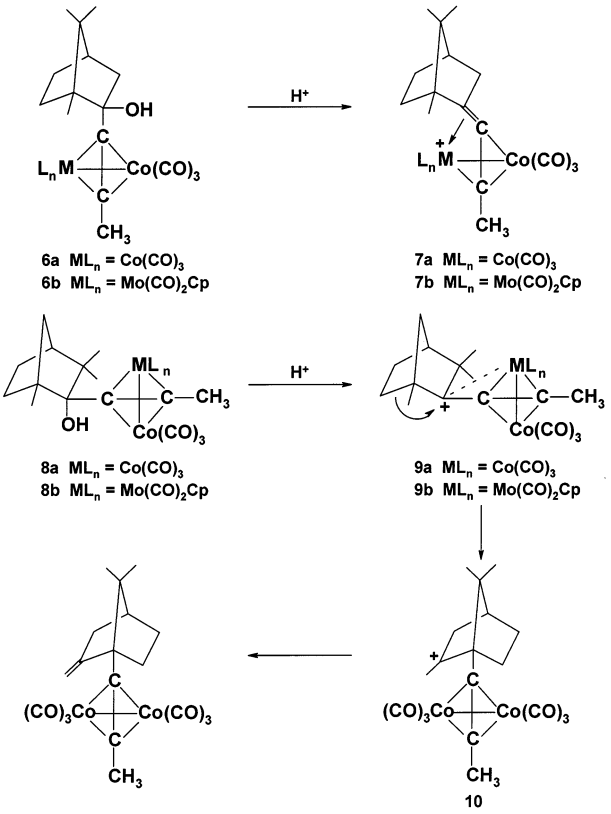
Scheme 2. Proposed Allyl Migrations in the Bornyl and Fenchyl Systems



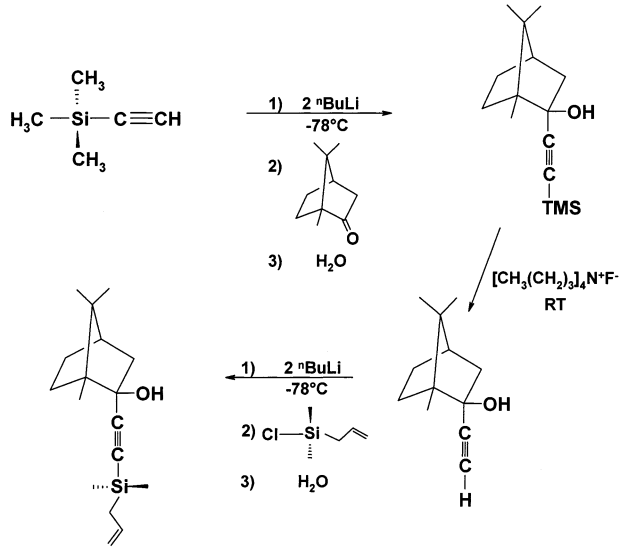
Scheme 3. Cationic Clusters Derived from Borneol and Fenchol



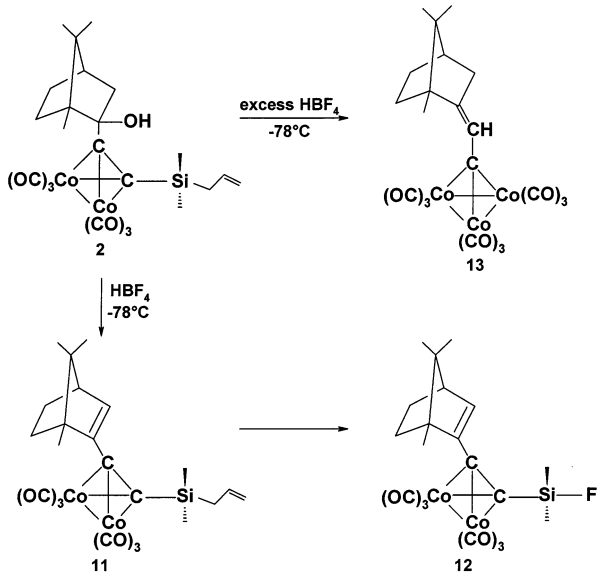
In the expectation that alkynyl anions would attack camphor from the endo face and fenchone from the exo face, these ketones were each treated with ((trimethylsilyl)ethynyl)lithium, at −78 °C. Removal of the TMS functionality with tetra-*n*-butylammonium fluoride and incorporation of the allyldimethylsilyl group proved successful, as shown in Scheme 4 for the bornyl system.

Addition of octacarbonyldicobalt to the appropriate alkynylallylsilanes afforded **2** and **4**, respectively, which were each treated with HBF_4 in ether at −78 °C and the products examined after chromatographic separation. It was immediately evident that the fenchyl system had yielded a multitude of products, each in very low yield. The mass spectra of these materials indicated that

Scheme 4. Synthetic Route to 2-*endo*-((Allyldimethylsilyl)ethynyl)borneol



Scheme 5. Products Derived from the Protonation of 2

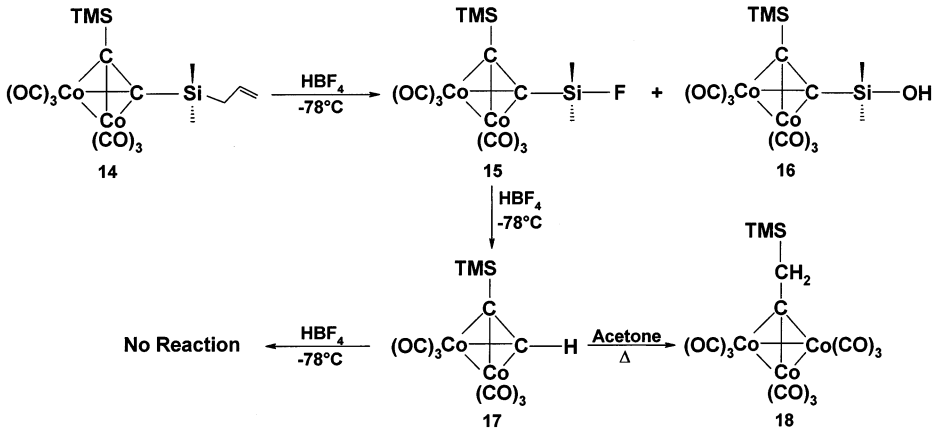


the anticipated allyl transfer product was, at best, a minor constituent among many others. We therefore chose to focus our efforts on the more tractable bornyl system.

As shown in Scheme 5, when the exo alcohol **2** was treated with an equimolar quantity of HBF_4 in ether at −78 °C, the 2-alkynyl-2-bornene **11** and the fluorosilane **12** were formed. However, when HBF_4 was added in excess and the reaction mixture warmed to room temperature over a 12 h period, chromatographic separation yielded a third isolable product, the tricobalt cluster **13**, involving an exocyclic elimination, as revealed by its 2-D $^1H-^1H$ COSY and $^1H-^{13}C$ shift-correlated NMR spectra. There was no evidence for production of the allyl migration product **3**.

One can readily envisage routes to **11** and **12**; the former simply arises from elimination of water from the starting alcohol, while the latter results from protonation of the allyl group in **11** to generate a β-silyl cation

Scheme 6. Products Derived from the Protonation of 14



with subsequent elimination of propene and concomitant formation of a silicon−fluorine bond.

Formation of the tricobalt cluster **13** was unexpected and implies the intermediacy of a terminal alkyne complex via cleavage of the allyldimethylsilyl functionality. Interestingly, protonation of [2-*endo*-((trimethylsilyl)ethynyl)borneol]$Co_2(CO)_6$ yields only the elimination product, [2-((trimethylsilyl)ethynyl)born-2-ene]$Co_2(CO)_6$, with no evidence for cleavage of the trimethylsilyl moiety. It has long been known that terminal alkyne−dicobalt complexes of the type $(RC{\equiv}CH)Co_2(CO)_6$ can rearrange under acidic conditions to yield the alkylidyne clusters $RCH_2CCo_3(CO)_9$.[7−9] However, the mechanism of this transformation has never been elucidated, and we advance some hypotheses later in this paper.

