Alkynylcyclohexanol Chairs and Twist-Boats: Co₂(CO)₆ as a Conformational Switch

Nicole M. Deschamps, John H. Kaldis, Philippa E. Lock, James F. Britten, and Michael J. McGlinchey*

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

mcglinc@mcmaster.ca

Received August 27, 2001

Treatment of 1-[axial]-(trimethylsilylethynyl)cyclohexan-1-ol with dicobalt octacarbonyl results in a conformational ring flip such that the bulky dicobalt–alkyne cluster moiety now occupies the favored equatorial site. However, when a 4-*tert*-butyl substituent is present, the coordinated alkynyl group retains its original axial or equatorial position. Complexation of *trans*-[diaxial]-1,4-bis-(triphenylsilylethynyl)cyclohexane-1,4-diol brings about a chair-to-chair conformational inversion such that both cluster fragments now occupy equatorial sites. In contrast, *cis*-1,4-bis(triphenyl-silylethynyl)cyclohexane-1,4-diol reacts with $Co_2(CO)_8$ to yield the twist-boat conformer in which the two axial hydroxy substituents exhibit *intra*-molecular hydrogen bonding. Likewise, the corresponding reaction of *cis*-1,4-bis(trimethylsilylethynyl)cyclohexane-1,4-diol with $Co_2(CO)_8$ leads to a twist-boat, but in this case, the molecules are linked through *inter*-molecular hydrogen bonds. Eight of these cobalt clusters have been characterized by X-ray crystallography, and the potential use of twist-boats in synthesis is discussed.

Introduction

Although the ability of the alkynyl dicobalt hexacarbonyl moiety to stabilize a neighboring carbocationic site is very well established,¹ its use as a stereocontrol element has been less widely exploited. We note that Melikyan and Nicholas have rationalized the Mn(OAc)₃mediated oxidative cycloaddition of β -dicarbonyl compounds with Co₂(CO)₆-complexed 1-alken-3-ynes in terms of a transition state whereby the bulky cluster unit is disposed pseudoequatorially; this favors a pseudoaxial approach by the incoming nucleophile.² Similarly, the stereospecificity of the Friedel–Crafts cyclization of cobalt-stabilized propargyl cations onto suitably activated arenes³ has been explained by invoking a transition state in which the ($-C \equiv CH$)Co₂(CO)₆ fragment adopts the less hindered pseudoequatorial site.⁴

It is particularly interesting to note that Isobe has reported the facile epimerization of a series of $Co_2(CO)_6$ -complexed alkynyl sugars such that the cluster adopts an equatorial rather than an axial site.⁵ We shall discuss the mechanism of this process presently.

(2) Melikyan, G. G.; Vostrowsky, O.; Bauer, W.; Bestmann, H. J.; Khan, M.; Nicholas, K. M. *J. Org. Chem.* **1994**, *59*, 222. Several years ago, we reported the X-ray crystal structures of 2-methyl-1-(phenylethynyl)cyclopentanol, 1, and of the corresponding dicobalt hexacarbonyl adduct, $2.^4$ In the former case, the alkynyl anion attacks the precursor ketone in a pseudoaxial fashion, cis to the methyl group. Addition of the $Co_2(CO)_6$ unit brings about a conformational flip such that the methyl and hydroxyl substituents become pseudoaxial and the cluster occupies a pseudoequatorial position, as in Scheme 1.

We here describe an extension of this concept whereby several cyclohexanones have been treated with alkynyl anions of increasing steric demand. The structures of these alkynols are compared with the conformations of the corresponding dicobalt hexacarbonyl complexes, eight of which have now been characterized in the solid state by X-ray crystallography.

Results and Discussion

The conformation adopted by a cyclohexane ring whether it be a chair, twist-boat, etc.—is critically dependent on the steric interplay between the substituents.⁶ The proclivity for a particularly bulky group, such as *tert*butyl, to occupy an equatorial site and thus "lock in" a given conformation is well known.⁷ In contrast, a needlelike substituent, such as an alkynyl moiety, imposes minimal steric interactions within the system and thus offers little opportunity for conformational control. As previously noted, treatment of the alkynylcyclopentanol **1** with dicobalt octacarbonyl yields the cluster complex

 $^{^{*}}$ To whom correspondence should be addressed. Phone: (905) 525-9140 ext 27318. Fax: (905) 522-2509.

 ^{(1) (}a) Nicholas, K. M. Acc. Chem. Res. 1986, 20, 207. (b) Caffyn, A. J. M.; Nicholas, K. M. In Comprehensive Organometallic Chemistry II; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 12, Chapter 7.1, pp 685–702. (c) McGlinchey, M. J.; Girard, L.; Ruffolo, R. Coord. Chem. Rev. 1995, 143, 331. (d) El Amouri, H.; Gruselle, M. Chem. Rev. 1996, 96, 1077. (e) Melikyan, G. G.; Bright, S.; Monroe, T.; Hardcastle, K. I.; Ciurash, J. Angew. Chem., Int. Ed. Engl. 1998, 37, 161. (f) Ruffolo, R.; Brook, M. A.; McGlinchey, M. J. Organometallics 1998, 17, 4992. (g) Guo, R.; Green, J. J. Chem. Soc., Chem. Commun. 1999, 2503 and references therein.

