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Toward Metal-Stabilized Silylium Cations: An EHMO Study of $[(HC{\equiv}C{-}SiH_2)Co_2(CO)_6]^+$ and X-ray Crystal Structures of $(Me_3SiC{\equiv}CSiPh_2H)Mo_2(CO)_4Cp_2$ and $[(Me_3SiC{\equiv}CSiMe_2)Co_2(CO)_6]_2O$

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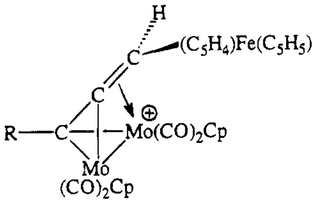
Extended Hückel molecular orbital calculations on the silicon cation $[(HC{\equiv}C{-}SiH_2)Co_2(CO)_6]^+$ reveal that the favored geometry for this silylium ion requires the SiH_2 group to lean toward a $Co(CO)_3$ vertex. This parallels the known behavior of carbocations with metal cluster vertices whereby the electron-deficient center is stabilized by a direct interaction with an organometallic fragment. These calculations also show that replacement of the $Co(CO)_3$ vertices by isolobal $CpMo(CO)_2$ groups noticeably enhances the stabilization of the silylium moiety. A number of possible precursors to metal-stabilized silylium ions have been synthesized, and the clusters $(Me_3SiC{\equiv}C{-}SiPh_2H)Mo_2(CO)_4Cp_2$, **9**, and $[(Me_3SiC{\equiv}C{-}SiMe_2)Co_2(CO)_6]_2O$, **15**, have been characterized by x-ray crystallography. **9** crystallizes in the monoclinic space group $P2_1/c$ with $a = 17.061(2)$ Å, $b = 9.756(2)$ Å, $c = 17.922(3)$ Å, $\beta = 96.64(3)3°$, $V = 2963.1(8)$ Å^3, and $Z = 4$. **15** crystallizes in the monoclinic space group $C2/c$ with $a = 14.093(2)$ Å, $b = 10.285(1)$ Å, $c = 27.689(3)$ Å, $\beta = 92.153(9)°$, $V = 4010.6(5)$ Å^3, and $Z = 4$.

Introduction

Potential routes to stable silylium ions continue to attract much attention,[1] and the recent crystallographic characterizations of $[Et_3Si\cdot toluene]^+[B(C_6F_5)_4]^-$, by Lambert,[2] and of $[i\text{-}Pr_3Si]^+[CB_{11}H_6Br_6]^-$, by Reed,[3] have eloquently stated the case for a non-silicophilic counterion.[4] The ability of transition metals to delocalize the positive charge from carbocationic ligands has been amply documented;[5] moreover, Tilley has characterized numerous complexes in which a transition metal is coordinated to an sp^2-hybridized silicon center.[6] These data support the idea that the stability of sp^2-hybridized silylium species might be enhanced by anchimeric assistance from an electron-rich transition metal center. Indeed, nearly 20 years ago, an attempt was made to generate a silylium ion bearing an α-ferrocenyl substituent.[7] However, this claim has been strongly challenged[8] and, in the absence of crystallographic evidence, must remain questionable. More recently, the complexes $(Ph_3SiOH)[Cr(CO)_3]_n$, where $n = 1$, 2 or 3, have been reported, but protonation does not yield chromium-stabilized silylium ions.[9]

It is noteworthy that, at least for carbocations, there is a hierarchy of organometallic fragments capable of stabilizing an electron-deficient site.[10] For example, in $[(C_5H_5)Fe(C_5H_4){-}CH{-}(C{\equiv}CR)Mo_2(CO)_4Cp_2]^+$, **1**, the cationic carbon could, in principle, interact directly with either a ferrocenyl group or an alkyne−dimolybdenum cluster; in fact, the x-ray crystal structure of **1** reveals that it is the latter which preferentially bonds to the C^+ center.[11]



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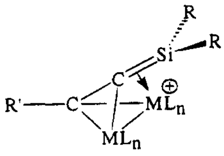

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We here present molecular orbital calculations which show that a silylium ion can be markedly stabilized by interaction with a transition metal center, as in **2**. Subsequently, we describe the synthesis and characterization of a number of clusters $(Me_3Si{-}C{\equiv}C{-}SiR_2H)$-

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

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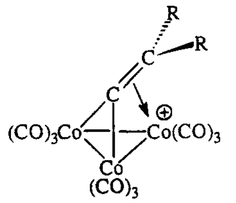
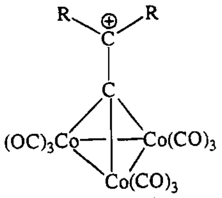
($L_nM{-}ML_n$), where ML_n = $CpMo(CO)_2$ or $Co(CO)_3$, which are potential precursors to metal-stabilized silylium ions.

Results and Discussion

EHMO Calculations. Following an initial suggestion by Seyferth that the vinylidene capping group in $[Co_3(CO)_9C{-}CR_2]^+$ would adopt the bent structure **3a** rather than the more symmetrical isomer **3b** with its



3a



3b

pseudo-3-fold axis,[12] this concept has received both theoretical and experimental support.[13,14] Extended Hückel molecular orbital calculations by Schilling and Hoffmann showed that, when the α-carbon is allowed to lean toward a cobalt vertex, the vacant p orbital on the sp^2-hybridized $-CH_2^+$ fragment can accept electron density from a filled metal d orbital. The net result is not only enhanced stabilization of the cationic center, *via* delocalization of the positive charge onto the metal vertex, but also a larger HOMO–LUMO gap.[13,15]

Replacement of the $Co(CO)_3$ vertices by isolobal $CpMo(CO)_2$ fragments yields cationic clusters, $[Cp_2Mo_2(CO)_4(RC{\equiv}C{-}CR_2)]^+$, many of which have been characterized by x-ray crystallography. Very recently, we have computed an energy hypersurface for the migration of a $C{=}CH_2$ fragment over a $[Cp_2Mo_2(CO)_4CH]^+$ triangular base, and it was shown that the structure in which the CH_2 group is oriented directly over a metal vertex lies at the bottom of the potential energy well.[16] Moreover, the calculated trajectory along which the methylene group migrates from one metal vertex to the other is beautifully paralleled by a series of x-ray crystal structures of cations $[Cp_2Mo_2(CO)_4(RC{\equiv}C{-}CR'R'')]^+$, in which the groups R′ and R″ range from H, methyl, and ferrocenyl to terpenoid and steroidal substituents.[16,17]