In light of the apparent facile cleavage of the allyldimethylsilyl moiety from **2**, the closely analogous cluster $[Me_3SiC{\equiv}CSiMe_2(allyl)]Co_2(CO)_6$ (**14**) was protonated with HBF_4 in ether at −78 °C and yielded $[Me_3SiC{\equiv}CSiMe_2F]Co_2(CO)_6$ (**15**) and $[Me_3SiC{\equiv}CSiMe_2OH]Co_2(CO)_6$ (**16**) (Scheme 6); the latter compound is not evident as an initial product and is apparently formed during chromatography on the silica column. After chromatographic purification, **15** was reprotonated in ether at −78 °C and afforded exclusively the terminal alkyne cluster **17**, verifying cleavage of the fluorodimethylsilyl functionality. It is worth noting that Knox and co-workers have demonstrated that protonation of similar monosilyl- and disilyl-substituted molybdenum−alkynyl clusters readily leads to desilylation.[10] Further protonation of **17** did not produce the expected tricobalt species, $Me_3SiCH_2CCo_3(CO)_9$ (**18**); however, when **17** was heated at reflux in acetone over a 36 h period, **18** was produced.

Concluding that either **2** or **12** can suffer desilylation under acidic conditions, we chose to study the behavior of (2-*endo*-ethynylborneol)$Co_2(CO)_6$ (**19**) to investigate the susceptibility of both the alkyne and hydroxyl sites toward protonation, under various conditions. Initially **19** was heated in refluxing acetone for 36 h, thereby generating two tricobalt clusters: the previously prepared **13** and its corresponding alcohol **20**, the structure

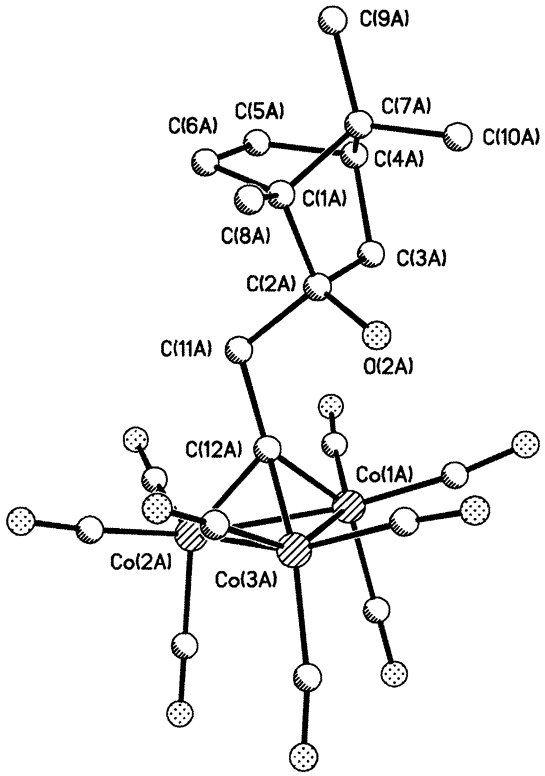


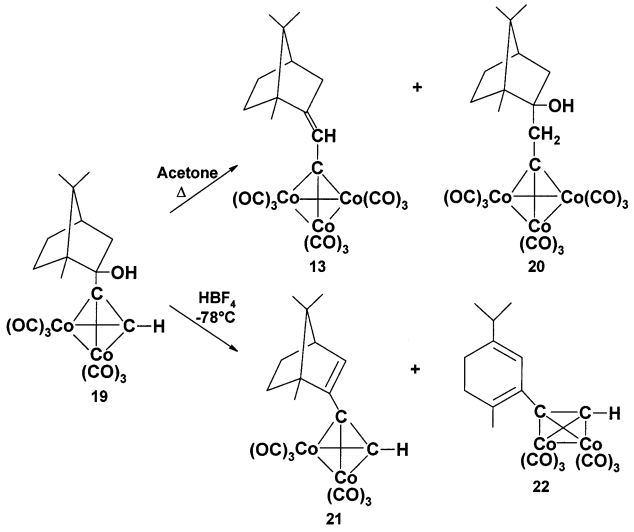
Figure 1. X-ray crystal structure of **20** showing the atom numbering system, with hydrogen atoms omitted for clarity.

of which was definitively established by X-ray crystallography. The endo positioning of the cluster in **20** is evident in Figure 1. In contrast, duplication of this reaction in diethyl ether resulted merely in reisolation of the starting material, **19**. It is perhaps somewhat surprising that such rearrangements have been shown to occur in acetone, and one cannot entirely eliminate the possibility that traces of an acidic impurity remain, even after purification of the solvent.

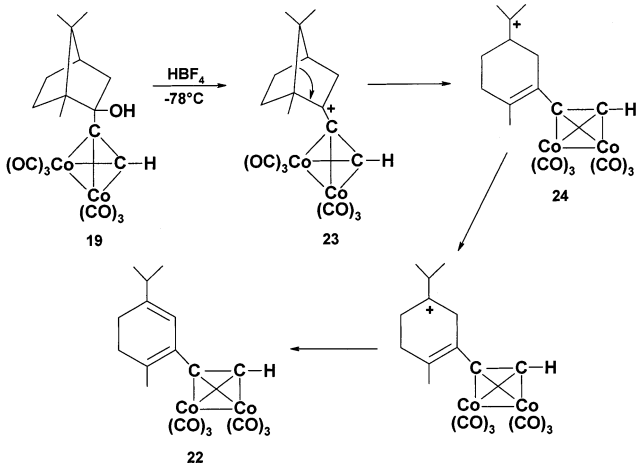
Treatment of the (2-*endo*-ethynylborneol)$Co_2(CO)_6$ complex **19** with HBF_4 in ether at −78 °C, and chromatographic separation of the mixture after warming to room temperature, furnished two major products: the 2-alkynyl-2-bornene complex **21** and a second complex, **22**, isomeric with **21**, as shown in Scheme 7. A third product, obtained in minimal yield, appears to have undergone ring opening and a carbonyl insertion but remains currently unidentified.

(7) Markby, R.; Wender, I., Friedel, R. A.; Cotton, F. A.; Sternberg, H. W. *J. Am. Chem. Soc.* **1958**, *80*, 6529.
(8) Krüerke, U.; Hübel, W. *Chem. Ind.* **1960**, 1264.
(9) Sutton, P. W.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 261.
(10) Beck, J. A.; Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 195.

Scheme 7. Products Derived from the Protonation of 19



Scheme 8. Ring Opening and Rearrangement of a Bornyl Cation

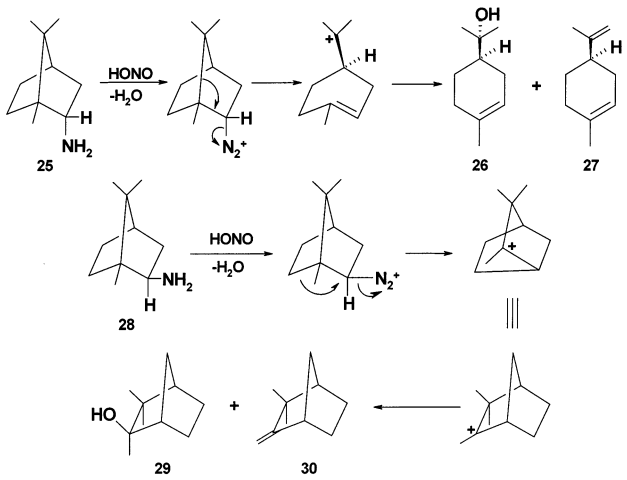


The identification of **22** relies on its mass and NMR spectra. The presence of the $(HC{\equiv}C)Co_2(CO)_6$ moiety is evident from the characteristic loss of six carbonyls in the mass spectrum, while the isopropyl group is readily observable in the ^1H and ^{13}C NMR spectra and was confirmed by $^1H-^1H$ COSY and $^1H-^{13}C$ shift-correlated experiments. These latter data also established that the methylene groups were adjacent; moreover, one pair of methylene protons exhibited a long-range correlation to the ring carbon bearing the isopropyl substituent. The final assignment as the 2-ethynyl-4-isopropyl-1-methylcyclohexa-1,3-diene complex **22** is unambiguous,[11] and a mechanistic rationale appears in Scheme 8.

