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Routes to Ruthenium−Cobalt Clusters and Dicobalt Complexes with New Alkoxysilyl- or Sulfur-Functionalized Alkynes. X-ray Structures of $[NEt_4][RuCo_3(CO)_{10}\{\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3\}]$ and $[Co_2(CO)_6\{\mu_2\text{-}\eta^2\text{-}HC_2CH_2NHC(O)NH(CH_2)_3Si(OEt)_3\}]$

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Two general approaches are presented and compared to covalently link metal clusters to alkynes terminated with a trialkoxysilyl or a thioether group. They consist in the direct reaction of the functional alkyne with the cluster or in the functionalization of an alkyne already coordinated to the cluster. These are applied to the tetrahedral mixed-metal cluster $[NEt_4][RuCo_3(CO)_{12}]$ ($NEt_4\cdot\mathbf{1}$). Complexes with the new alkynes $HC{\equiv}C(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3$ ($\mathbf{L^1}$), $HC{\equiv}CCH_2NHC(O)NH(CH_2)_3Si(OEt)_3$ ($\mathbf{L^2}$), and $HC{\equiv}CCH_2NHC(O)NHC_6H_4SMe$ ($\mathbf{L^3}$) have been characterized, and the crystal structures of $[NEt_4][RuCo_3(CO)_{10}\{\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3\}]$ ($NEt_4\cdot\mathbf{2a}$) and $[Co_2(CO)_6\{\mu_2\text{-}\eta^2\text{-}HC_2CH_2NHC(O)NH(CH_2)_3Si(OEt)_3\}]$ (**9**) have been determined by X-ray diffraction.

Introduction

The current interest in stable functional metal clusters that could be subsequently covalently anchored onto surfaces or act as precursors to new cluster-derived nanomaterials has led us to consider the use of alkynes as a way to introduce the desired functionality, such as a $-Si(OR)_3$ group, owing to its ability to condense with surface OH groups of inorganic supports and to form sol−gel materials,[1] or a thiol or thioether for, for example, the formation of organized monolayers on gold surfaces.[2] Indeed, reactions of alkynes with carbonyl-metal clusters afford a considerable diversity of structural types and bond activation processes,[3] and the stability of the products is largely due to the formation of covalent metal−carbon bonds, usually involving a triangular or rectangular face of the metal polyhedron. If one considers the large family of tetrahedral metal clusters, the products generally obtained are of the butterfly type, with the organic fragment interacting with the metals in a μ_4-η^2-bonding mode.[3,4] Alternatively, these clusters may be viewed as having a *closo* structure in which the two carbon atoms originating from the alkyne are part of the skeleton. The stability of the metal−carbon σ bonds explains that subsequent reactions may occur by breaking of metal−metal bond(s) and partial cluster fragmentation rather than by splitting of the organic moiety.[5]

Covalent linking rather than dative bonding of a functional ligand to a metal cluster represents a significant advantage to avoid leaching phenomena and is also gaining increasing attention in heterogeneous catalysis.[6] Two strategies may be envisaged to link covalently a metal cluster to a functional alkyne: either by the reaction of a metal cluster with the desired functional alkyne (route A_2 in Scheme 1) or by the functionalization of an organic backbone already linked to the metal cluster (route B_2 in Scheme 1).

It is not obvious that both methods may be used indiscriminately, but if they can, a comparative study of their respective advantages/disadvantages should be particularly instructive. In all cases, the chemo- and regioselectivity of the reactions represent central issues to be investigated. A prerequisite in approach *A* is that the functional group *-FG* will not compete with the alkyne in the reaction with the cluster (A_2). Approach

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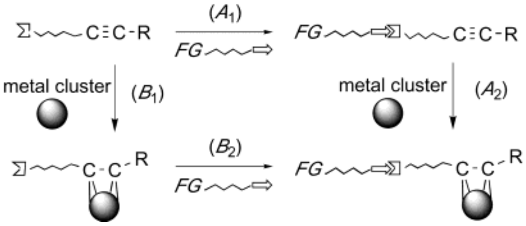
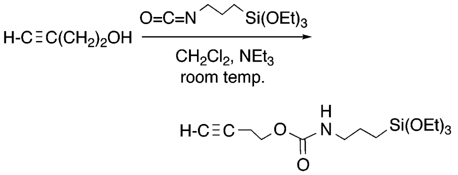
Scheme 1. General Approaches for the Incorporation of Functional Alkynes into Metal Clusters, *FG* = −Si(OR)$_3$ or −SR