We here present the analogous hypersurface for a $C{=}SiH_2$ fragment sited above a $[Co_2(CO)_6CH]^+$ basal triangle. The molecular geometry was based on a typical (alkyne)$Co_2(CO)_6$ cluster with Co–Co, Co–C, and C–C values of 2.49, 1.99, and 1.35 Å, respectively. To define the geometry of the cationic cluster which undergoes rearrangement, we place the origin, ⊙, of our coordinate system at the centroid of the Co(1)–Co(2)–C(3) basal triangle. The carbynyl capping atom, C(2), is defined by a vector starting at the origin and making an angle of 71° with the line C(3)–⊙. The distance was taken as 0.81 Å (for the Co_2C_2 clusters) and as 1.25 Å (for the Mo_2C_2 clusters).[18] The coordinates of the α-$\mathbf{E}H_2$ unit, where **E** = C or Si, are defined in terms of the C(2)–**E** distance (1.45 and 1.85 Å for CH_2 and SiH_2, respectively) and the three angles θ, ϕ, and ω. As shown in Figure 1, θ is the angle ⊙–C(2)–**E** which decreases from 180° as the CH_2 or SiH_2 unit is allowed to lean toward the metal–metal bond. As the $\mathbf{E}H_2$ group swivels away from the mirror plane which bisects the metal–metal bond and contains C(1) and C(2), the dihedral angle ϕ opens up from 0 toward 90°, at which point the C(2)–**E** bond is parallel to the metal–metal vector. The third degree of freedom, the twist angle ω, defines the orientation of the $\mathbf{E}H_2$ plane with respect to the basal plane. When all three components of the $\mathbf{E}H_2$ unit lie in the molecular mirror plane ($\phi = 0°$), the ω values are 0° for H_{endo} and 180° for H_{exo}, where H_{endo} is defined as the hydrogen closer to the M–M vector. As the $\mathbf{E}H_2$ fragment swivels toward M(1), one might anticipate that the values $\omega(H_{endo})$ and $\omega(H_{exo})$ would gradually evolve toward +90 and −90°, respectively. To generate the hypersurface shown in Figure 2, the angles θ and ϕ were incremented in units of 2°; at each point defined by a (θ, ϕ) pair, the torsion angle ω was varied from 0 to 180° in 15° increments and the minimum energy ω value for each (θ, ϕ) position was plotted. These data not only allow the evaluation of a global minimum (*i.e.* the structure which presumably would be found by x-ray diffraction if the metal-stabilized silylium ion could be isolated as a single crystal) but also yield the favored pathway by which the cation can migrate from one metal vertex to the other.

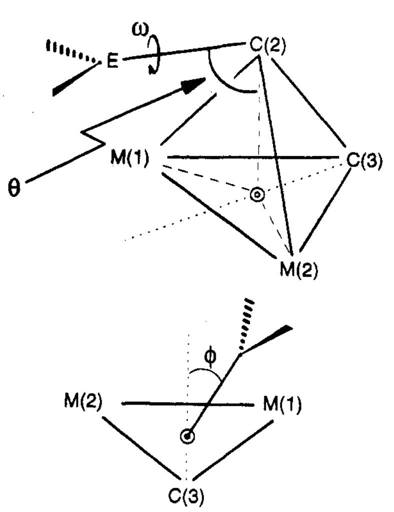


Figure 1. Definition of the coordinate system used in the EHMO calculations.

In the molybdenum-stabilized carbocations previously studied both by EHMO calculations and by a Bürgi–Dunitz analysis of a series of x-ray crystal structures,[17] the α-CH_2 group is found to pass through a symmetrical transition state in which the methylene moiety lies in the molecular mirror plane and perpendicular to the Mo–Mo bond vector. In contrast, in $[Co_2(CO)_6(HC{\equiv}C{-}SiH_2)]^+$ the SiH_2 fragment can rotate freely about the C(2)–Si axis when $\phi = 0°$. At this point, the SiH_2 group is found to bend only slightly (6° toward the

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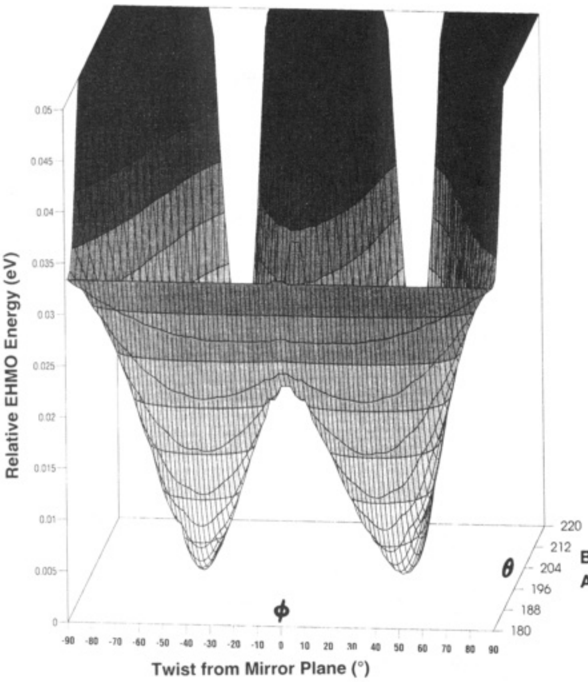


Figure 2. EHMO-calculated energy hypersurface for the migration of SiH_2 in $[Co_2(CO)_6(HC{\equiv}C{-}SiH_2)]^+$.

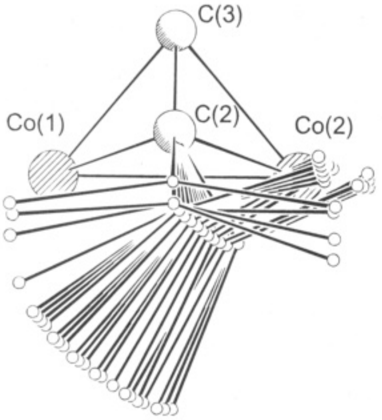


Figure 3. Migration pathway of the SiH_2^+ group on a cobalt cluster.