^{(3) (}a) Grove, D. D.; Miskevich, F.; Smith, C. C.; Corte, J. R. *Tetrahedron Lett.* **1990**, 6277. (b) Grove, D. D.; Corte, J. R.; Spencer, R. P.; Pauly, M. E.; Rath, N. P. *J. Chem. Soc., Chem. Commun.* **1994**, 49.

⁽⁴⁾ Malisza, K. L.; Girard, L.; Hughes, D. W.; Britten, J. F.; McGlinchey, M. J. Organometallics **1995**, *14*, 4676.

^{(5) (}a) Tanaka, S.; Tsukiyama, T.; Isobe, M. *Tetrahedron Lett.* **1993**, *34*, 5757. (b) Tanaka, S.; Isobe, M. *Tetrahedron* **1994**, *50*, 5633.

⁽⁶⁾ Weser, J.; Golan, O.; Fiyjer, L.; Biali, S. E. *J. Org. Chem.* **1996**, *61*, 8277 and references therein.

^{(7) (}a) Eliel, E. L. Stereochemistry of Carbon Compounds; McGraw-Hill: New York, 1962; pp 208–221. (b) Kellie, G. M.; Riddell, F. G. Top. Stereochem. **1974**, *8*, 224–269. (c) Bucourt, R. Top. Stereochem. **1974**, *8*, 159–224.



2 in which the formerly pseudoaxial alkyne linkage now occupies a pseudoequatorial site.⁴ However, the conformational flexibility of five-membered rings⁸ is much greater than is found in cyclohexane systems for which the chair is generally favored.

When cyclohexanone was allowed to react with (trimethylsilylethynyl)lithium and then hydrolyzed, the resulting alkynol, 3, was characterized by NMR spectroscopy as the conformer in which the entering nucleophile occupies an axial site.9 After identification of all the proton and carbon resonances by use of standard ¹H-¹H COSY and ¹H-¹³C shift-correlated techniques, observation of nuclear Overhauser interactions between the hydroxyl proton and the hydrogens only at C-2 and C-6 clearly established the equatorial positioning of the OH group. Subsequent incorporation of the $Co_2(CO)_6$ unit yielded the complex 4 in which the cyclohexane ring has flipped to allow the cluster fragment to occupy the equatorial position, as illustrated in Scheme 2. The structure of 4 was unequivocally determined by X-ray diffraction.¹⁰

It is clearly relevant to note that Braga, Grepioni, and their co-workers have reported the X-ray crystal structures of both 1-(tert-butylethynyl)cyclohexan-1-ol, 5, and of its nickel and platinum complexes **6a**,**b**, shown in Scheme 3. As with the conversion of **3** to **4**, the alkynyl substituent in 5 has moved from an axial to an equatorial site in 6; however, the authors made no mention of this conformational change since their primary focus was on the intermolecular hydrogen bonding patterns in the crystal lattice.11

Alkynols Derived from 4-tert-Butylcyclohexanone. The next question concerns the relative ability of a *tert*-

Imhof, W.; Görls, H.; Klettke, T. Organometallics 1997, 16, 4910.



Figure 1. Molecular structures of (A) 11 and (B) 12 (50% thermal ellipsoids).

butyl versus an $(RC \equiv C)Co_2(CO)_6$ substituent to maintain its equatorial alignment. To this end, trans-4-tert-butyl-1-(phenylethynyl)cyclohexan-1-ol, 7, was treated with $Co_2(CO)_8$ to furnish 8, whose solid-state structure was determined by X-ray diffraction.¹⁰ It is evident that the equatorial preference of the tert-butyl group remains dominant; the axially disposed cluster moiety in 8 causes the cyclohexane ring to flatten only marginally and the planar phenyl substituent is oriented so as to minimize steric interactions with the *tert*-butyl group at the 4-position.

In an attempt to increase the steric bulk of the alkynyl substituent, 4-tert-butylcyclohexanone was treated with (trimethylsilvlethynyl)lithium: subsequent hydrolysis vielded two alkynols that were readily separable by column chromatography on silica gel. The isomers with axial and equatorial alkynyl groups, 9 and 10, respectively, were formed in a 5:2 ratio (Scheme 4).