B offers the potential of using a larger diversity of organic substituents but requires that the first step (B_1), i.e., the binding of the alkyne to the cluster, occur with maximum selectivity and efficiency. It also requires that at least one intact organic function remain available for further transformation (B_2). It appeared to us that, to the best of our knowledge, strategy *B* has not been previously applied to cluster chemistry. We decided to explore and compare these two approaches, using the mixed-metal cluster $[RuCo_3(CO)_{12}]^-$ (**1**) as precursor (as NEt_4^+ salt throughout). This cluster is known to react with alkynes[5,7] and offers the advantage over the related $[Co_4(CO)_{12}]$ to allow a study of the metalloselectivity of the reaction.

Results and Discussion

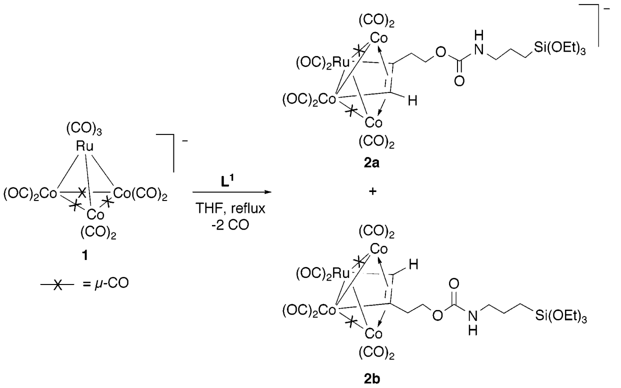
The new alkyne $\mathbf{L^1}$ was prepared in high yield by condensation of 3-butyn-1-ol and 3-(triethoxysilyl)propylisocyanate in the presence of triethylamine (eq 1). It was characterized by ^1H, ^{13}C, and ^{29}Si NMR and IR spectroscopy (see Experimental Section).



(1)

$\mathbf{L^1}$

Reaction of $\mathbf{L^1}$ with **1** afforded cluster **2** by selective alkyne insertion into a Co−Co bond (eq 2). Its ^1H NMR spectrum contains two singlets for the alkyne CH proton at δ 8.74 and 8.27, indicating that two isomers **2a**/**2b** have been formed, in a 3:2 ratio, which differ in the orientation of the alkyne with respect to the Co−Ru hinge but could not be separated by column chromatography. Formation of such isomers is not uncommon in mixed-metal clusters, but the stereoelectronic factors that govern their ratio are not yet clear.[8] On the basis of experiments carried out with related $RuCo_3$ clusters bearing the alkyne HC≡CMe(=CH$_2$),[9] we suggest that the more deshielded ^1H NMR signal should be assigned to the Co-bound CH proton. The cluster identified by X-ray diffraction, **2a**, has the CH group attached to Co (Figure 1). The main bonding parameters in this 60-electron cluster are given in the caption of Figure 1 and are comparable to those in related molecules.[3,5] The four metal atoms form a butterfly skeleton where the ruthenium atom occupies a hinge position. The alkyne is coordinated to the concave side such that the C−C bond is parallel to the hinge of the butterfly. It coordinates to all metal atoms in a μ_4-η^2-mode, leading to a distorted *closo* $RuCo_3C_2$ octahedral framework with 7 skeletal electron pairs. For comparison, we explored the pos-



(2)