Co—Co bond, presumably to allow some stabilization of the electron-deficient silicon center by both cobalt atoms. As ϕ increases and the SiH_2 unit moves toward one Co-$(CO)_3$ vertex, the molecule falls into a potential well. As the cluster cation descends into this well, increases in ϕ are accompanied by a smooth decrease in the bend angle θ, from 174° at $\phi = 0°$ to 164° at $\phi = 32°$. We have previously shown for the migration of the CH_2^+ group in $[(C_5H_4{-}C_5H_4)Mo_2(CO)_4(R{-}C{\equiv}C{-}CH_2)]^+$ that the migrating cation orients itself (as a function of ω) so as to best align the vacant p orbital with the nearest metal center; this behavior can also be seen in Figure 3. The EHMO-derived energetically most favorable structures for both carbenium and silylium ions stabilized on either a cobalt or molybdenum center are depicted in Figure 4.

Another factor which was considered involved the pyramidalization of the $\mathbf{E}H_2$ fragments when bonded to a transition metal center. It was shown previously that an 8° "folding-back" of the methylene hydrogens in $[(C_5H_4{-}C_5H_4)Mo_2(CO)_4(R{-}C{\equiv}C{-}CH_2)]^+$ led to a slight stabilization. In $[(C_5H_5)_2Mo_2(CO)_4(HC{\equiv}C{-}\mathbf{E}H_2)]^+$, the system is stabilized to the tune of 5.8 or 5.0 kJ mol^{-1} for $\mathbf{E}$ = C or Si, respectively. The corresponding values for the analogous $[Co_2(CO)_6(HC{\equiv}C{-}\mathbf{E}H_2)]^+$ systems are 1.9 kJ mol^{-1} for the carbenium ion and zero for the SiH_2^+ complex. Overall, according to the EHMO calculations, the energetic advantage arising from allowing the $\mathbf{E}H_2^+$ fragment to lean toward a metal vertex is 41 kJ mol^{-1} for $Mo_2{-}CH_2^+$, 22 kJ mol^{-1} for $Mo_2SiH_2^+$, 24 kJ mol^{-1} for Co_2-CH_2^+, and ≈3 kJ mol^{-1} for $Co_2{-}SiH_2^+$. The predicted M—$\mathbf{E}H_2^+$ distances for the above-listed cations are Mo—C 2.65 Å , Mo—Si 2.99 Å , Co—C 2.53 Å, and Co—Si 3.08 Å , respectively.

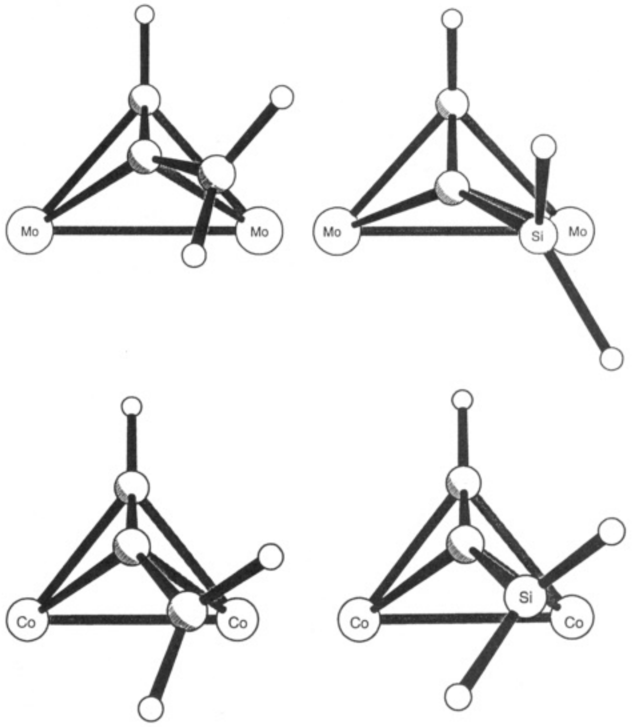
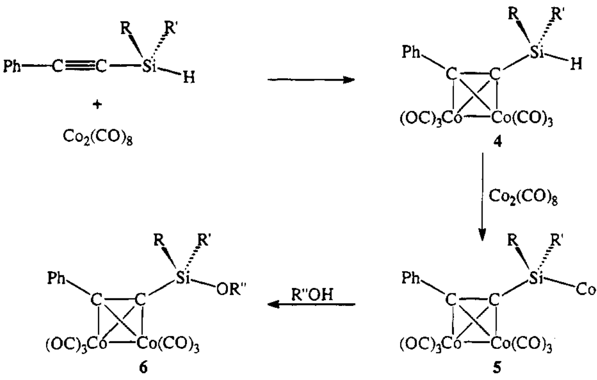


Figure 4. Calculated structures for carbenium and silylium ions stabilized by dimetallic clusters.

Of course, these EHMO-calculated energies should not be regarded as definitive values; however, such semi-empirical approaches are valuable indicators of trends. Other computationally more demanding methods, such as density functional theory, while they give more reliable energies, are not amenable to the convenient generation of hypersurfaces without continued access to a supercomputer. EHMO, Fenske—Hall calculations, and other such approaches are still valuable components of the experimentalist's armory. One can summarize the situation for metal-stabilized silylium systems as follows: the stabilization of an Si^+ center by a $CpMo(CO)_2$ fragment is comparable to that found for a $Co(CO)_3$-stabilized carbocation. In contrast, the anchimeric assistance provided to an Si^+ center by a $Co(CO)_3$ vertex is expected to be rather minimal. It is evident that carbenium ions are better stabilized by metals than are silylium ions and also that a (C_5H_5)-$Mo(CO)_2$ vertex is more effective than a $Co(CO)_3$ group. This latter facet is amply illustrated by the recently reported x-ray crystal structure of the [(2—propynylbornyl)$Mo(CO)_2(C_5H_5)Co(CO)_3]^+$ cation in which the carbocationic charge is alleviated by direct interaction with the molybdenum atom.[10]

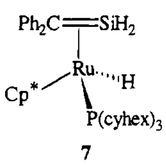
Synthetic Aspects. It is known that alkynylsilanes, such as Ph—C≡C—$SiMe_2H$ or Ph—C≡C-SiH(Me)Cl,

Scheme 1. Reaction of an (alkyne)$Co_2(CO)_6$ Cluster To Give a Siloxy Derivative



react with dicobalt octacarbonyl to yield the corresponding (alkyne)$Co_2(CO)_6$ tetrahedral clusters, **4**. However, one must take care to avoid the addition of excess $Co_2(CO)_8$; otherwise cleavage of the Si—H linkage leads to the formation of a silicon—cobalt bond, as in **5**. Furthermore, as shown in Scheme 1, these latter molecules are readily susceptible to nucleophilic attack, especially by alcohols, giving siloxy derivatives **6**.[19–21]

The $CpMo(CO)_2$ vertex is perhaps the most favorable organometallic fragment for the stabilization of carbocations;[10] however, these species may also be regarded as alkenes coordinated to a molybdenum cation, as in **1**. Similarly, the ruthenium-stabilized silaalkene, $(C_5Me_5)Ru(H)(\eta^2\text{-}Ph_2Si{=}CH_2)P(C_6H_{11})_3$, **7**, has been synthesized and crystallographically characterized by Tilley.[22] These results suggest that a molybdenum-stabilized silylium moiety, **2**, might be a viable objective, and so our initial goal was to prepare a precursor possessing a potential leaving group.