Ring opening of the dimethyl bridge in cation **23** to yield the tertiary cation **24** is favored by the antiperiplanar alignment of the C(1)−C(7) linkage with the *endo*-C(2)−Co bond. A 1,2-hydride shift, to generate the isopropyl group, and subsequent elimination leads directly to the conjugated diene−yne complex **22**.

(11) The ^{13}C NMR spectra of **22** match closely with the data for 1-isopropyl-4-methylcyclohexa-1,3-diene (α-terpinene): Bohlmann, F.; Zeisberg, R.; Klein, E. *Org. Magn. Reson.* **1975**, *7*, 426.

Scheme 9. Rearrangements of endo and exo Bornyl Diazonium Ions



A search for purely organic precedents led us to the now classic work given in ref 12, in which it was shown that 2-*endo*-bornylamine (**25**) furnishes, upon diazotization, the bridge-opened products **26** and **27**. In complete contrast, 2-*exo*-bornylamine (**28**) is perfectly aligned for a Wagner−Meerwein rearrangement and gives **29** and **30**, as in Scheme 9.

One can now appreciate how the fenchyl cluster **4** might yield a plethora of products, not merely via generation and rearrangement of a terminal alkyne cluster, but also through Wagner−Meerwein skeletal rearrangements of the terpene skeleton, which are known to be very extensive in fenchol itself.[13]

These results, while rationalizing the observed products, do not explain the failure of the bornyl−allylsilane dicobalt complex **2** to undergo an allyl migration, and one should consider steric effects that might hinder formation of the crucial seven-membered-ring cationic intermediate **31**. To this end, the structure of this intermediate has been modeled[14] (Figure 2), and one can see that the presence of the spiro-C(2) center brings about unfavorable interactions between the allyl unit and one of the methyl groups attached to C(7). Presumably, this effect hinders the allyl transfer process and makes the terpene skeletal rearrangements and the cluster transformations more competitive.

$(RC{\equiv}CH)Co_2(CO)_6$ to $RCH_2CCo_3(CO)_9$ Transformation. Currently, the most widely used route to alkylidyne−tricobalt nonacarbonyl clusters involves the reaction of the appropriate trichloromethyl precursor, $RCCl_3$, with $Co_2(CO)_8$.[15] However, the very first (and entirely serendipitous) synthesis of such a cluster arose from the reaction of the parent compound, $(HC{\equiv}CH)$-$Co_2(CO)_6$, with aqueous sulfuric acid in methanol;[7] the resulting product, $CH_3CCo_3(CO)_9$, was characterized

(12) (a) Hückel, W.; Kern, H. J. *Justus Liebigs Ann. Chem.* **1969**, *728*, 49. (b) Banthorpe, D. V.; Morris, D. G.; Bunton, C. A. *J. Chem. Soc. B* **1971**, 687.

(13) (a) Lutz, R. P.; Roberts, J. D. *J. Am. Chem. Soc.* **1962**, *84*, 3715. (b) Sorensen, T. S. *Acc. Chem. Res.* **1976**, *9*, 257.

(14) (a) HyperChem Pro Version 5.1; Hypercube Inc., 1115 NW 4th Street, Gainesville, FL 32601, 1997. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (c) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

(15) (a) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97. (b) Bor, G.; Markó, L.; Markó, B. *Chem. Ber.* **1962**, *95*, 333. (c) Dent, W. T.; Duncanson, L. A.; Guy, R. G.; Reed, H. W. B.; Shaw, B. L. *Proc. Chem. Soc.* **1961**, 169.

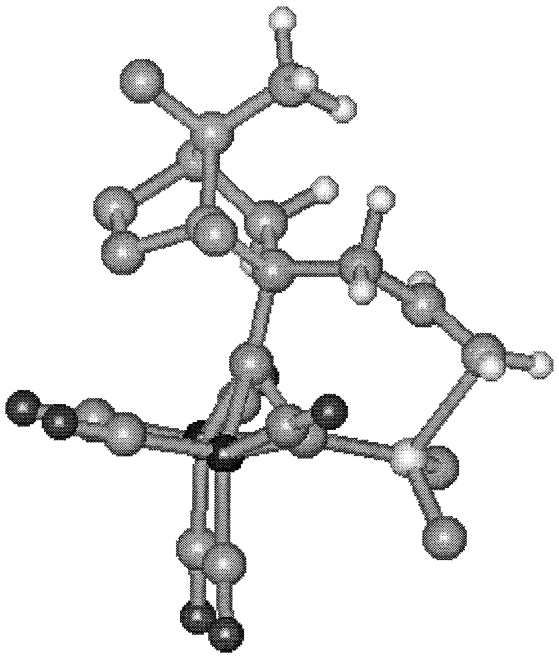


Figure 2. Semiempirically derived model of **31** (PM3 Hamiltonian), showing only pertinent hydrogen interactions.[14]

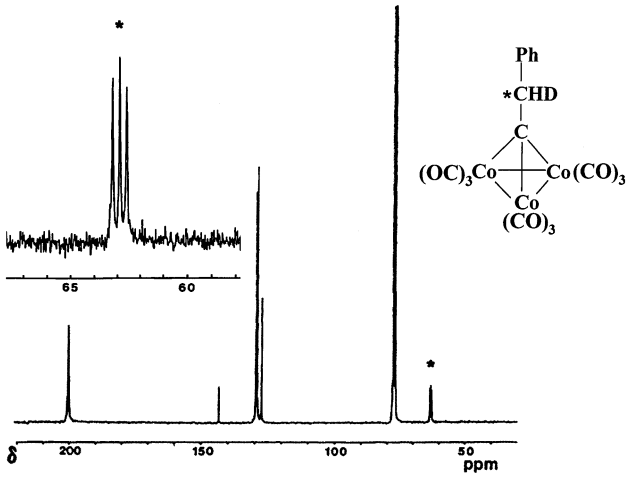


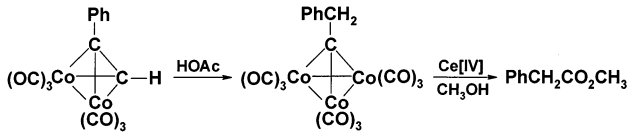
Figure 3. ^{13}C NMR spectrum of **32** in $CDCl_3$.

spectroscopically by Hübel[8] and X-ray crystallographically by Dahl.[9] Subsequently, Pauson used this reaction (Scheme 10) to convert terminal alkynes into the corresponding esters.[16]

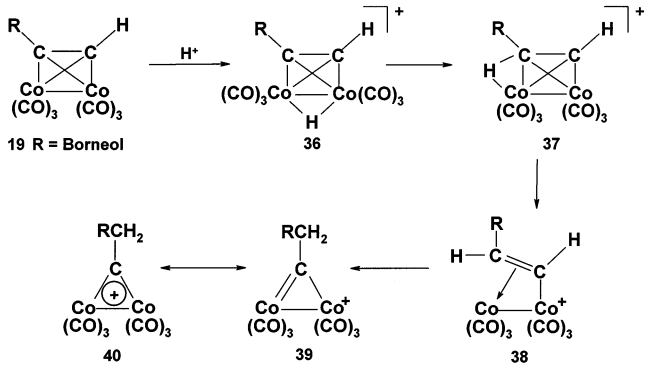
Any mechanistic description must first determine the source of the methylene hydrogens in the final product. This was readily accomplished by reaction of (PhC≡C*D*)-$Co_2(CO)_6$ with acetic acid (CH_3CO_2H), which furnished PhC*HD*$CCo_3(CO)_9$ (**32**); likewise, treatment of (PhC≡C*H*)$Co_2(CO)_6$ with CH_3CO_2D also led to **32**. Figure 3 shows the ^{13}C NMR resonance of the −CHD− linkage in **32,** which appears as a deuterium-coupled triplet at 62.9 ppm. These experiments established unequivocally that one of the methylene hydrogens was originally bonded to the terminal alkyne carbon, while the acid provides its partner.