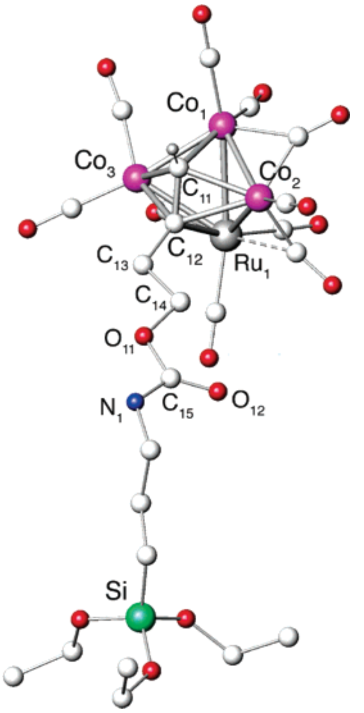


Figure 1. View of the molecular structure of the anionic cluster in NEt$_4$·**2a**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms have been placed mathematically except for H(11). Selected bond lengths (Å) and angles (deg): Ru(1)−Co(1) = 2.745(2), Ru(1)−Co(2) = 2.557(2), Ru(1)−Co(3) = 2.5240(19), Ru(1)−C(12) = 2.160(10), Co(1)−Co(2) = 2.464(2), Co(1)−Co(3) = 2.449(2), Co(1)−C(11) = 1.985(10), Co(2)···Co(3) = 3.560, Co(2)−C(11) = 2.091(10), Co(2)−C(12) = 2.048(9), Co(3)−C(11) = 2.073(11), Co(3)−C(12) = 2.170(10), C(11)−C(12) = 1.378; Co(2)−Ru(1)−Co(1) = 55.25(6), Co(3)−Ru(1)−Co(1) = 55.21(5), Co(2)−Co(1)−Ru(1) = 57.81(6), Co(3)−Co(1)−Ru(1) = 58.51(7), Co(1)−Co(3)−Ru(1) = 66.98(6). Dihedral angle between the wings = 117°. The carbonyl ligand C(8)O(8) conforms to the semibridging category of Crabtree−Lavin.[10]

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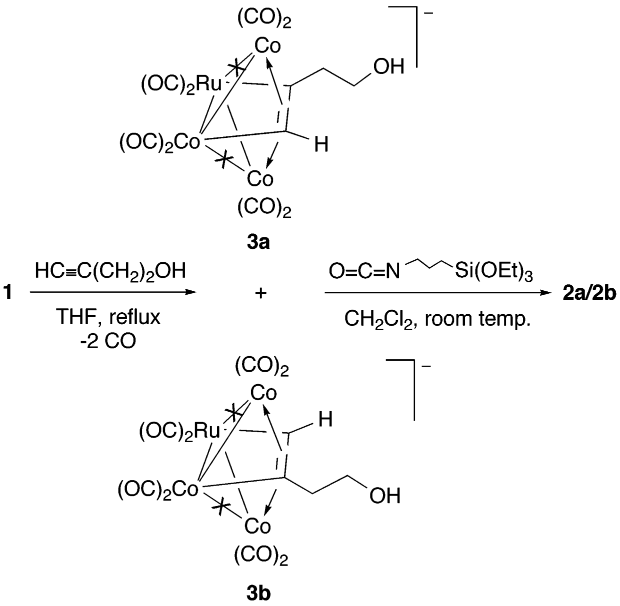
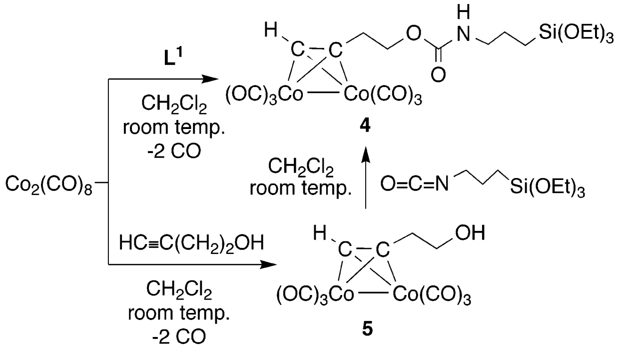
Scheme 2



Scheme 3. Alternative Procedures for the Synthesis of 4

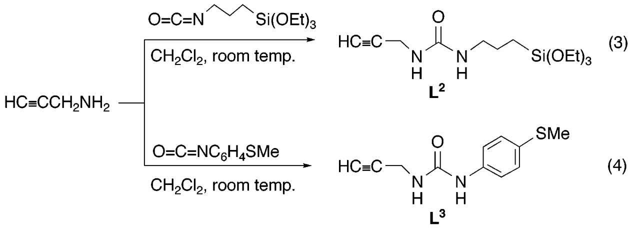


sibility of obtaining **2** following strategy *B* in Scheme 1 and thus first reacted **1** with 3-butyn-1-ol (Scheme 2). This afforded the new cluster $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2OH]^-$ (**3**), and again two ^{1}H NMR CH resonances were observed, at δ 8.74 and 8.25 in a 5:1 ratio, for isomers **3a**/**3b**.