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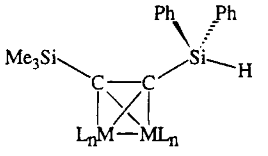

8 $ML_n = Co(CO)_3$
9 $ML_n = CpMo(CO)_2$

The reaction of the silaalkyne $Me_3Si{-}C{\equiv}C{-}SiPh_2H$ with $Co_2(CO)_8$ or with the metal—metal triple-bonded dimer $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ yields the tetrahedral clusters $Co_2(CO)_6(Me_3Si{-}C{\equiv}C{-}SiPh_2H)$, **8**, and $Cp_2Mo_2(CO)_4(Me_3Si{-}C{\equiv}C{-}SiPh_2H)$, **9**, which were readily identifiable by their ^1H, ^{13}C, and ^{29}Si NMR spectra, and also by their characteristic ν_{Si-H} stretches at 2144 and 2171 cm^{-1}, respectively. Recrystallization of the dimolybdenum complex, **9**, from THF/hexane gave red parallelepipeds suitable for an x-ray diffraction study. The silaalkyne cluster **9** crystallizes in the monoclinic space $P2_1/c$, and a view of the molecule appears as Figure 5. The Mo—C distances within the tetrahedral core vary from 2.142 to 2.237 Å and are within the normal range.[23] However, the complexed alkyne linkage, C(2)—C(3) = 1.420(5) Å , is rather long compared to analogous bonds found in other $Cp_2Mo_2(CO)_4(RC{\equiv}CR)$ clusters, where the C≡C distances normally lie in the range 1.35—1.37 Å .[23] This effect presumably arises as a result of the bulk of the trimethylsilyl and diphenylsilyl substituents and is also seen in the angles Si(1)—C(2)—C(3) and C(2)—C(3)—Si(4) which are 140 and 149°, respectively, rather than the normal C—C—R value of ≈137°. The lengthened C(2)—C(3) distance is counterbalanced by the rather short Mo(1)—Mo(2) distance of 2.783(1) Å, considerably shorter than the Mo—Mo bond length of ≈2.97 Å normally found in these $Cp_2Mo_2(CO)_4(RC{\equiv}CR)$ clusters. The crystallographic data were of sufficient quality to allow the hydrogen attached to Si(4) to be located; it lies 4 Å from the nearest molybdenum, and apparently, there is no tendency toward a Si⋯H⋯Mo agostic interaction in this molecule. This observation is in accord with the ^{29}Si NMR data which yield a $^1J(Si{-}H)$ value of 211 Hz; for comparison, in the free ligand, $Me_3Si{-}C{\equiv}C{-}SiPh_2H$, $^1J(Si{-}H)$ is 212 Hz.

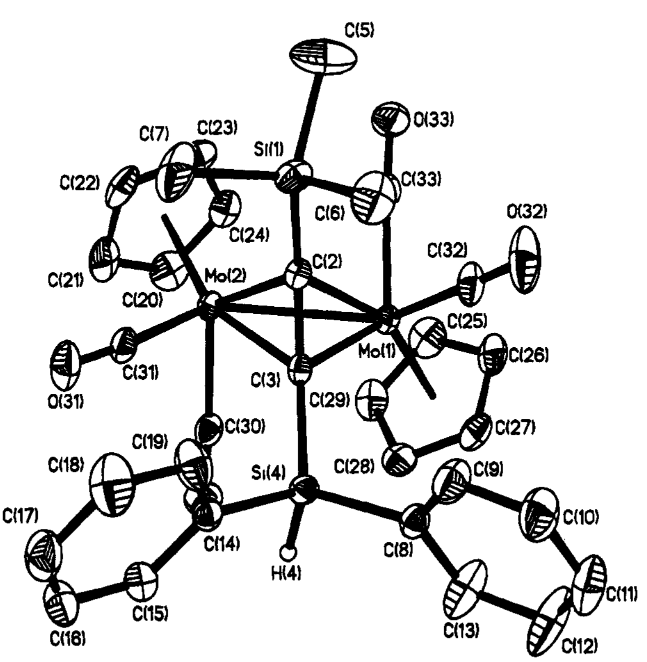

Figure 5. View of **9** showing the atomic numbering scheme. *Salient bond lengths (Å)*: Mo(1)—Mo(2) 2.783(1), Mo(1)—C(2) 2.223(3), Mo(1)—C(3) 2.142(3), Mo(2)—C(2) 2.146(3), Mo(2)—C(3) 2.237(3), C(2)—C(3) 1.420(5), C(2)—Si(1) 1.901(3), C(3)—Si(4) 1.923(3).

A common feature of $Cp_2Mo_2(CO)_4(RC{\equiv}CR)$ systems is the presence of one semibridging carbonyl and three clearly terminal CO ligands.[24] However, such is not the case in $Cp_2Mo_2(CO)_4(Me_3Si{-}C{\equiv}C{-}SiPh_2H)$, **9**; all four molybdenum—carbonyl linkages are terminal with M—C≡O angles of 175 ± 2°. Indeed, when viewed along the metal—metal bond (see Figure 6), the $Cp_2Mo_2(CO)_4C_2$ moiety is seen to have almost idealized C_2 symmetry. Again, one may attribute the adoption of this structure to the presence of the two bulky substituents on the alkyne. This behavior is reminiscent of

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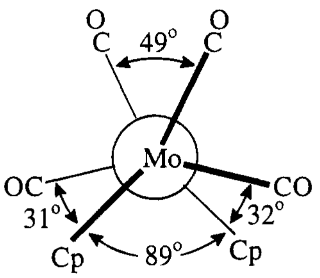
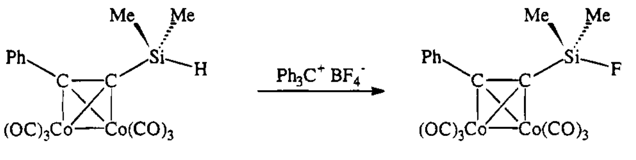


Figure 6. Newman projection of **9**, viewed along the molybdenum–molybdenum bond.