The direction of attack by alkynyl anions on alkylsubstituted 5- and 6-membered ring systems (initially investigated by Cadiot and Chodkiewicz¹²) cannot be predicted simply from Cram's rule.¹³ The torsional strain transition-state model proposed by Felkin,¹⁴ and subsequently supported by Anh and Eisenstein,¹⁵ has been

^{(8) (}a) Reference 7a, pp 248-252. (b) Malloy, T. B., Jr.; Bauman, L. E. Top. Stereochem. **1979**, *11*, 97.

⁽⁹⁾ The synthesis of 1-(trimethylsilylethynyl)cyclohexan-1-ol has been reported previously, but only low-field NMR data are available: (a) Wenkert, E.; Leftin, M. H.; Michelotti, E. L. J. Org. Chem. **1985**, 50, 1122. (b) Iritani, K.; Yanagihara, N.; Utimoto, K. J. Org. Chem. 1986, 51, 5499.

⁽¹⁰⁾ X-ray crystal structures of molecules 4, 8, and 26 are shown in (11) Braga, D.; Grepioni, F.; Walther, D.; Heubach, K.; Schmidt, A.;

^{(12) (}a) Battioni, J.-P.; Chodkiewicz, W.; Cadiot, P. C. R. Seances Acad. Sci. Ser. C 1967, 264, 991. (b) Battioni, J.-P.; Capmau, M.-L.; Chodkiewicz, W. Bull. Soc. Chim. Fr. 1969, 976. (c) Battioni, J.-P.; Chodkiewicz, W. Bull. Soc. Chim. Fr. 1969, 981.

⁽¹³⁾ Cram, D. J.; Abd Elhafez, F. A. J. Am. Chem. Soc. 1952, 74, 5828.

^{(14) (}a) Cherest, M.; Felkin, H.; Prudent, N. Tetrahedron Lett. 1968, 2201. (b) Cherest, M.; Felkin, H. Tetrahedron Lett. 1968, 2205.

^{(15) (}a) Anh, N. T.; Eisenstein, O. Nouv. J. Chim. 1977, 1, 61. (b) Anh, N. T. Top. Curr. Chem. 1980, 88, 145.



used to rationalize the experimentally observed stereoselectivities of nucleophilic additions to cyclic ketones. In this model, it is suggested that the direction of nucleophilic attack is controlled not only by steric effects but also by the torsional strain imposed on the system in the transition state. In the case of cyclohexanones, this involves a distorted chair conformation whereby the axial transition state is perfectly staggered, whereas equatorial attack proceeds through a transition state that affords partial eclipsing.¹⁶

The X-ray crystal structures of the dicobalt hexacarbonyl clusters **11** and **12** (derived from **9** and **10**, respectively) show that the conformations of the cyclohexane rings in these complexes are not markedly perturbed. However, the data do allow a comparison of the solid-state structures of these isomers (Figure 1). They reveal that the conformation of the cyclohexane chair at the *tert*-butyl end of the molecule remains reasonably constant; the angle between the planes defined by C(3)-C(4)-C(5) and C(2)-C(3)-C(5)-C(6) is $53^{\circ} \pm 0.5^{\circ}$. There is slightly more variation at the cluster end whereby the interplanar angle between C(2)-C(1)-C(6) and C(2)-C(3)-C(5)-C(6) ranges from 44° to 47°.

The X-ray crystallographic characterizations of the cobalt clusters **11** and **12** allowed the unequivocal assignment of their precursors **9** and **10** as possessing, respectively, axial and equatorial alkynyl substituents. The ¹³C NMR spectra of the alkynols show clear chemical shift differences: in **9**, the C(1) absorption is found at δ 69.7, while in **10** the C(1) peak occurs δ 66.0, suggesting that for systems of this type the C(1) resonance of the isomer with the equatorial alkynyl moiety is approximately 4 ppm more shielded than its axial counterpart.

Replacement of the trimethylsilylethynyl substituent by a triphenylsilylethynyl group again yields a mixture of 4-*tert*-butyl-(1-alkynyl)cyclohexan-1-ols; in this case,

⁽¹⁶⁾ For more recent analyses of this concept, see: (a) Wu, Y.-D.; Tucker, J. A.; Houk, K, N. *J. Am. Chem. Soc.* **1991**, *113*, 5018. (b) Frenking, G.; Köhler, K. F.; Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1146. (c) Wu, Y.-D.; Houk, K, N. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1019.



Figure 2. Molecular structures of (A) 18 and (B) 20 (30% thermal ellipsoids).

the axial isomer, **13**, is more favored than its equatorial partner, **14**, by a 4:1 ratio. These assignments are based on the C(1) NMR absorptions which again differ by \sim 4 ppm. Although both **13** and **14** yield crystalline complexes (**15** and **16**, respectively) when treated with Co₂(CO)₈, it has not yet proven possible to acquire acceptable X-ray data sets on these cobalt clusters. Nevertheless, it is evident that increasing the bulk of the attacking nucleophile disfavors the formation of axial isomers.