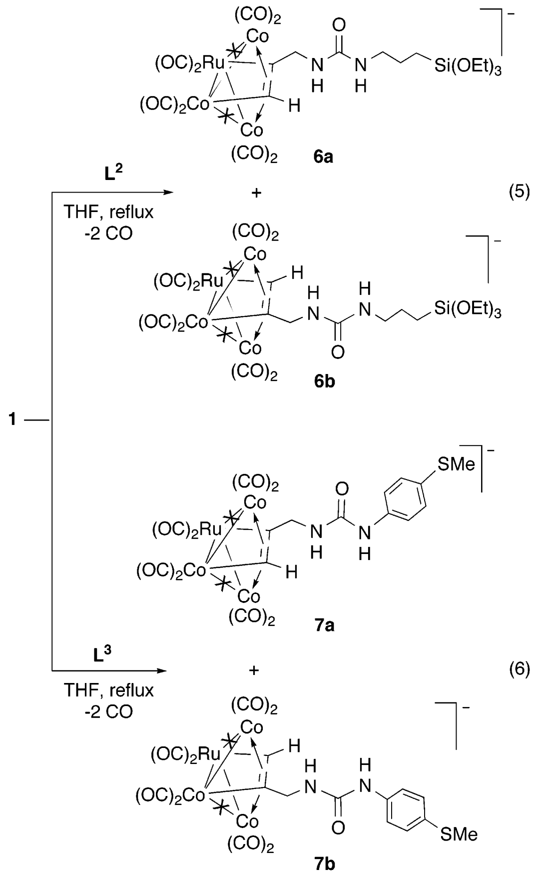
These clusters were then reacted with 3-(triethoxysilyl)propylisocyanate (route B_2) to afford the corresponding isomeric clusters **2a** and **2b** in a 5:1 ratio (Scheme 2). Interestingly, the reaction proceeded without the need for additional triethylamine, in contrast to the synthesis of $\mathbf{L^1}$. Although addition of NEt_3 may increase the rate of condensation, it also leads to some decomposition of the precursor cluster. Owing to the ionic nature of these clusters, it is difficult to monitor the progress of the reaction by TLC. Furthermore, clusters **2** and **3** are both violet. IR spectroscopy indicates the formation of the product, which has a characteristic ν(C=O) absorption at 1720 cm^{-1}, but does not indicate if the reaction has reached completion. The reaction mixture was therefore stirred for 2 days at room temperature.

For comparison and in order to better characterize coordinated $\mathbf{L^1}$, the latter was reacted with $[Co_2(CO)_8]$, and complex **4** was obtained in high yield (Scheme 3). The latter was also obtained, in comparable yield, when strategy *B* was followed. First, $[Co_2(CO)_8]$ was reacted with 3-butyn-1-ol to give **5**, which was then reacted with 3-(triethoxysilyl)propylisocyanate to afford **4** (Scheme 3). Interestingly, **4** was obtained even in the absence of triethylamine, but the reaction is more rapid if the latter is used.

We then examined the behavior of alkynes carrying an amine instead of an alcohol function. The new alkynes $\mathbf{L^2}$ and $\mathbf{L^3}$ were prepared in quantitative yield by condensation of propargylamine with a functional isocyanate[11] (route A_1, eqs 3, 4) and reacted with **1**



(route A_2). This afforded clusters **6a/6b** in a 5:1 ratio and **7a/7b** in 2:1 ratio, respectively (eqs 5, 6).



For comparison, we reacted **1** with propargylamine (Scheme 4). This afforded two isomeric clusters, **8a** and **8b**, in 88% yield (route B_1). These clusters were characterized by IR and ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the isomeric mixture **8a/8b** contains two singlets at δ 8.72 and 8.41 in a 2:1 ratio, respectively, for the alkyne CH proton. These clusters were too unstable to be stored for a prolonged period of time and