We now remind ourselves of an important observation made independently by Curtis[17] and by Knox:[18] that

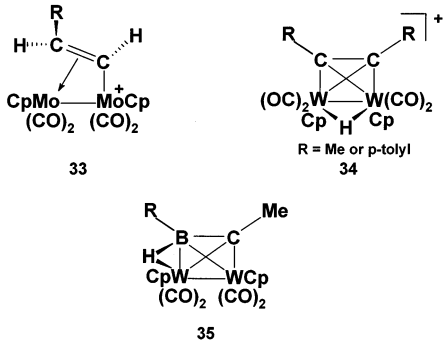
Scheme 10. Conversion of Phenylacetylene to Methyl Phenylacetate



Scheme 11. Proposed Mechanism for Acid-Promoted Rearrangement of Terminal Alkyne Dicobalt Complexes



protonation of the terminal dimolybdenum−alkyne clusters $Cp_2Mo_2(CO)_4(RC{\equiv}CH)$ generates the μ-η^1:η^3-vinyl complex **33**. Curtis also noted that, in all cases



studied, the vinyl units have the *E* configuration, thus implying that the initial site of attack by the proton was at the metal−metal bond, with subsequent migration to the coordinated alkyne.[17] This assertion is greatly strengthened by Stone's isolation of $[Cp_2W_2(CO)_4(\mu\text{-H})(RC{\equiv}CR)]^+$ (**34**), in which the hydrogen bridges the tungsten vertexes.[19] Moreover, Stone has also characterized $Cp_2W_2(CO)_4[Et(\mu\text{-H})B{\equiv}CMe]$ (**35**), whereby the hydrogen bridges the tungsten−boron bond.[20]

One can now venture a hypothesis based upon these observations which, when taken together with the isolobal analogy,[21] lend themselves to a viable mechanistic proposal. Scheme 11 presents a series of steps involving (a) initial protonation across a cobalt−cobalt bond, as in **36**, (b) bridging and then transfer of this hydrogen to the *internal* carbon of the alkyne linkage,

(16) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E. *J. Organomet. Chem.* **1974**, *73*, 383.

(17) Gerlach, R. F.; Duffy, D. N.; Curtis, M. D. *Organometallics* **1983**, *2*, 1172.

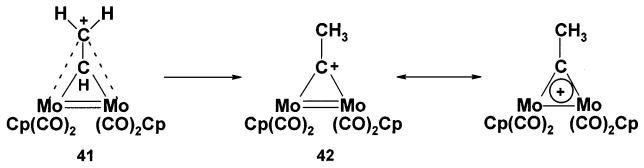
(18) Beck, J. A.; Knox, S. A. R.; Riding, G. H.; Taylor, G. E.; Winter, M. J. *J. Organomet. Chem.* **1980**, *202*, C49.

(19) Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Stone, F. G. A. *J. Organomet. Chem.* **1983**, *258*, C37.

(20) Carriedo, G. A.; Elliot, G. P.; Howard, J. A. K.; Lewis, D. B.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1585.

(21) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

Scheme 12. Proposed Route to a Dimetallacyclopropenium Intermediate



37 → **38**, and (c) migration of the *terminal* hydrogen so as to generate the required methylene group, thus placing the cationic charge either on a metal vertex, as in **39**, or on the bridging carbon atom. However, a more attractive resonance structure would regard this species as a Hückel-type 2π aromatic cyclopropenium cation, **40**, in which two of the CH units have been replaced by isolobal $Co(CO)_3$ vertexes.[21]

It is particularly noteworthy that the previously mentioned $[(\mu\text{-}\eta^1\text{:}\eta^3\text{-}CH{=}CH_2)Mo_2(CO)_4Cp_2]^+$ complex, **33**, is fluxional, whereby the cyclopentadienyl environments, and also the geminal vinylic protons, undergo site exchange. Knox has suggested a mirror-symmetric transition state, **41**, such that the vinyl fragment bridges the molybdenum−molybdenum bond.[18] We note that an intermediate of this type would facilitate migration of the unique hydrogen and lead directly to the dimetallacyclopropenium structure **42**, as depicted in Scheme 12.

We freely admit that this is merely a proposed mechanistic pathway for the dicobalt system, but we also note that several of the intermediates invoked, in particular **36**−**38**, have been unequivocally characterized where the $Co(CO)_3$ vertexes have been replaced by other isolobal metal vertexes such as $(C_5H_5)Mo(CO)_2$ or $(C_5H_5)W(CO)_2$, in **34**, **35**, and **33**, respectively. The final step, whereby the third metal is incorporated to generate the tetrahedral cluster, remains unclear at present and may involve reduction of the dimetallacyclopropenium cation to the corresponding radical that subsequently couples with $(CO)_4Co^{\bullet}$ or a related species.

To conclude, we report that (propargyl alcohol)$Co_2(CO)_6$ systems derived from terminal alkynes can exhibit a wide variety of reactivity patterns. Moreover, we trust that our mechanistic speculations concerning the acid-promoted conversion of $(RC{\equiv}CH)Co_2(CO)_6$ complexes into alkylidyne−nonacarbonyltricobalt clusters, $RCH_2CCo_3(CO)_9$, will prompt others to attempt to provide a more precise explanation of this fascinating transformation.

Experimental Section

Materials. All syntheses were carried out under a dry nitrogen atmosphere in an enclosed round-bottom flask, with constant stirring. All reactants and products were weighed in a glovebag. Solvents were dried and distilled according to standard procedures. All chemicals were purchased and used as supplied by the Aldrich Chemical Co., with the exception of dicobalt octacarbonyl and allyldimethylchlorosilane obtained from Strem Chemicals Inc. and Gelest Inc., respectively. Silica gel, 230−400 mesh, was used for flash column chromatography. Melting points (uncorrected) were determined with a Thomas-Hoover Unimelt capillary melting point apparatus. Elemental analyses are from Guelph Chemical Laboratories, Guelph, Ontario, Canada.

Instrumentation. ^1H and ^{13}C solution NMR spectra were acquired on Bruker DRX-500, WM 250, and AC-200 spectrometers; spectra were recorded at ambient temperatures and referenced to the residual proton or ^{13}C solvent signal. One-dimensional ^1H, ^{13}C, and ^{13}C DEPT and two-dimensional $^1H-^1H$ COSY, $^1H-^{-3}C$ shift-correlated, and long-range $^1H-^{13}C$ shift-correlated experiments recorded on the Bruker DRX-500 spectrometer were measured on nonspinning samples that were prepared by filtering the dissolved compound through a small glass pipet containing glass wool and silica gel. Mass spectra were acquired with a Finnigan EI/CI mass spectrometer system, using direct electron impact and chemical ionization methods. Chemical ionization was induced using NH_3 as the collision gas. High-resolution mass spectra (HRMS) were obtained using a Micromass GCT, GC time-of-flight mass spectrometer.

General Synthetic Procedures. Each reaction was conducted at −78 °C in a dry ice/2-propanol bath and monitored to completion using thin-layer chromatography, before it was warmed to room temperature and quenched with H_2O. In a typical reaction, addition of (1*R*)-(+)-camphor (1.63 g, 10.70 mmol) to a mixture of (trimethylsilyl)acetylene (1.51 mL, 10.70 mmol) and *n*-butyllithium (10.70 mmol) in ether (30 mL) gave, after hydrolysis and flash chromatography with a 2:1 mixture of CH_2Cl_2/hexanes as eluent, (2-*endo*-trimethylsilyl)ethynylborneol[22] (2.17 g, 8.67 mmol; 81%), as a white solid. Treatment with tetra-*n*-butylammonium fluoride (5.42 mL, 8.67 mmol) in ether (30 mL) yielded, after flash chromatography with a 2:1 mixture of CH_2Cl_2/hexanes as eluent, 2-*endo*-ethynylborneol (93%),[23] as a white solid. Subsequent treatment of the alkynol with an equimolar quantity of $Co_2(CO)_8$ in THF at room temperature for 12 h yielded (2-*endo*-ethynylborneol)$Co_2(CO)_6$ (**19**) as a dark red solid (90%), after chromatographic separation with hexanes. When an equimolar amount of HBF_4 in ether was added to **19** in ether (30 mL) at −78 °C, and the mixture was warmed gradually to room temperature, removal of solvent and chromatographic separation with hexanes yielded **21** (53%) and **22** (32%).