Alkynols Derived from Cyclohexane-1,4-dione. The observation that a triphenylsilylethynyl group could adopt either an axial or an equatorial position when a bulky substituent was already present at C(4) suggested that both cis and trans isomers of 1,4-bis(triphenylsilylethynyl)cyclohexane-1,4-diol might be readily available. Assuming that the initial attack occurred at an axial site, to give 17, the second alkynyl unit could then adopt either an axial, 18, or an equatorial, 19, orientation, as depicted in Scheme 5. Treatment of cyclohexane-1,4-dione with 2 equiv of (triphenylsilylethynyl)lithium yielded three products; the trans dialkynol 18 was obtained as colorless crystals and characterized by X-ray crystallography. The solid-state structure of 18 appears as Figure 2A and illustrates clearly the diaxial nature of the alkynyl substituents. The molecule has an inversion center, the crystal packing is apparently dominated by the bulk of the triphenylsilyl groups, and hydrogen bonding does not seem to play a significant role in this particular case.

The other two products from this reaction were identified spectroscopically as the isomeric disubstituted material **19**, along with a small quantity of the monoalkyne **17**. However, since these latter two materials could not be cleanly separated by chromatography, they were treated with dicobalt octacarbonyl and the separation achieved at the cluster stage. Similarly, the diaxial isomer **18** was allowed to react with $Co_2(CO)_8$ to give the corresponding trans cluster **20** whose solid-state structure is shown in Figure 2B. The most obvious result is that the cyclohexane ring has undergone a conformational flip whereby addition of a dicobalt hexacarbonyl moiety to each of the axial alkynyl units in **18** has resulted in the formation of the diequatorial isomer **20**.

The most dramatic effects are found for the cis complex **21**, the X-ray structure of which appears as Figure 3A. The molecule adopts a well-defined twist-boat conformation with overall C_2 molecular symmetry. The angle between the C(2)–C(1)–C(3) and C(2)–C(3)–C(2A)–



Figure 3. Molecular structures of (A) **21** and (B) **25** (30% thermal ellipsoids).

C(3A) planes is \sim 33°, and the distance between O(1) and O(1A) is 2.705(10) Å, appropriate for *intra*molecular hydrogen bonding. The net result of converting two alkyne substituents into cobalt clusters has been to provide a convenient route to a twist-boat cyclohexane-1,4-diol; decomplexation with iodine allows facile reversal of this conformational change.

The analogous reaction of cyclohexane-1,4-dione with 2 equiv of (trimethylsilylethynyl)lithium again afforded the *trans*- and *cis*-dialkynols, **22** and **23**. Treatment with $Co_2(CO)_8$ gave the bis-complexed *trans*- and *cis*-dialkynols **24** and **25**, respectively, together with a small quantity of the monocomplexed *trans*-dialkynol **26**, which was also characterized by X-ray crystallography.¹⁰ The ring-flipped nature of complex **26** further illustrates the tendency of the cluster moiety to favor an equatorial site.

Table 1. Idealized and Experimental Torsion Angles in Cyclohexane Twist-Boats

torsion angle (deg)	idealized twist-boat ^a	Berti ^b	Dieks ^c	Biali 1,2,3, 4^d	Biali 1,2,4,5 ^e	cobalt–TPS $(1)^{f}$	cobalt–TPS $(2)^{f}$	cobalt–TMS ^g
C6-C1-C2-C3	+65	+63.5	+61.8	+60.1	+64.5	+57.8	+58.2	+61.2
C1-C2-C3-C4	-31	-36.5	-42.4	-28.5	-24.7	-37.8	-38.0	-29.4
C2-C3-C4-C5	-31	-20.6	-17.5	-24.0	-37.1	-17.6	-21.3	-30.2
C3-C4-C5-C6	+65	+61.8	+61.8	+48.8	+64.5	+56.1	+60.0	+61.2
C4-C5-C6-C1	-31	-37.6	-42.3	-16.1	-24.7	-37.1	-40.1	-29.4
C5-C6-C1-C2	-31	-25.4	-17.8	-37.2	-36.9	-20.9	-18.5	-30.2

^{*a*} From ref 7c. ^{*b*} Data from ref 17. ^{*c*} Data from ref 20. ^{*d*} Data from ref 18. ^{*e*} Data from ref 19. ^{*f*} This work; there are two independent molecules of **21** in the unit cell. ^{*g*} This work; molecule **25**.

Gratifyingly, the bis-cluster complex **25**, derived from the *cis*-dialkynol, yielded a twist-boat conformation with overall C_2 molecular symmetry, as shown in Figure 3B. In contrast to the triphenylsilylated twist-boat, **21**, the O(1)····O(4) distance in **25** is now 3.099(12) Å, probably too long to support *intra*molecular hydrogen bonds. However, in the solid state, the molecules of **25** pack in pairs such that the four oxygens are in a pseudotetrahedral arrangement with *inter*molecular O···O distances of approximately 2.776(11) Å, indicative of hydrogen bonding. One can readily envisage silicon, germanium, or a transition metal occupying the cavity in such a tetrahedral coordination site!