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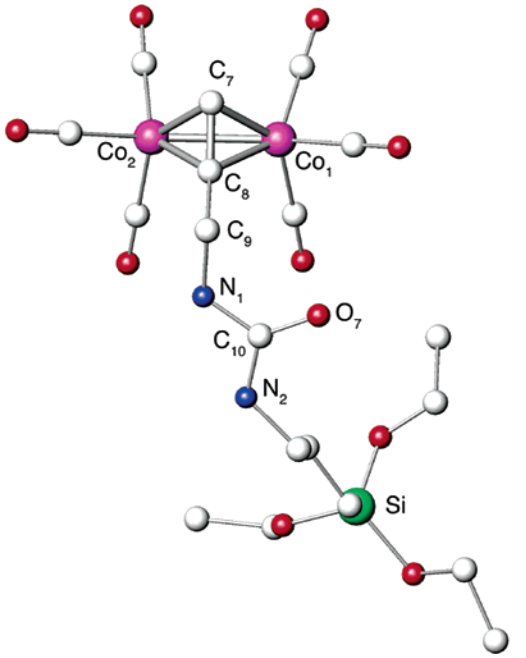
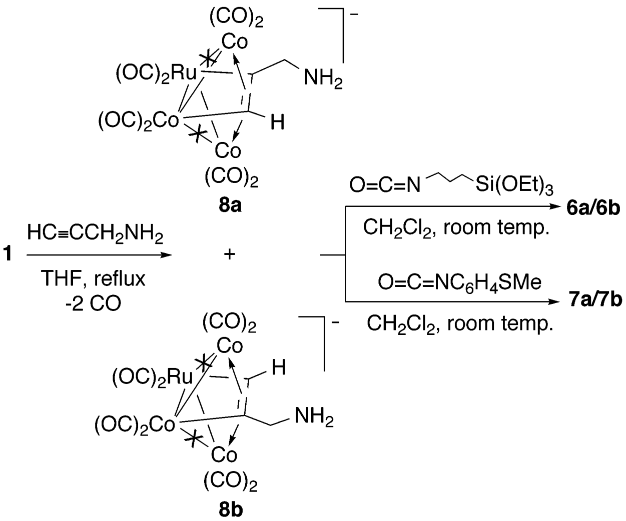


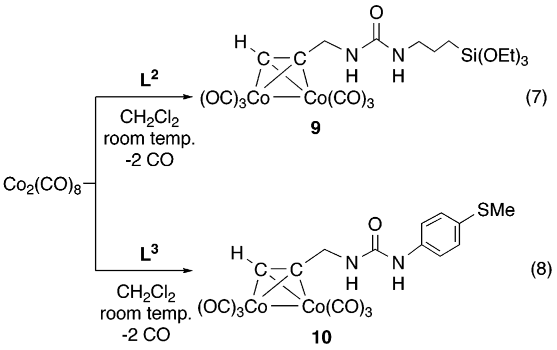
Figure 2. View of the molecular structure of **9** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Co(1)–Co(2) = 2.474(1), Co(1)–C(7) = 1.956(6), Co(1)–C(8) = 1.970(6), Co(2)–C(7) = 1.949(6), Co(2)–C(8) = 1.963(6), C(7)–C(8) = 1.323(8); C(7)–Co(1)–C(8) = 39.4(2), C(7)–Co(2)–C(8) = 39.5(2), Co(1)–C(7)–Co(2) = 78.6(2), Co(1)–C(8)–Co(2) = 78.0(2).

Scheme 4



were reacted immediately with 3-(triethoxysilyl)propylisocyanate (route *B*$_2$). This afforded the corresponding isomeric clusters **6a** and **6b** in a 1:2 ratio (Scheme 4). Similarly, their reaction with 4-(methylthio)phenylisocyanate yielded **7a** and **7b**, in a 2:1 ratio. Method *A* gave a better yield of functional cluster compared to *B* owing to the limited stability of the intermediate clusters **8**.

Since single crystals of the functionalized cluster **6** or **7** could not be obtained, we reacted $\mathbf{L^2}$ and $\mathbf{L^3}$ with $[Co_2(CO)_8]$ in order to better characterize the new, coordinated alkynes and obtained **9** and **10**, respectively (eqs 7, 8). Interestingly, these two complexes could not be obtained according to method *B* since propargylamine reacts with $[Co_2(CO)_8]$ to give $[\{Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}HC{\equiv}CCH_2NH\}_2CO]$.[12] Complex **9** was characterized by X-ray diffraction (Figure 2) and shows the usual Co_2C_2 tetrahedral core.[13] The $-Si(OEt)_3$ group appears sterically unhindered, which is promising for further condensation reactions using the dicobalt or the cluster complexes, and such studies are in progress.



In conclusion, we have examined and compared two complementary approaches to covalently link dinuclear complexes and metal clusters to functional alkynes terminated with an alkoxysilyl or a thioether function. The strategies depicted in Scheme 1 should be rather general and since they are not necessarily interchangeable, they should be useful in providing different potential access to a given class of functional clusters. Their use as precursors in materials science is the subject of ongoing work.