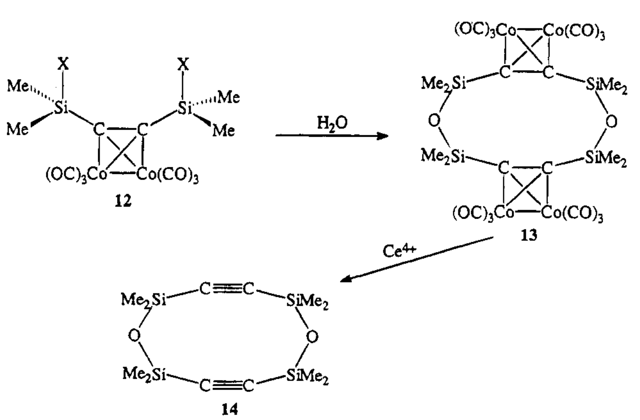
Knox's $Cp_2Mo_2(CO)_4(Me_3Si{-}C{\equiv}C{-}SiMe_3)$ cluster, which also adopts a C_2 structure with terminal carbonyls.[25]

In an attempt to generate a molybdenum-stabilized silylium ion, $Cp_2Mo_2(CO)_4(Me_3Si{-}C{\equiv}C{-}SiPh_2H)$, **9**, was treated with $Ph_3C^+\ BF_4^-$ but the complex was recovered unchanged. One can speculate that the steric problems engendered by the approach of the bulky trityl cation in its attempt to abstract a hydride from the $Ph_2Si{-}H$ moiety in **9** thwarted the process. This result should be contrasted with the report by Corriu that the reaction of $Co_2(CO)_6(Ph{-}C{\equiv}C{-}SiMe_2H)$, **10**, with $Ph_3C^+\ BF_4^-$ led to the isolation of the fluorosilane complex $Co_2(CO)_6(Ph{-}C{\equiv}C{-}SiMe_2F)$, **11**.[26] However, in the latter case, the potential steric problems are likely to be less severe than for **9**.



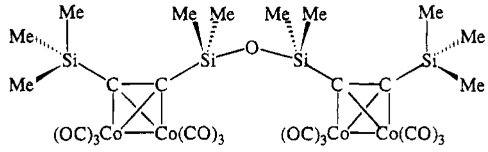
10 11

As shown in Scheme 1, addition of more than 1 equiv of $Co_2(CO)_8$ to an alkynylsilane not only yields a Co_2C_2 tetrahedral cluster but also leads to the formation of a silicon–$Co(CO)_4$ linkage, which is itself very susceptible to hydrolysis, and leads to siloxanes.[19-21] Furthermore, it has been noted that siloxanes are also obtained upon hydrolysis of cobalt clusters bearing $SiMe_2H$ or $SiMe_2Cl$ substituents. Typically, aqueous hydrolysis of $(XSiMe_2{-}C{\equiv}C{-}SiMe_2X)Co_2(CO)_6$, **12**, where X = H or Cl, is reported to yield the cyclic dimer **13**, but only mass spectroscopic evidence is available. However, the free ligand, *i.e.* octamethyl-3,5,8,10-tetrasila-4,9-dioxacyclodeca-1,6-diyne, **14**, has been crystallographically characterized.[27]



12 13 14

In the course of his pioneering studies, Seyferth described the syntheses of numerous alkynylsilanes (including $Me_3Si{-}C{\equiv}C{-}SiMe_2H$) and their general reaction to yield tetrahedral clusters when treated with $Co_2(CO)_8$.[28] However, no further mention was made of the product(s) derived from $Me_3Si{-}C{\equiv}C{-}SiMe_2H$. We find that treatment of 1-(dimethylsilyl)-2-(trimethylsilyl)ethyne with an equimolar quantity of $Co_2(CO)_8$ in pentane yields the siloxane **15**. The product was initially identified by its NMR and mass spectra; the latter revealed the presence of two cobalt cluster fragments and their associated carbonyl ligands. Recrystallization from hexane gave black parallelepipeds suitable for an x-ray diffraction study. The siloxane cluster **15** crystallizes in the monoclinic space group $C2/c$, and a view of the molecule appears as Figure 7.



15

The bond lengths within the Co_2C_2 tetrahedron (Co–Co, 2.491(1) Å ; Co–C, 1.99–2.00 Å ; C–C, 1.326(3) Å) are within the normal ranges for such molecules.[29] As with the dimolybdenum cluster, **9**, the $Si{-}C{\equiv}C$ angles are wider than normal (144° vs ≈135°), but there are no unusual bond lengths. The Si–O–Si angle of 151.5° is typical of siloxanes bearing bulky substituents.[30] The molecule possesses a 2-fold axis, and a view along the Si(1)–Si(1a) vector is entirely analogous to a staggered ethane in which the largest substituents are aligned almost antiparallel. Figure 8 provides such a "Newman projection" along the silicon–silicon axis. The dihedral angle between the two cluster capping carbons, C(2) and C(2a), is 172°.

The closest structurally characterized analogue to **15**, of which we are aware, is $Co_2(CO)_6(Ph{-}C{\equiv}C{-}SiCl(Me){-}Co(CO)_4)$, and its dimensions closely match those found for **15**.[21] One can readily envisage a route to **15** which involves generation of a tetrahedral cluster $Co_2(CO)_6(Me_3Si{-}C{\equiv}C{-}SiMe_2H)$, oxidative addition to give $Co_2(CO)_6(Me_3Si{-}C{\equiv}C{-}SiMe_2{-}Co(CO)_4)$, and finally, hydrolysis to the siloxane.