Crystallographically characterized cyclohexane twistboats are relatively rare. Twenty-five years ago, Berti et al. reported the structure of 2,3-dibromo-4-tert-butylcyclohexyl p-nitrobenzoate,17 and Biali has recently described two other cases, cis, trans, trans-1,2,3,4- and cis, syn, cis-1, 2, 4, 5-tetracyclohexylcyclohexane.^{18,19} There are also several examples in the Cambridge Crystallographic Database of metal complexes containing multiple polycyclohexyl-phosphines or -silanes in which severe crowding gives rise to the occasional maverick nonchair cyclohexyl ring. To our knowledge, the only crystallographically characterized 1,4-disubstituted twistboat cyclohexane, reported by Dieks and co-workers,²⁰ possesses both a porphyrin ring and a 2-methyl-1,4naphthoquinone. In that system, the torsion angles within the cyclohexane ring differ quite substantially from those expected for an idealized twist-boat geometry.7c For comparison, the torsion angles for all the previously reported twist-boats and for the cobalt-containing boats 21 and 25 are listed in Table 1; it is evident that the structure of the trimethylsilyl-substituted twist-boat 25 is remarkably close to the reported idealized geometry. It would be interesting to reevaluate the most favored twist-boat geometry of cyclohexane-1,4-diol using modern calculation techniques.

In principle, the accessibility of a boat conformer of *cis*-cyclohexane-1,4-diol can be turned into a synthetic advantage. For example, it has been reported that treatment of *cis*-cyclohexane-1,4-diol with dibutyldichlorogermane yields a mixture of cyclic germanoxane polymers, as depicted in Scheme 6; however, under conditions of very high dilution, small quantities of the cyclic dimer are obtained.²¹ In contrast, use of *cis*-2,5-di-*tert*-butylcy-clohexane-1,4-diol (for which infrared data indicate strong



intramolecular hydrogen bonding, consistent with a twist-boat conformation²²) furnishes the monomer **27** in 75% yield. Nevertheless, the product still contains bulky alkyl groups that would be difficult to remove, whereas use of cobalt carbonyl clusters to effect a temporary augmentation of the steric bulk of an appropriately positioned substituent can be used for stereochemical control.

Epimerization of Alkynyl Sugars. The elegant work of Tanaka and Isobe⁵ on the cobalt cluster-mediated epimerization of the alkynyl sugar 28 into 29 merits some comment. As noted by these authors, complexation of the alkynyl substituent by dicobalt hexacarbonyl and subsequent protonation leads to a metal-stabilized propargyl cation. However, they did not discuss the mechanism of epimerization which must be considered in terms of the structure and dynamics of the cationic intermediate. It has been previously noted that generation of cobaltstabilized cations preferentially proceeds through an antiperiplanar transition state such that the elimination of water is anchimerically assisted by the metal.²³ This process maintains the stereochemical integrity of the developing sp²-carbon center. However, a symmetryallowed antarafacial migration from one cobalt vertex to the other inverts the configuration of the cationic center.²⁴ Scheme 7 depicts such a process for the alkynyl sugar 28 whereby protonation and ring opening affords the cation 30; antarafacial migration (such that the smaller substituent maintains the position proximal to the metal-metal bond) generates the diastereomeric cation 31. Subsequent ring closure from the exo face yields a

⁽¹⁷⁾ Bellucci, G.; Berti, G.; Colapietro, M.; Spagna, R.; Zambonelli, L. J. Chem. Soc., Perkin Trans. 2 1976, 1213.

⁽¹⁸⁾ Columbus, I.; Hoffman, R. E.; Biali, S. E. J. Am. Chem. Soc. **1996**, *118*, 6890.

 ⁽¹⁹⁾ Golan, O.; Cohen, S.; Biali, S. E. J. Org. Chem. 1999, 64, 6505.
(20) Dieks, H.; Senge, M. O.; Kirste, B.; Kurreck, H. J. Org. Chem.
1997, 62, 8666.

⁽²¹⁾ Sara, A. N. J. Organomet. Chem. 1973, 47, 331.

⁽²²⁾ Stolow, R. D. J. Am. Chem. Soc. 1961, 83, 2592.

⁽²³⁾ El Hafa, H.; Cordier, C.; Gruselle, M.; Besace, Y.; Jaouen, G.; McGlinchey, M. J. *Organometallics* **1994**, *13*, 5149.