2-*endo*-((Allyldimethylsilyl)ethynyl)borneol was prepared analogously by using 2 equiv of *n*-butyllithium for the initial reaction with 2-ethynylborneol, followed by the addition of allyldimethylchlorosilane to yield the product as a yellow oil (76%). ^1H NMR (200.13 MHz, $CDCl_3$): δ 5.77 (ddt, 1H, $SiCH_2CH{=}CH_2$, $^3J_{H-H}$ = 16.4, 10.5, and 8.1 Hz), 4.91 (m, 1H) and 4.87 (m, 1H) ($SiCH_2CH{=}CH_2$), 2.17 (ddd, 1H, H_3, $^2J_{H-H}$ = 13.4 Hz, $^3J_{H-H}$ = 3.7 and 3.7 Hz), 2.03 (s, 1H, OH), 1.53−1.88 (m, 6H), 1.42 (m, 1H), 1.09 (m, 1H), 1.01 (s, 3H) and 0.83 (s, 3H) (Me_8, Me_9), 0.90 (s, 3H, Me_{10}), 0.12 (s, 6H, $SiMe_2$). ^{13}C NMR (50.13 MHz): δ 133.9 ($SiCH_2CH{=}CH_2$), 113.7 ($SiCH_2CH{=}CH_2$), 111.1 ($C{\equiv}CSi$), 85.5 (C_2), 77.9 ($C{\equiv}Si$), 53.3 (C_1), 48.2 (C_3), 47.7 (C_7), 45.3 (C_4), 32.3 (C_6), 26.7 (C_5), 24.0 ($SiCH_2CH{=}CH_2$), 21.2 and 20.9 ($Me_{8/9}$), 10.2 (Me_{10}), −2.3 ($SiMe_2$). MS (DEI, *m*/*z* (%)): 276 (3) $[(M)]^+$, 259 (25) $[(M - OH)]^+$, 235 (7) $[(M - C_3H_5)]^+$, 217 (6) $[(M - H_2O - C_3H_5)]^+$, 159 (7) $[(M - H_2O - (CH_3)_2SiCH_2CH{=}CH_2)]^+$. MS (DCI, NH_3, *m*/*z* (%)): 277 (4) $[(M + H)]^+$, 276 (14) $[(M)]^+$, 259 (60) $[(M - OH)]^+$, 235 (5) $[(M - C_3H_5)]^+$, 217 (3) $[(M - H_2O - C_3H_5)]^+$. HRMS: *m*/*z* calcd for $C_{17}H_{28}OSi$ 276.1909 $[(M)]^+$, found 276.1899.

[2-*endo*-((allyldimethylsilyl)ethynyl)borneol]$Co_2(CO)_6$ (2): dark red solid (88%); mp 96−97 °C. ^1H NMR (500.13 MHz, $CDCl_3$): δ 5.81 (m, 1H, $SiCH_2CH{=}CH_2$), 4.97 (m, 1H) and 4.93 (m, 1H) ($SiCH_2CH{=}CH_2$), 2.41 (m, 1H, H_3, $^2J_{H-H}$ = 12.2 Hz), 1.98 (s, 1H, OH), 1.84 (m, 2H, $SiCH_2CH{=}CH_2$), 1.83 (m, 1H, H_4), 1.82 (m, 1H, H_5), 1.60 (m, 1H, H_3), 1.57 (m, 1H, H_6), 1.43 (m, 1H, H_6), 1.28 (m, 1H, H_5), 1.17 (s, 3H) and 0.91 (s, 3H) ($Me_{8/9}$), 0.94 (s, 3H, Me_{10}), 0.35 (s, 6H, $SiMe_2$). ^{13}C NMR (125.77 MHz): δ 195.0 (6CO), 133.8 ($SiCH_2CH{=}CH_2$), 122.0 ($CCSi$), 114.7 ($SiCH_2CH{=}CH_2$), 83.3 (C_2), 78.6 ($CCSi$), 54.0 (C_1),

(22) van der Linden, J. B.; van Asten, P. F. T. M.; Braverman, S.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 51.

(23) Capmau, M. L.; Chodkiewicz, W.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1968**, *8*, 3233.

53.8 (C_3), 51.0 (C_7), 45.4 (C_4), 30.6 (C_6), 27.7 (C_5), 25.3 ($SiCH_2$-$CH{=}CH_2$), 21.7 and 21.5 ($Me_{8/9}$), 10.7 (Me_{10}), −0.8 ($SiMe_2$). MS (DEI, *m/z* (%)): 506 (2) $[(M - 2CO)]^+$, 478 (3) $[(M - 3CO)]^+$, 450 (11) $[(M - 4CO)]^+$, 422 (5) $[(M - 5CO)]^+$, 394 (14) $[(M - 6CO)]^+$, 352 (15) $[(M - 6CO - C_3H_6)]^+$. MS (DCI, NH_3, *m/z* (%)): 545 (100) $[(M - OH)]^+$, 517 (52) $[(M - OH - CO)]^+$, 489 (41) $[(M - OH - 2CO)]^+$, 461 (33) $[(M - OH - 3CO)]^+$, 450 (94) $[(M - 4CO)]^+$, 433 (52) $[(M - OH - 4CO)]^+$, 394 (43) $[(M - 6CO)]^+$, 352 (46) $[(M - 6CO - C_3H_6)]^+$, 335 (27) $[(M - Co - 6CO)]^+$, 276 (58) $[(M - Co_2(CO)_6)]^+$, 259 (85) $[(M - OH - Co_2(CO)_6)]^+$, 217 (3) $[(M - Co_2(CO)_6 - H_2O - C_3H_5)]^+$. Anal. Calcd for $C_{23}H_{28}O_7Co_2Si$: C, 49.12; H, 5.02. Found: C, 49.70; H, 5.61.

Protonation of [2-*endo*-((allyldimethylsilyl)ethynyl)-borneol]$Co_2(CO)_6$ (2) and subsequent chromatographic separation yielded [2-((allyldimethylsilyl)ethynyl)born-2-ene]$Co_2(CO)_6$ (**11**; 45%) and [2-*endo*-((dimethylfluorosilyl)ethynyl)born-2-ene]$Co_2(CO)_6$ (**12**; 36%) as dark red oily solids.

Data for **11** are as follows. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 6.25 (broad, 1H, H_3), 5.82 (m, 1H, $SiCH_2CH{=}CH_2$) and 4.98 (m, 2H, $SiCH_2CH{=}CH_2$), 1.21−2.48 (broad, 7H), 1.10 (s, 3H, Me), 0.86 (s, 6H, 2Me), 0.35 (s, 6H, $SiMe_2$). ^{13}C NMR (50.13 MHz): δ 200.7 (6CO), 145.8 (C_2), 139.9 (C_3), 134.0 ($SiCH_2CH{=}CH_2$), 114.4 ($SiCH_2CH{=}CH_2$), 79.7 (*C*CSi), 78.2 (C*C*Si), 57.4 (C_1), 56.6 (C_7), 52.4 (C_4), 31.9 (C_6), 29.7 (C_5), 25.4 ($SiCH_2CH{=}CH_2$), 19.6 ($Me_{8/9}$), 2.9 (Me_{10}), −0.8 and −0.9 ($SiMe_2$). MS (DEI, *m/z* (%)): 488 (1) $[(M - 2CO)]^+$, 432 (3) $[(M - 4CO)]^+$, 404 (6) $[(M - 5CO)]^+$, 376 (21) $[(M - 6CO)]^+$, 317 (4) $[(M - Co - 6CO)]^+$, 217 (4) $[(M - Co_2(CO)_6 - C_3H_5)]^+$. MS (DCI, NH_3, *m/z* (%)): 545 (2) $[(M + H)]^+$, 517 (2) $[(M + H - CO)]^+$, 489 (2) $[(M + H - 2CO)]^+$, 461 (4) $[(M + H - 3CO)]^+$, 450 (20) $[(M + NH_4 - 4CO)]^+$, 433 (11) $[(M + H - 4CO)]^+$, 376 (7) $[(M - 6CO)]^+$, 317 (5) $[(M - Co - 6CO)]^+$, 276 (12) $[(M + NH_4 - Co_2(CO)_6)]^+$, 259 (27) $[(M + H - Co_2(CO)_6)]^+$, 99 (52) $[(Me_2SiCH_2CH{=}CH_2)]^+$.