To conclude, we have presented evidence from molecular orbital calculations at the extended Hückel level that a silylium ion would be stabilized by interaction with a metal fragment; in this respect, a $(C_5H_5)Mo(CO)_2$ moiety is shown to be better able to alleviate the electron deficiency at silicon than is a $Co(CO)_3$ fragment. However, this stabilization of an SiR_2^+ unit will be less than that observed already for carbocations. Routes to

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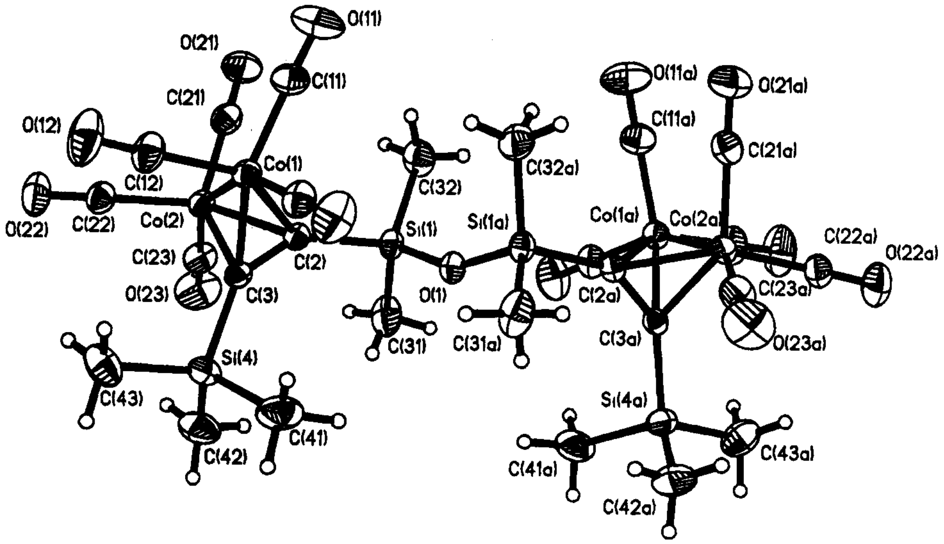

Figure 7. View of **15** showing the atomic numbering scheme. *Salient bond lengths (Å)*: Co(1)—Co(2) 2.491(1), Co(1)—C(2) 1.991(2), Co(1)—C(3) 1.995(2), Co(2)—C(2) 2.001(2), Co(2)—C(3) 1.991(2), C(2)—C(3) 1.326(3), C(2)—Si(1) 1.851(2), C(3)—Si(4) 1.853(2), Si(1)—O(1) 1.628(1). *Salient bond angles (deg)*: Si(1)—C(2)—C(3) 144.6(2), C(2)—(C3)—Si(4) 144.6(2).

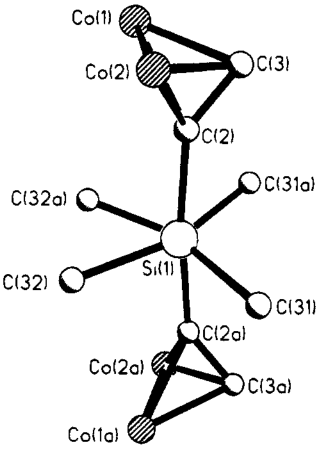

Figure 8. Newman projection of **15**, viewed along the silicon—silicon vector.

metal-stabilized silylium systems require the juxtaposition of the organometallic fragment prior to generation of the silicon cation; subsequent removal of an appropriate leaving group should lead to silylium ion formation. However, the steric demands of the conventional hydride-abstracting reagents are severe, and we are currently exploring the use of other potential leaving groups, as well as counterions of lower silicophilicity.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen, using standard Schlenk techniques. Solvents were dried according to standard procedures. Fast atom bombardment (FAB) mass spectra were obtained on a VG analytical ZAB-SE spectrometer with an accelerating potential of 8 kV and a resolving power of 10 000. NMR spectra were obtained using Bruker AM 500, AC 300, and AC 200 spectrometers. ^{1}H, ^{13}C, and ^{29}Si chemical shifts were reported relative to tetramethylsilane. Infrared spectra were obtained on a Bio-Rad FTS-40 spectrometer, using NaCl windows.

$Me_3SiC{\equiv}C{-}SiMe_2H$. *n*-Butyllithium (11.08 mL of a 1.6 M hexane solution, 17.72 mmol) was added dropwise to a solution of (trimethylsilyl)ethyne (1.737 g, 17.72 mmol) in THF (30 mL) at −78 ° C *via* cannula over a 30 min period, and the solution was then allowed to warm to room temperature. After stirring for 2 h, the solution was cooled to −78 °C and dimethylchlorosilane (2 mL, 1.94 g, 17.72 mmol) in THF (5 mL) was added dropwise; the solution was allowed to warm to room temperature and stirred for 24 h. The desired product was extracted by using a buffer solution ($NaH_2PO_4/KHPO_4$) of pH 6.8. After removal of hexane the organic phase yielded $Me_3SiCC{-}SiMe_2H$ (2.66 g, 17.0 mmol; 96%) as an oil. ^{1}H NMR ($CDCl_3$, 200 MHz): 4.10 (septet, $^2J_{Si-H}$ = 5.4 Hz, 1H, Si—H), 0.20 (d, $^2J_{Si-H}$ = 5.4 Hz, 6H, $SiMe_2$); 0.14 (s, 9H, Me_3Si). ^{13}C NMR ($CDCl_3$, 50.3 MHz): 115.78, 110.54 (C≡C); −0.18 (Me_3Si); −3.05 ($SiMe_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): −39.1 (doublet of septets, $^1J_{Si-H}$ = 200 Hz, Me_2SiH), −18.9 (decet, $^2J_{Si-H}$ = 6.7 Hz, Me_3Si). IR (neat liquid): ν_{SiH} 2134 cm^{-1}.

$[Me_3SiC{\equiv}C{-}SiMe_2(\mu^2\text{-}Co_2(CO)_6)]_2O$ (15). Dicobalt octacarbonyl (3.40 g, 10 mmol) dissolved in THF (30 mL) was added dropwise to $Me_3SiC{\equiv}C{-}SiMe_2H$ (1.56 mL, 10 mmol) in THF (30 mL) over a 30 min period. The solution was allowed to stir for 24 h at room temperature. After removal of solvent *in vacuo*, the residue was subjected to flash chromatography on silica gel. Elution with hexane gave dark red crystals of **15** (3.59 g, 4 mmol; 80%). ^{1}H NMR (CD_2Cl_2, 200 MHz): 0.38 (s, 6H, $SiMe_2$), 0.30 (s, 9H, Me_3Si). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 202.9 (Co—CO's); 93.2, 91.0 (cluster C's); 3.8 (Me_3Si); 1.9 (Me_2Si). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): −3.1 (septet, $^2J_{Si-H}$ = 6.8 Hz, Me_2Si), 0.79 (decet, $^2J_{Si-H}$ = 6.7 Hz, Me_3Si). IR (hexane): ν_{CO} 2087, 2049, 2020 cm^{-1}. Mass spectrum DEI, *m/z* (%): 814 (35) $[(M - 3CO)]^+$, 758 (30) $[(M - 5CO)]^+$, 702 (68) $[(M - 6CO)]^+$, 674 (100) $[(M - 8CO)]^+$, 646 (20) $[(M - 9CO)]^+$, 618 (20) $[(M - 10\ CO)]^+$.