^{(24) (}a) Padmanabhan, S.; Nicholas, K. M. *J. Organomet. Chem.* **1984**, *212*, C23. (b) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128. (c) Edidin, R. T.; Norton, J. R.; Mislow, K. Organometallics **1982**, *1*, 561. (d) Schilling, B. E. R.; Hoffmann, R.

J. Am. Chem. Soc. **1979**, *101*, 3456. (e) D'Agostino, M. F.; Frommann, R.

C. S.; McGlinchey, M. J. J. Organomet. Chem. 1990, 394, 145.

Scheme 7



chair conformation in which the bulky alkynylcobalt cluster moiety occupies the favored equatorial site.

Concluding Remarks

To our knowledge, the present examples are the only ones in which the chair—twist-boat interconversion can be controlled by incorporation of a readily removable functionality. This approach, whereby a dicobalt hexacarbonyl moiety can function as a conformational switch, has considerable potential for the selective manipulation of other ring systems, and our ongoing studies will be the basis for future communications.

Experimental Section

Materials. All syntheses were carried out under a dry nitrogen atmosphere in an enclosed round-bottom flask, with constant stirring, and all reagents 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, obtained from Strem Chemicals Inc. Silica gel, 230–400 mesh, was used for flash column chromatography.

Instrumentation. ¹H and ¹³C solution NMR spectra were measured on spinning samples by using Bruker AC-200 or AC-300 spectrometers. The NOE experiments for **3** were carried out, using a nonspinning sample, on a Bruker DRX 500 spectrometer. All NMR spectra were recorded at ambient temperatures and referenced to the residual proton or ¹³C solvent signal. Low-resolution 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 NH₃ as the collision gas. Electrospray ionization methods were used to acquire the mass spectra for compounds **15**, **16**, **18**, **20**, **21**, and **23–26**, employing a Quattro L.C. triple quadrupole mass spectrometer (Micromass Canada, Inc.).

General Synthetic Procedure. Each reaction was conducted at -78 °C in a dry ice/2-propanol bath and monitored to completion using thin-layer chromatography, before the mixture was allowed to warm to room temperature and quenched with H₂O. In a typical reaction, *n*-butyllithium (7.64 mmol) in ether (30 mL) was added to a cold solution of trimethylsilylethyne (1.08 mL, 7.64 mmol) dropwise via a syringe over a 1 h period. After the mixture was stirred for 3 h at -78 °C, a solution of 4-*tert*-butylcyclohexanone (1.178 g,

7.64 mmol) in ether (6 mL) was added dropwise. The solution was allowed to warm to room temperature, stirred for 24 h, and quenched with water. After ether extraction, washing with brine, drying over magnesium sulfate, and removal of solvent in vacuo, the resulting white solid was flash chromatographed on silica gel using 50/50 hexane/dichloromethane as eluent to give trans-4-tert-butyl-1-(trimethylsilylethynyl)cyclohexane-1ol, 9 (62%), and the corresponding cis isomer 10 (24%) as colorless crystals. Subsequently, each alkynol was stirred at room temperature for 24 h with an equimolar quantity of Co2-(CO)₈ in THF under a nitrogen atmosphere. Removal of the solvent and flash chromatography on silica gel using 50/50 hexane/dichloromethane as eluent yielded dark red crystals of the clusters 11 and 12, respectively. Crystals suitable for X-ray diffraction were grown for 4, 8, 11, 12, 18, 20, 21, 25, and **26** by slow evaporation from a 50/50 solution of diethyl ether and hexanes.

1-(Trimethylsilylethynyl)cyclohexan-1-ol, 3:⁹ colorless crystals (70%); mp 72–73 °C; ¹H NMR δ 3.29 (1H, s), 1.70 (2H, m) 1.57 (2H, m), 1.48–1.35 (5H, m), 1.16 (1H, m), 0.13 (9H, s); ¹³C NMR δ 112.0, 86.1, 66.8, 39.7, 24.9, 22.7, 0.1.

1-(Trimethylsilylethynyl)cyclohexan-1-ol[Co₂(CO)₆], 4: dark red crystals (79%); mp 104–105 °C; ¹H NMR δ 1.85– 1.57 (11H, m), 0.31 (9H, s); ¹³C NMR δ 200.5, 122.8, 73.5, 42.1, 25.7, 22.56, 1.1.

trans-4-*tert*-Butyl-1-(phenylethynyl)cyclohexanol, 7: colorless crystals (72%); mp 125–126 °C; ¹H NMR δ 7.36 (5H, m), 5.47 (1H, s), 1.96 (2H, m), 1.68 (2H, m), 1.38 (4H, m), 1.01 (1H, t of t), 0.84 (9H, s); ¹³C NMR δ 130.9, 128.6, 128.1, 122.7, 94.1, 83.7, 67.9, 46.4, 40.2, 31.9, 27.4, 24.3.

trans-4-*tert*-Butyl-1-(phenylethynyl)cyclohexanol[Co₂-(CO)₆], 8: dark red crystals (90%); mp > 156 °C dec; ¹H δ 7.43 (2H, m), 6.97 (3H, m), 4.30 (1H, s), 2.03 (2H, m), 1.63–1.07 (m, 6H), 0.85 (1H, m), 0.54 (9H, s); ¹³C NMR δ 130.3, 127.7, 74.1, 69.1, 48.0, 43.2, 32.2, 27.5, 24.3.