Data for **12** are as follows. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 6.36 (broad, 1H, H_3), 1.22−2.49 (broad, 5H), 1.11 (s, 3H), and 0.87 (s, 6H) ($Me_{8,9,10}$), 0.55 (s, 6H, $SiMe_2$). ^{13}C NMR (50.13 MHz): δ 200.1 (6CO), 145.9 (C_2), 140.9 (C_3), 97.0 (*C*CSi), 78.3 (C*C*Si), 57.4 (C_1), 56.7 (C_7), 52.5 (C_4), 31.8 (C_6), 25.3 (C_5), 19.6 and 19.4 ($Me_{8/9}$), 12.3 (Me_{10}), 0.8 and 0.4 ($SiMe_2$). MS (DEI, *m/z* (%)): 438 (1) $[(M - 3CO)]^+$, 410 (3) $[(M - 4CO)]^+$, 382 (4) $[(M - 5CO)]^+$, 354 (3) $[(M - 6CO)]^+$, 236 (6) $[(M - Co_2(CO)_6)]^+$, 221 (12) $[(M - Co_2(CO)_6 - Me)]^+$. MS (DCI, NH_3, *m/z* (%)): 523 (2) $[(M + H)]^+$, 495 (1) $[(M + H - CO)]^+$, 456 (2) $[(M + NH_4 - 3CO)]^+$, 428 (8) $[(M + NH_4 - 4CO)]^+$, 237 (25) $[(M + H - Co_2(CO)_6)]^+$.

(2-norbornylidene)CHCCo$_3$(CO)$_9$ (13). Method 1. A 5-fold excess of HBF_4 in ether was added dropwise to [2-*endo*-((allyldimethylsilyl)ethynyl)borneol]$Co_2(CO)_6$ (**2**; 0.11 g, 0.20 mmol) in an NMR tube at −78 °C, and the mixture was warmed gradually to room temperature over 12 h. Chromatographic separation yielded a dark red solid (19%), mp 47−48 °C.

Method 2. [2-*endo*-ethynylborneol]$Co_2(CO)_6$ (**19**; 1.95 g, 4.37 mmol) was heated at reflux in acetone (30 mL) for 36 h and, after flash chromatography, yielded **13** (38%). ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 7.37 (s, 1H, C≡C*H*), 2.39 (m, 1H, H_3), 2.36 (m, 1H, H_3), 1.88 (m, 1H, H_4), 1.80 (m, 1H, H_5), 1.70 (m, 1H, H_6, $^2J_{H-H}$ = 11.5 Hz), 1.28 (m, 1H, H_6), 1.18 (m, 1H, H_5, $^3J_{H-H}$ = 8.9 Hz), 0.99 (s, 3H, Me_{10}), 0.92 (s, 3H) and 0.75 (s, 3H) ($Me_{8/9}$). ^{13}C NMR (125.77 MHz): δ 200.5 (9CO), 152.4 (*C*≡CH), 139.5 (C≡*C*H), 53.1 (C_1), 48.2 (C_7), 45.2 (C_4), 38.0 (C_3), 29.7 (C_6), 27.6 (C_5), 19.6 and 19.0 ($Me_{8/9}$), 12.9 (Me_{10}). MS (DEI, *m/z* (%)): 562 (3) $[(M - CO)]^+$, 534 (1) $[(M - 2CO)]^+$, 506 (1) $[(M - 3CO)]^+$, 478 (4) $[(M - 4CO)]^+$, 450 (4) $[(M - 5CO)]^+$, 422 (4) $[(M - 6CO)]^+$, 394 (2) $[(M - 7CO)]^+$, 366 (3) $[(M - 8CO)]^+$, 338 (3) $[(M - 9CO)]^+$. MS (DCI, NH_3, *m/z* (%)): 591 (6) $[(M + H)]^+$, 563 (4) $[(M + H - CO)]^+$, 535 (3) $[(M + H - 2CO)]^+$. Anal. Calcd for $C_{21}H_{17}O_9Co_3 \cdot (C_2H_5)_2O$: C, 45.20; H, 4.10. Found: C, 45.42; H, 3.63. HRMS: *m/z* calcd for $C_{21}H_{17}O_9Co_3$ 589.8869 $[(M)]^+$, found 589.8884.

[2-*endo*-((trimethylsilyl)ethynyl)borneol]$Co_2(CO)_6$: dark red solid (89%), mp 77−78 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 2.40 (m, 1H, H_3), 1.98 (s, 1H, OH), 1.82 (m, 2H), 1.67 (m, 1H), 1.62 (m, 1H), 1.45 (m, 1H), 1.26 (m, 1H), 1.18 (s, 3H, Me), 0.94 (s, 3H, Me), 0.91 (s, 3H, Me), 0.37 (s, 9H, $SiMe_3$). ^{13}C NMR (125.77 MHz): δ 200.6 (6CO), 121.9 (*C*CSi), 83.2 (C_2), 80.3 (C*C*Si), 54.0 (C_1), 53.7 (C_3), 51.0 (C_7), 45.4 (C_4), 30.6 (C_6), 27.7 (C_5), 21.7 and 21.5 ($Me_{8/9}$), 10.7 (Me_{10}), 1.5 (Me_3Si). MS (DEI, *m/z* (%)): 368 (3) $[(M - 6CO)]^+$, 233 (2) $[(M - OH - Co_2(CO)_6)]^+$. MS (DCI, NH_3, *m/z* (%)): 519 (2) $[(M - OH)]^+$, 424 (8) $[(M - 4CO)]^+$, 250 (4) $[(M - Co_2(CO)_6)]^+$, 233 (100) $[(M - OH - Co_2(CO)_6)]^+$, 153 (17) $[(M - C_2Co_2(CO)_6 - SiMe_3)]^+$. HRMS: *m/z* calcd for $C_{21}H_{26}O_7SiCo_2$ 536.0112 $[(M)]^+$, found 536.0106.

[2-((Trimethylsilyl)ethynyl)born-2-ene]$Co_2(CO)_6$. Protonation of the precursor alcohol yielded the elimination product [2-((trimethylsilyl)ethynyl)born-2-ene]$Co_2(CO)_6$ exclusively, as a dark red solid (81%), mp 46−47 °C. Reflux in acetone resulted primarily in decomposition, with 37% yield. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 6.29 (broad s, 1H, H_3), 2.40 (broad s, 1H), 1.92 (m, 1H), 1.61 (m, 1H), 1.42 (m, 1H), 1.24 (m, 1H), 1.09 (s, 3H, Me), 0.82 (s, 6H, 2Me), 0.34 (s, 9H, SMe_3). ^{13}C NMR (50.13 MHz): δ 200.6 (6CO), 146.0 (*C*CSi), 139.8 (C_3), 99.2 (C_2), 81.3 (C*C*Si), 57.3 (C_1), 56.6 (C_7), 52.3 (C_4), 31.8 (C_6), 25.4 (C_5), 19.6 and 19.4 ($Me_{8/9}$), 12.7 (Me_{10}), 1.4 (Me_3Si). MS (DEI, *m/z* (%)): 490 (1) $[(M - CO)]^+$, 462 (4) $[(M - 2CO)]^+$, 434 (4) $[(M - 3CO)]^+$, 406 (9) $[(M - 4CO)]^+$, 378 (17) $[(M - 5CO)]^+$, 350 (7) $[(M - 6CO)]^+$, 291 (3) $[(M - Co - 6CO)]^+$, 232 (20) $[(M - Co_2(CO)_6)]^+$, 217 (33) $[(M - Co_2(CO)_6 - CH_3)]^+$, 73 (79) $[(SiMe_3)]^+$. MS (DCI, NH_3, *m/z* (%)): 519 (8) $[(M + H)]^+$, 491 (6) $[(M + H - CO)]^+$, 480 (4) $[(M + NH_4 - 2CO)]^+$, 452 (3) $[(M + NH_4 - 3CO)]^+$, 424 (11) $[(M + NH_4 - 4CO)]^+$, 233 (54) $[(M + H - Co_2(CO)_6)]^+$, 177 (13) $[(M + NH_4 - Co_2(CO)_6 - SiMe_3)]^+$. HRMS: *m/z* calcd for $C_{21}H_{24}O_6SiCo_2$ 536.0006 $[(M)]^+$, found 536.0016.

Protonation of [(trimethylsilyl)(allyldimethylsilyl)-ethyne]$Co_2(CO)_6$ (14). 14 was prepared according to the method of Ruffolo et al.[24] and protonated, thereby affording $[Me_3SiC{\equiv}CSiMe_2F]Co_2(CO)_6$ (**15**)[24] and $[Me_3C{\equiv}CSiMe_2OH]$-$Co_2(CO)_6$ (**16**). The latter was apparently produced during purification of **15** by column chromatography.