$Me_3SiC{\equiv}C{-}SiPh_2H$. Analogously to the synthesis of $Me_3SiC{\equiv}C{-}SiMe_2H$, (trimethylsilyl)ethyne (1.74 g, 17.72 mmol) in THF (30 mL), *n*-butyllithium (17.72 mmol), and diphenylchlorosilane (3.86 g, 17.72 mmol) in THF (5 mL) gave $Me_3SiC{\equiv}C{-}SiPh_2H$ (3.97 g, 14.18 mmol; 80%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.85 (m,

Table 1. X-ray Structure Summary

	9	**15**
	Crystal Data	
empirical formula	$C_{31}H_{30}Mo_2O_4Si_2$	$C_{26}H_{30}Co_4O_{13}Si_4$
color	red	black
habit	parallelepiped	parallelepiped
cryst size, mm	0.3 × 0.3 × 0.2	0.36 × 0.34 × 0.27
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a, Å	17.061(2)	14.093(2)
b, Å	9.756(2)	10.285(1)
c, Å	17.922(3)	27.689(3)
β, deg	96.64(3)	92.153(9)
V, Å^3	2963.1(8)	4010.6(5)
Z	4	4
fw	714.6	898.6
d (calc), Mg/m^3	1.602	1.488
μ, cm^{-1}	9.62	17.97
F(000)	1440	1816
	Data Collection	
diffractometer used	Siemens P4	Siemens P4
radiation (λ, Å)	Mo Kα (0.710 73)	
temp, K	300	300
monochromator	highly oriented graphite crystal	
2θ range, deg	5.0–60.0	4.0–60.0
scan type	$\theta-2\theta$	$\theta-2\theta$
scan speed, deg/min in ω	var; 4.00–40.00	var; 2.00–40.00
no. of std rflns	3 measured every 97 rflns	
index ranges	$-1 \le h \le 23$, $-1 \le k \le 13$, $-25 \le l \le 25$	$-1 \le h \le 19$, $-1 \le k \le 14$, $-38 \le l \le 38$
no. of rflns collcd	10 440	7184
no. of ind rflns	8627 (R_{int} = 2.34%)	5850 (R_{int} = 2.13%)
no. of obsd rflns	6090 ($F \ge 4.0\sigma(R)$)	4245 ($F \ge 4.0\sigma(F)$)
abs corr	Difabs	Difabs
	Solution and Refinement	
system used	Siemens SHELXTL PLUS (PC version)	
solution	direct methods	
refinement method	full-matrix least squares	
quantity minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000F^2$	
no. of params refined	415	274
R, %	3.93	3.69
R_W, %	4.51	3.76
GOF	1.10	1.43
Δ/σ (max)	0.277, 0.011	0.046, 0.007
data-to-param ratio	14.7:1	15.5:1
largest diff peak, e Å^{-3}	0.50	0.37
largest diff hole e Å^{-3}	−0.50	−0.33

Table 2. Atomic Coordinates (×10) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 9

	x	*y*	*z*	*U*(eq)[a]
Mo(1)	1671(1)	1971(1)	115(1)	30(1)
Mo(2)	3307(1)	2137(1)	1881)	29(1)
Si(1)	2664(1)	−1070(1)	−771(1)	40(1)
Si(4)	2527(1)	−107(1)	1685(1)	31(1)
C(2)	2562(2)	393(3)	−87(2)	30(1)
C(3)	2532(2)	627(3)	691(2)	28(1)
C(5)	2403(4)	−618(6)	−1814(3)	93(3)
C(6)	2079(3)	−2568(4)	−560(3)	66(2)
C(7)	3654(3)	−1677(5)	−632(4)	83(2)
C(8)	1634(2)	−1039(4)	1828(2)	36(1)
C(9)	1429(3)	−2299(5)	1495(3)	57(2)
C(10)	786(3)	−2970(5)	1664(3)	68(2)
C(11)	326(3)	−2384(6)	2146(4)	72(2)
C(12)	506(3)	−1168(7)	2469(5)	98(3)
C(13)	1159(3)	−494(5)	2322(3)	78(2)
C(14)	3368(2)	−1224(4)	1973(2)	35(1)
C(15)	3914(2)	−776(5)	2562(3)	48(1)
C(16)	4554(3)	−1534(6)	2774(3)	62(2)
C(17)	4665(3)	−2752(6)	2407(3)	64(2)
C(18)	4139(3)	−3202(5)	1835(4)	74(2)
C(19)	3502(3)	−2458(5)	1616(3)	58(2)
C(20)	3683(3)	4291(4)	−192(3)	57(2)
C(21)	4303(3)	3407(5)	−170(3)	59(2)
C(22)	4132(3)	2418(5)	−764(3)	59(2)
C(23)	3425(3)	2694(5)	−1153(3)	49(1)
C(24)	3142(3)	3856(4)	−799(3)	48(1)
C(25)	1130(3)	4134(5)	133(3)	57(2)
C(26)	579(2)	3148(5)	256(3)	58(2)
C(27)	801(3)	2514(5)	981(3)	54(2)
C(28)	1479(3)	3116(5)	1303(3)	50(1)
C(29)	1679(3)	4106(4)	776(3)	54(2)
C(30)	3296(2)	2882(4)	1253(2)	40(1)
C(31)	4092(2)	847(4)	670(2)	40(1)
C(32)	1034(2)	351(4)	−187(3)	50(1)
C(33)	1669(2)	2195(4)	−1020(3)	46(1)
O(30)	3337(2)	3381(4)	1865(2)	63(1)
O(31)	4586(2)	187(3)	920(2)	63(1)
O(32)	644(2)	−532(4)	−386(3)	93(2)
O(33)	1619(2)	2409(4)	−1688(2)	68(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

4H, aromatic), 7.58 (m, 6H, aromatic), 0.43 (s, 3H, Me$_3$Si). ^{13}C NMR (CD$_2$Cl$_2$, 50.3 MHz): δ 135.50, 128.57 (*meta* and *ortho C's*); 132.37 (*ipso*); 130.61 (*para*); 120.44, 106.22 (C$\equiv$C); −0.16 (Me$_3$Si). ^{29}Si NMR (CH$_2$Cl$_2$, 59.6 MHz) -42.08 (decet, $^1J_{Si-H}$ = 212 Hz, SiPh$_2$H), −18.74 ppm (doublet, $^2J_{Si-H}$ = 6.4 Hz, Me$_3$Si). IR (THF): ν_{SiH} 2143 cm^{-1}.