*trans***4**-*tert***-Butyl-1-(trimethylsilylethynyl)cyclohexan1-ol, 9:** colorless crystals (62%); mp 145 °C (lit.²⁵ mp 145–147 °C); ¹H NMR δ 2.60 (1H, s), 1.95–1.32 (9H, m), 0.84 (9H, s), 0.14 (9H, s); ¹³C NMR δ 109.1, 89.6, 69.7, 46.8, 40.2, 32.2, 27.5, 24.7, 0.0.

cis-4-*tert*-Butyl-1-(trimethylsilylethynyl)cyclohexan-1ol, 10: colorless crystals (24%); mp 68–69 °C; ¹H NMR δ 2.15 (1H, s), 2.02–1.20 (9H, m), 0.82 (9H, s), 0.12 (9H, s); ¹³C NMR δ 111.4, 85.8, 66.0, 47.2, 39.3, 32.4, 27.4, 21.8, 0.0.

trans-4-*tert*-Butyl-1-(trimethylsilylethynyl)cyclohexan-1-ol[Co₂(CO)₆], 11:²⁶ dark red crystals (63%); mp 89–90 °C; ¹H NMR δ 3.71 (1H, s), 1.92–1.82 (5H, m), 1.23–1.19 (4H, m), 0.88 (9H, s), 0.31 (9H, s); ^{13}C NMR δ 200.6, 120.9, 79.3, 74.3, 47.9, 42.8, 32.5, 28.0, 24.5, 1.6.

cis-4-*tert*-Butyl-1-(trimethylsilylethynyl)cyclohexan-1ol[Co₂(CO)₆], 12:²⁶ dark red crystals (58%); mp 105–106 °C; ¹H NMR δ 3.72 (1H, s), 1.89–1.49 (9H, m), 0.87 (9H, s), 0.30 (9H, s); ¹³C NMR δ 200.5, 122.61, 73.14, 47.8, 42.5, 32.4, 27.5, 23.5, 1.1.

trans-4-*tert*-Butyl-1-(triphenylsilylethynyl)cyclohexan-1-ol, 13: colorless crystals (58%); mp 121–122 °C; ¹H NMR δ 7.69–7.26 (15H, m), 2.18–1.34 (9H, m), 0.88 (9H, s); ¹³C NMR δ 135.5, 133.5, 129.9, 127.9, 113.8, 84.4, 70.1, 47.2, 40.3, 32.3, 27.6, 24.4.

cis-4-*tert*-Butyl-1-(triphenylsilylethynyl)cyclohexan-1ol, 14: colorless crystals (14%); mp 187–188 °C; ¹H NMR δ 7.69–7.26 (15H, m), 2.17–1.28 (9H, m), 0.89 (9H, s); ¹³C NMR δ 135.5, 133.5, 129.9, 127.9, 116.1, 81.1, 66.4, 47.2, 39.3, 32.4, 27.3, 21.8.

trans-4-*tert*-Butyl-1-(triphenylsilylethynyl)cyclohexan-1-ol[Co₂(CO)₆], 15: dark red crystals (50%); mp 103–104 °C; ¹H NMR δ 7.77–7.26 (15H, m), 1.97–1.25 (9H, m), 1.04 (9H, s); ¹³C NMR δ 200.1, 136.4, 134.0, 130.0), 127.9), 122.9, 74.2, 45.0, 41.2, 32.7, 27.7, 23.5.

cis-4-*tert*-Butyl-1-(triphenylsilylethynyl)cyclohexan-1ol[Co₂(CO)₆], 16: dark red crystals (80%); mp 150–152 °C; ¹H NMR δ 7.75–7.29 (15H, m), 1.83–1.28 (9H, m), 0.86 (9H, s); ¹³C NMR δ 200.6, 136.3, 134.0, 130.0, 127.9, 73.1, 47.4, 41.6, 32.3, 27.5, 23.3.

4-Hydroxy-4-(triphenylsilylethynyl)cyclohexanone, 17, trans-1,4-Bis(triphenylsilylethynyl)cyclohexane-1,4-diol, 18, and cis-1,4-Bis(triphenylsilylethynyl)cyclohexane-1,4-diol, 19. Addition of cyclohexane-1,4-dione to triphenylsilylacetylene and *n*-butyllithium in Et₂O gave a mixture of 17–19. The dialkynol 18 was separated from the mixture as a white crystalline solid, mp 225–226 °C (37%), by flash column chromatography on silica gel, whereas 17, mp 154 °C, was only partially isolated and predominantly coeluted with 19 from the column. Compound 19 was not isolated from the mixture but was treated directly with Co₂(CO)₈.