15: dark red oily solid (72%). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 0.48 (d, 6H, $SiMe_2F$, $^3J_{H-F}$ = 6.8 Hz), 0.30 (s, 9H, $SiMe_3$). ^{13}C NMR (50.13 MHz): δ 200.1 (6CO), 0.9 ($SiMe_3$), 0.4 ($SiMe_2F$, $^2J_{C-F}$ = 16.3 Hz). MS (DEI, *m/z* (%)): 432 (53) $[(M - CO)]^+$, 404 (22) $[(M - 2CO)]^+$, 376 (24) $[(M - 3CO)]^+$, 348 (26) $[(M - 4CO)]^+$, 320 (46) $[(M - 5CO)]^+$, 292 (48) $[(M - 6CO)]^+$, 233 (50) $[(M - Co - 6CO)]^+$. MS (DCI, NH_3, *m/z* (%)): 478 (2) $[(M + NH_4)]^+$, 441 (1) $[(M - F)]^+$, 433 (3) $[(M + H - CO)]^+$, 410 (11) $[(M - HF - 2CH_3)]^+$, 383 (15) $[(M - SiMe_2F)]^+$, 354 (27) $[(M - H - SiMe_2F - CO)]^+$, 326 (43) $[(M - H - SiMe_2F - 2CO)]^+$, 250 (58) $[(M + NH_4 - Co - 6CO)]^+$. HRMS: *m/z* calcd for $C_{13}H_{15}O_6FSi_2Co_2$ 459.9055 $[(M)]^+$, found 459.9046.

16: dark red oily solid (10%). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.46 (broad s, 1H, O*H*), 0.39 (s, 6H, $SiMe_2OH$), 0.29 (s, 9H, $SiMe_3$). ^{13}C NMR (50.13 MHz): δ 200.7 (6CO), 91.7 and 90.2 (*C*≡*C*), 1.6 ($SiMe_2OH$), 0.9 ($SiMe_3$). MS (DCI, NH_3, *m/z* (%)): 476 (10) $[(M + NH_4)]^+$, 459 (26) $[(M + H)]^+$, 431 (15) $[(M + H - CO)]^+$, 410 (20) $[(M - H_2O - 2CH_3)]^+$, 392 (51) $[(M + NH_4 - 3CO)]^+$, 382 (16) $[(M - H - SiMe_2OH)]^+$, 364 (47) $[(M + NH_4 - 4CO)]^+$, 354 (55) $[(M - H - SiMe_2OH - CO)]^+$, 326 (100) $[(M - H - SiMe_2OH - 2CO)]^+$, 248 (94) $[(M + NH_4 - Co - 6CO)]^+$, 190 (31) $[(M + NH_4 - Co_2(CO)_6)]^+$.

Protonation of ($Me_3SiC{\equiv}CSiMe_2F$)$Co_2(CO)_6$ (15) with HBF_4 in ether at −78 °C gave $[Me_3SiC{\equiv}CH]Co_2(CO)_6$ (**17**)[25] in 32% yield.

$Me_3SiCH_2CCo_3(CO)_9$ (18).[26] When **15** was heated at reflux in acetone for 36 h, it afforded **18** in 12% yield: dark red solid,

(24) Ruffolo, R.; Kainz, S.; Gupta, H. K.; Brook, M. A.; McGlinchey, M. J. *J. Organomet. Chem.* **1997**, *547*, 217.
(25) Krüerke, U.; Hübel, W. *Chem. Ber.* **1961**, *94*, 2829.

mp 37 °C (lit.[26] mp 36−37 °C). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.81 (s, 2H, CH_2CCo_3), 0.20 (s, 9H, $SiMe_3$). ^{13}C NMR (50.13 MHz): δ 200.6 (6CO), 56.9 (CH_2CCo_3), −1.0 ($SiMe_3$). MS (DEI, *m*/*z* (%)): 528 (11) $[(M)]^+$, 500 (84) $[(M - CO)]^+$, 472 (41) $[(M - 2CO)]^+$, 444 (39) $[(M - 3CO)]^+$, 416 (55) $[(M - 4CO)]^+$, 388 (98) $[(M - 5CO)]^+$, 360 (100) $[(M - 6CO)]^+$, 332 (60) $[(M - 7CO)]^+$, 304 (38) $[(M - 8CO)]^+$, 276 (71) $[(M - 9CO)]^+$, 217 (22) $[(M - Co - 9CO)]^+$.

(2-*endo*-ethynylborneol)$Co_2(CO)_6$ (19): dark red solid (90%), mp 53−54 °C. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 6.09 (s, 1H, CC*H*), 2.46 (m, 1H, H_3), 2.40 (m, 1H, H_3), 1.90 (s, 1H, OH), 1.79 (m, 2H), 1.55 (m, 1H), 1.52 (m, 1H), 1.45 (m, 1H), 1.17 (s, 3H, Me), 0.92 (s, 3H, Me), 0.89 (s, 3H, Me). ^{13}C NMR (50.13 MHz): δ 199.8 (6CO), 105.6 (*C*CH), 82.8 (C*C*H), 74.5 (C_2), 54.7 (C_3), 53.7 (C_1), 51.0 (C_7), 45.4 (C_4), 30.4 (C_6), 27.7 (C_5), 21.5 and 21.3 ($Me_{8/9}$), 10.6 (Me_{10}). MS (DEI, *m*/*z* (%)): 408 (1) $[(M - 2CO)]^+$, 380 (3) $[(M - 3CO)]^+$, 324 (4) $[(M - 5CO)]^+$, 296 (11) $[(M - 6CO)]^+$. MS (DCI, NH_3, *m*/*z* (%)): 447 (13) $[(M - OH)]^+$, 419 (3) $[(M - OH - CO)]^+$, 408 (3) $[(M - 2CO)]^+$, 352 (9) $[(M - 4CO)]^+$, 296 (1) $[(M - 6CO)]^+$, 237 (2) $[(M - Co - 6CO)]^+$, 161 (40) $[(M - OH - Co_2(CO)_6)]^+$. Anal. Calcd for $C_{18}H_{18}O_7Co_2 \cdot {}^1/_2(C_2H_5)_2O$: C, 47.92; H, 4.62. Found: C, 48.35; H, 4.81. HRMS: *m*/*z* calcd for $C_{17}H_{18}O_6Co_2$ 435.9767 $[(M - CO)]^+$, found 435.9754.

[2-(2-Hydroxybornyl)]$CH_2CCo_3(CO)_9$ (20). The synthesis and purification of this product were identical with method 2 for **13**: dark red solid (24%), mp 88 °C dec. Crystals suitable for X-ray diffraction were grown for **20** by slow evaporation from a 50/50 solution of CH_2Cl_2 and hexanes. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 4.00 (d, 1H, C*H*$_2$CCo$_3$, $^2J_{H-H} = 16.6$ Hz), 3.81 (d, 1H, H_{11}, $^2J_{H-H} = 16.5$ Hz), 2.12 (m, 1H, H_3, $^2J_{H-H} = 13.1$ Hz), 1.83 (m, 1H, H_4, $^3J_{H-H} = 6.3$ Hz), 1.80 (m, 1H, H_3), 1.75 (m, 1H, H_5), 1.59 (s, 1H, OH), 1.51 (m, 1H, H_6), 1.47 (m, 1H, H_6), 1.13 (s, 3H) and 0.90 (s, 3H) ($Me_{8/9}$), 1.07 (m, 1H, H_5), 0.92 (s, 3H, Me_{10}). ^{13}C NMR (125.77 MHz): δ 200.4 (9CO), 81.1 (C_2), 64.7 (CH_2CCo_3), 53.8 (C_1), 48.6 (C_7), 46.0 (C_3), 45.4 (C_4), 30.1 (C_6), 27.0 (C_5), 21.6 and 21.0 ($Me_{8/9}$), 10.1 (Me_{10}). MS (DEI, *m*/*z* (%)): 478 (3) $[(M - H_2O - 4CO)]^+$, 450 (4) $[(M - H_2O - 5CO)]^+$, 422 (4) $[(M - H_2O - 6CO)]^+$, 304 (13) $[(M - H_2O - Co_2(CO)_6)]^+$, 276 (22) $[(M - H_2O - CO - Co_2(CO)_6)]^+$. MS (DCI, NH_3, *m*/*z* (%)): 591 (9) $[(M - OH)]^+$, 563 (5) $[(M - OH - CO)]^+$, 535 (3) $[(M - OH - 2CO)]^+$, 395 (100) $[(M - OH - 7CO)]^+$. Anal. Calcd for $(C_{21}H_{18}O_9Co_3)_2O$: C, 42.10; H, 3.03. Found: C, 42.10; H, 3.20 (loss of water from the alcohol to form the ether). HRMS: *m*/*z* calcd for $C_{20}H_{19}O_9Co_3$ 579.9025 $[(M - CO)]^+$, found 579.9095.