[(Me$_3$SiC$\equiv$C−SiPh$_2$H)Co$_2$(CO)$_6$] (8). Analogously to the synthesis of **15**, Me$_3$SiC$\equiv$C−SiPh$_2$H (475 mg, 1.70 mmol) and dicobalt octacarbonyl (580 mg, 1.70 mmol) yielded **8** (0.796 g, 1.41 mmol; 83%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz): δ 7.45 (m, 4H, aromatic), 7.14 (m, 6H, aromatic), 0.30 (s, 9H, Me$_3$Si). ^{13}C NMR (CD$_2$Cl$_2$, 50.3 MHz): δ 200.6 (Co CO's); 135.3, 128.5 (*meta* and *ortho C's*); 134.5 (*ipso*); 130.6 (*para*); 1.1 (Me$_3$Si). ^{29}Si NMR (CH$_2$Cl$_2$): δ −17.9 (doublet, $^1J_{Si-H}$ = 252 Hz, Ph$_2$Si), 2.5 (decet, Me$_3$Si). IR (hexane): ν_{CO} 2020, 2050, 2087 cm^{-1}; ν_{SiH} 2145 cm^{-1}. Mass spectrum DEI *m/z* (%): 482 (5) [(M − 3CO)]$^+$, 454 (35) [(M − 4CO)]$^+$, 426 (80) [(M − 5CO)]$^+$, 398 (100) [(M − 6CO)]$^+$.

[(Me$_3$SiC$\equiv$C−SiPh$_2$H)Mo$_2$(CO)$_4$(C$_5$H$_5$)$_2$] (9). Me$_3$SiC$\equiv$C−SiPh$_2$H (1.4 g, 10 mmol) in dry THF (30 mL) was added dropwise *via* cannula to a freshly prepared solution of (C$_5$H$_5$)$_2$(CO)$_4$Mo$_2$ (4.40 g, 11 mmol) over 45 min. The solution was allowed to stir at room temperature for 24 h. After removal of the solvent, the residue was recrystallized from THF/hexane (2:1) to yield red crystals of **9** (5.57 g, 7.8 mmol; 78%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz): δ 7.25 (m, 10H, aromatic), 4.78 (s, 11H, C$_p$-H's and Si−H), 0.07 (s, 9H, Me$_3$Si). ^{13}C NMR (CD$_2$Cl$_2$, 50.3 MHz): δ 229.0 (Mo−CO's); 137.2 (*ipso*); 135.7, 128.1 (*meta* and *ortho C's*); 129.9 (*para*); 90.2 (C$_p$−C's); 3.5 (Me$_3$Si). ^{29}Si NMR (CH$_2$Cl$_2$, 59.6 MHz): δ 6.6 (decet, Me$_3$Si), −10.8 (doublet, $^1J_{Si-H}$ = 211 Hz, SiPh$_2$H). IR (hexane): ν_{CO} 1883, 1950, 1981 cm^{-1}; ν_{SiH} 2171 cm^{-1}.

X-ray Crystallography. X-ray crystallographic data were collected on a Siemens P4 diffractometer, equipped with a rotating anode and using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The background measurements were obtained by using a stationary crystal and stationary counter at the beginning and end of the scan time. The two compounds were solved by using the direct methods routine contained in the SHELXTL-Plus program library.[31] All hydrogen atoms for both structures, **9** and **15**, were found in the Fourier difference maps and were refined individually. The riding model of hydrogen atoms with fixed isotropic

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[31] Sheldrick, G. M. SHELXTLPC, Release 4.1; Siemens Crystallographic Research System: Madison, WI, 1990.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for 15

	x	*y*	*z*	*U*(eq)[a]
Co(1)	9128(1)	1177(1)	3815(1)	40(1)
Co(2)	10754(1)	1536(1)	4174(1)	39(1)
Si(1)	10793(1)	1880(1)	2918(1)	40(1)
Si(4)	9585(1)	4523(1)	3955(1)	49(1)
O(1)	10000	2269(3)	2500	49(1)
C(2)	10239(2)	1995(2)	3512(1)	36(1)
C(3)	9896(2)	2806(2)	3835(1)	36(1)
C(31)	11764(3)	3091(5)	2916(1)	76(1)
C(32)	11231(3)	211(4)	2810(1)	67(1)
C(41)	8839(4)	5086(4)	3433(2)	90(2)
C(42)	10700(3)	5487(4)	4012(2)	75(1)
C(43)	8922(3)	4630(4)	4522(2)	77(1)
C(11)	9241(2)	−495(3)	3625(1)	59(1)
C(12)	8512(2)	1115(3)	4376(1)	62(1)
C(13)	8135(2)	1656(3)	3437(1)	53(1)
C(21)	11198(2)	−106(3)	4104(1)	52(1)
C(22)	10457(2)	1682(3)	4800(1)	51(1)
C(23)	11858(2)	2391(3)	4212(1)	59(1)
O(11)	9314(2)	−1531(2)	3503(1)	101(1)
O(12)	8123(2)	1061(3)	4721(1)	103(1)
O(13)	7501(2)	1970(3)	3202(1)	86(1)
O(21)	11481(2)	−1124(2)	4063(1)	77(1)
O(22)	10283(2)	1783(3)	5194(1)	83(1)
O(23)	12556(12)	2932(3)	4245(1)	99(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

U values is employed for all solutions. The method of refinement was full-matrix least-squares in each case. The scattering factors were taken from ref 32. Crystallographic data are collected in Tables 1 through 3.

Molecular orbital calculations were performed *via* the extended Hückel method using weighted H_{ij} 's,[33] orbital drawings were obtained by use of the program CACAO.[34]

Acknowledgment. Financial support from NSERC Canada is gratefully acknowledged. We thank Dr. J. F. Britten for crystallographic advice, Dr. Richard Smith of the McMaster Regional Centre for Mass Spectrometry, and Dr. Carlo Mealli, CNR, Florence, Italy for providing the program CACAO.

Supplementary Material Available: Tables listing bond lengths, bond angles, positional parameters, and displacement coefficients for **9** and **15** (9 pages). Ordering information is given on any current masthead page.

OM940354X

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