17: ¹H NMR δ 7.66–7.34 (15H, m), 2.62–2.12 (9H, m); ¹³C NMR δ 209.6, 135.4, 132.9, 130.1, 128.1, 111.9, 85.1, 66.8, 38.8, 37.3.

18: ¹H NMR δ 7.67–7.34 (30H, m), 2.19–2.01 (10H, m); ¹³C NMR δ 135.5, 133.2, 130.0, 128.0, 113.3, 84.2, 67.9, 36.1.

trans-1,4-Bis(triphenylsilylethynyl)cyclohexane-1,4diol[Co₂(CO)₆]₂, 20: dark red crystals (82%); mp >192 °C dec; ¹H NMR δ 7.78–7.36 (30H, m), 2.09–1.50 (10H, m); ¹³C NMR δ 199.8, 136.4), 133.9), 130.0), 127.9, 72.6, 37.1.

A small quantity of the monocomplexed dialkyne, 4-hydroxy-4-(triphenylsilylethynyl)cyclohexanone[Co₂-(CO)₆], was also isolated as a dark red oil: ¹H NMR δ 7.73–

(26) The clusters **11** and **12** have been reported previously, but no spectroscopic or structural data are available: Daly, S. M.; Armstrong, R. W. *Tetrahedron Lett.* **1989**, *30*, 5713.

7.44 (15H, m), 2.76–1.50 (9H, m); $^{13}\mathrm{C}$ NMR δ 210.6, 199.8, 136.2, 133.9, 130.4, 128.1, 2.1, 40.2, 37.3.

cis-1,4-Bis(triphenylsilylethynyl)cyclohexane-1,4-diol-[Co₂(CO)₆]₂, 21: dark red crystals; mp >150 °C dec; ¹H NMR δ 7.72–7.33 (30H, m), 1.91–1.55 (8H, m); ¹³C NMR δ 199.8, 136.3, 133.9), 130.2, 128.0, 72.9, 37.3.

trans-1,4-Bis(trimethylsilylethynyl)cyclohexane-1,4diol, 22: colorless crystals (56%); mp 188–190 °C; ¹H NMR δ 2.10–1.89 (10H, m), 0.16 (18H, s); ¹³C NMR δ 108.5, 89.0, 68.0, 36.5, -0.1.

cis-1,4-Bis(trimethylsilylethynyl)cyclohexane-1,4-diol, 23: colorless crystals (21%); mp 146–147 °C; ¹H NMR δ 2.58 (2H, s), 1.87 (8H, s), 0.12 (18H, s); ¹³C NMR δ 109.1, 108.7, 88.8, 88.0, 67.8, 66.8, 36.4, 35.7, -0.1.

trans-1,4-Bis(trimethylsilylethynyl)cyclohexane-1,4diol[Co₂(CO)₆]₂, 24: dark red crystals (80%); mp >165 °C dec; ¹H NMR δ 2.21 (4H, d), 1.76 (4H, d), 1.36 (1H, s), 0.36 (9H, s); ¹³C NMR δ 200.3, 121.5, 72.9, 38.2, 1.1.

cis-1,4-Bis(trimethylsilylethynyl)cyclohexane-1,4-diol-[Co₂(CO)₆]₂, 25: dark red crystals (53%); mp >129 °C dec; ¹H NMR δ 2.75 (2H, s), 2.25–1.80 (8H, m), 0.34 (18H, s); ¹³C NMR δ 200.2, 120.4, 78.8, 73.2, 38.0, 1.1.

trans-1,4-Bis(trimethylsilylethynyl)cyclohexane-1,4diol[Co₂(CO)₆], 26: dark red crystals (18%); mp > 154 °C dec; ¹H NMR δ 2.12–1.38 (10H, m), 0.32 (9H, s), 0.16 (9H, s); ¹³C NMR δ 200.2, 121.7, 110.1, 87.1, 72.5, 65.7, 36.6, 35.0, 1.0, -0.1.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged. J.H.K. and P.E.L. thank NSERC and the Province of Ontario for graduate scholarships. Mass spectra were acquired courtesy of Dr. Kirk Green of the McMaster Regional Mass Spectrometry Centre. We thank Professors Dario Braga and Fabrizia Grepioni (University of Bologna, Italy) for helpful discussions.

Supporting Information Available: Spectroscopic and other characterization data for all molecules. Crystallographic data (excluding structure factors) for the molecules reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-169852 (4), 169853 (8), 169854 (11), 169855 (12), 169856 (18), 169857 (20), 170373 (21), 169858 (25), and 169859 (26). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0108820