Protonation of (2-*endo*-ethynylborneol)$Co_2(CO)_6$ (19) at −78 °C yielded (2-ethynyl-2-bornene)$Co_2(CO)_6$ (**21**; 53%), mp 41−43 °C, and (2-ethynyl-4-isopropyl-1-methylcyclohexa-1,3-diene)$Co_2(CO)_6$ (**22**) as a dark red oily solid (32%). Repetition at room temperature afforded **21** (74%) and **22** (13%).

Data for **21** are as follows. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 6.38 (broad, 1H, H_3), 6.21 (s, 1H, CC*H*), 2.41 (m, 1H), 1.47−1.93 (m, 4H), 1.05 (s, 3H, Me), 0.80 (s, 6H, 2Me). ^{13}C NMR (50.13 MHz): δ 200.1 (6CO), 145.7 (C_2), 141.1 (C_3), 83.4 (*C*CH), 73.4 (CC*H*), 57.3 (C_1), 56.4 (C_7), 52.6 (C_4), 31.6 (C_6), 25.1 (C_5), 19.6 and 19.4 ($Me_{8/9}$), 12.0 (Me_{10}). MS (DEI, *m*/*z* (%)): 446 (3) $[(M)]^+$, 418 (15) $[(M - CO)]^+$, 390 (35) $[(M - 2CO)]^+$, 362 (25) $[(M - 3CO)]^+$, 334 (46) $[(M - 4CO)]^+$, 306 (41) $[(M - 5CO)]^+$, 278 (18) $[(M - 6CO)]^+$. MS (DCI, NH_3, *m*/*z* (%)): 447 (100) $[(M + H)]^+$, 419 (40) $[(M + H - CO)]^+$, 380 (10) $[(M + NH_4 - 3CO)]^+$, 352 (27) $[(M + NH_4 - 4CO)]^+$, 178 (11) $[(M + NH_4 - Co_2(CO)_6)]^+$, 161 (19) $[(M + H - Co_2(CO)_6)]^+$. Anal. Calcd for $C_{18}H_{16}O_6Co_2 \cdot (C_2H_5)_2O$: C, 50.79; H, 5.04. Found: C, 50.84; H, 4.91.

Data for **22** are as follows. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 6.34 (s, 1H, CC*H*), 5.40 (s, 1H, H_3), 2.87 (m, 2H, H_5), 2.74 (m, 2H, H_6), 2.30 (m, H_7), 1.87 (broad, 3H, Me_{10}), 1.06 and 1.05 (broad, 6H, 2Me). ^{13}C NMR (125.77 MHz): δ 200.1 (6CO), 141.4 (C_4), 133.4 (C_1), 123.0 (C_2), 114.7 (C_3), 89.6 (*C*CH), 74.7 (C*C*H), 35.2 (C_6), 34.3 (C_7), 33.9 (C_5), 21.1 (2Me), 21.0 (Me). MS (DEI, *m*/*z* (%)): 446 (4) $[(M)]^+$, 418 (9) $[(M - CO)]^+$, 390 (6) $[(M - 2CO)]^+$, 362 (5) $[(M - 3CO)]^+$, 334 (8) $[(M - 4CO)]^+$, 306 (18) $[(M - 5CO)]^+$, 278 (21) $[(M - 6CO)]^+$. MS (DCI, NH_3, *m*/*z* (%)): 447 (100) $[(M + H)]^+$, 419 (7) $[(M + H - CO)]^+$, 391 (4) $[(M - H - 2CO)]^+$, 380 (5) $[(M + NH_4 - 3CO)]^+$, 352 (5) $[(M + NH_4 - 4CO)]^+$, 161 (13) $[(M + H - Co_2(CO)_6)]^+$.

PhCHDCCo$_3$(CO)$_9$ (32). Following Pauson's method,[16] addition of glacial acetic acid to D(PhC≡CD)$Co_2(CO)_6$ or of CH_3CO_2D to (PhC≡CH)$Co_2(CO)_6$ gave **32** in 17% and 24% yields, respectively. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 7.3−7.4 (m, 5H, Ph), 4.8 (s, 1H). ^{13}C NMR (62.86 MHz): δ 199.8 (6CO), 143.1, 129.3, 128.8, 127.7 (Ph C's), 62.9 (t, *C*HD, $^1J_{C-D} = 19.5$ Hz). MS (EI+, *m*/*z*): 533 $[(M)]^+$, 505 $[(M - CO)]^+$, 477 $[(M - 2CO)]^+$, 449 $[(M - 3CO)]^+$, 421 $[(M - 4CO)]^+$, 393 $[(M - 5CO)]^+$, 365 $[(M - 6CO)]^+$, 337 $[(M - 7CO)]^+$, 309 $[(M - 8CO)]^+$, 281 $[(M - 9CO)]^+$.

X-ray Crystal Structure Determinations. X-ray crystallographic data were collected from a single crystal of **20** mounted on a glass fiber. Data were collected using a P4 Bruker diffractometer, equipped with a Bruker SMART 1K charge coupled device (CCD) area detector, using the program SMART,[27] and a rotating anode, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The crystal-to-detector distance was 4.987 cm, and the data collection was carried out in 512 × 512 pixel mode, utilizing 2 × 2 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected by a 12° scan in 40 frames over three different sections of reciprocal space (120 frames in total). A hemisphere of data was collected with high redundancy, to better than 0.8 Å resolution at 298 K. Upon completion of the data collection, the first 40 frames were re-collected in order to improve the decay correction analyses. Processing was carried out using the program SAINT,[28] which applied Lorentz and polarization corrections to the three-dimensionally integrated diffraction spots. The program SADABS[29] was utilized for the scaling of the diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections for each data set. The structures were solved by using the direct-methods procedure in the Bruker SHELXTL program library[30] and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for the bridging methylene carbon, cluster carbon, carbonyl, and cobalt atoms. A slight rotational disorder of the borneol ligand prevented anisotropic refinement of this functionality. Hydrogen atoms were added as fixed contributors at calculated positions with isotropic thermal parameters, on the basis of the carbon atom to which they were bonded. The unit cell consisted of two crystallographically unrelated molecules ($Z = Z' = 2$).

X-ray crystal data for **20**: $C_{21}H_{19}Co_3O_{10}$, red plate (0.03 × 0.10 × 0.17 mm), triclinic, *P*1, a = 7.761(4) Å, b = 12.739(7) Å, c = 13.332(8) Å, α = 90.486(14)°, β = 106.479(12)°, γ = 91.064(18)°, V = 1263.6(13) Å^3, $Z = 2$, ρ_{calcd} = 1.598 g cm^{-3}, T = 299(2) K, μ = 1.996 mm^{-1}; R1 = 0.0567, wR2 = 0.0872 (based on F^2) for 425 variables and 9539 reflections (6746 independent); R(int) = 0.0656 with $I < 2\sigma(I)$, and 1.59 < θ < 25.00°.

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Crystallographic data (excluding structure factors) for the molecule reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 190592 (**20**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223−336−033; e-mail, deposit@ccdc.cam.ac.uk).

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged. J.H.K. thanks the NSERC and the Province of Ontario for graduate scholarships, and P.M. was the recipient of a DAAD student exchange fellowship from the University of Duisberg. Mass spectra were acquired courtesy of Dr. Kirk Green of the McMaster Regional Mass Spectrometry Center. We thank Dr. D. G. Morris (University of Glasgow) for valuable discussions concerning the rearrangement behavior of bornyl cations.

Supporting Information Available: Tables giving X-ray crystallographic data for 20 and figures giving NMR spectra for some of the compounds prepared in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020727R