Experimental Section

All reactions and manipulations were carried out under an inert atmosphere of purified nitrogen using standard Schlenk tube techniques. Solvents were dried and distilled under nitrogen before use: hexane, pentane, and tetrahydrofuran over sodium-benzophenone, dichloromethane over phosphorus pentoxide. Nitrogen (Air Liquide, R-grade) was passed through BASF R3-11 catalyst and molecular sieves columns to remove residual oxygen and water. Elemental C, H, N, and S analyses were performed by the Service de Microanalyses du CNRS (ULP Strasbourg). Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. The ^1H NMR spectra were recorded at 300.13 MHz, $^{13}C\{^1H\}$ NMR spectra at 75.48 or 100.62 MHz, and $^{29}Si\{^1H\}$ at 79.48 MHz on a Bruker AC300, AVANCE 300 or AVANCE 400 instrument. The ratios between the isomeric clusters **a** and **b** determined from the alkyne CH resonance may not always represent the situation at thermodynamic equilibrium.

Synthesis of $\mathbf{HC{\equiv}C(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3}$ ($\mathbf{L^1}$). To a solution of 3-butyn-1-ol (19.75 mmol, 1.5 mL) and dry triethylamine (17.85 mmol, 2.35 mL) in 10 mL of CH_2Cl_2, cooled in an ice bath, was added dropwise a solution of 3-(triethoxysilyl)propylisocyanate (4.45 mL, 17.85 mmol) in 5 mL of CH_2Cl_2. After stirring overnight at room temperature, the resulting solution was filtered, and the excess of 3-butyn-1-ol and the solvent were evaporated under reduced pressure

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to afford **L^1** as a colorless liquid (5.27 g, 16.60 mmol, 93%). IR (CH_2Cl_2, cm^{-1}): 3304 (s, $\nu_{\equiv CH}$), 2274 (vs, $\nu_{C\equiv C}$), 1720 (vs, $\nu_{C=O}$), and 1517 (vs, δ_{NH}). ^1H NMR ($CDCl_3$): δ 0.53 (m, 2H, $SiCH_2$), 1.12 (t, $^3J(HH) = 7$ Hz, 9H, CH_3), 1.52 (m, 2H, $CH_2CH_2CH_2$), 1.92 (t, $^4J(HH) = 2.74$ Hz, 1H, $HC\equiv$), 2.41 (dt, $^3J(HH) = 7$ Hz, $^4J(HH) = 2.74$ Hz, 2H, $\equiv CCH_2$), 3.06 (m, 2H, NCH_2), 3.72 (q, $^3J(HH) = 7$ Hz, 6H, OCH_2CH_3), 4.05 (t, $^3J(HH) = 7$ Hz, 2H, OCH_2), 5.27 (br, NH). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ 7.46 (s, $SiCH_2$), 18.16 (s, OCH_2CH_3), 19.32 (s, $CH_2CH_2CH_2$), 23.13 (s, $\equiv CCH_2$), 42.84 (s, NCH_2), 58.34 (s, OCH_2CH_3), 62.54 (s, OCH_2), 69.58 (s, $HC\equiv C$), 80.38 (s, $HC\equiv C$), 156.07 (s, C=O). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −45.93.

Synthesis of $HC\equiv CCH_2NHC(O)NH(CH_2)_3Si(OEt)_3$ (L^2). A solution of 3-(triethoxysilyl)propylisocyanate (1.64 g, 1.66 mL, 6.65 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a solution of propargylamine (7.32 mmol, 0.50 mL) in 15 mL of CH_2Cl_2, cooled in an ice bath. After stirring overnight at room temperature, the solvent was evaporated under vacuum and the product was quantitatively obtained as a pale yellow solid (2.00 g, 6.61 mmol). IR (KBr, cm^{-1}): 3332 (s, $\nu_{\equiv CH}$), 1624 (vs, $\nu_{C=O}$), and 1586 (vs, δ_{NH}). ^1H NMR ($CDCl_3$): δ 0.58 (m, 2H, $SiCH_2$), 1.11 (t, 9H, $^3J(HH) = 7$ Hz, CH_3), 1.56 (quint, 2H, $^3J(HH) = 7$ Hz, $CH_2CH_2CH_2$), 2.17 (t, $^4J(HH) = 2.5$ Hz, 1H, $\equiv CH$), 3.11 (q, $^3J(HH) = 7$ Hz, 2H, NCH_2CH_2), 3.75 (q, $^3J(HH) = 7$ Hz, 6H, OCH_2), 3.90 (dd, $^3J(HH) = 5.8$ Hz, $^4J(HH) = 2.5$ Hz, 2H, $\equiv CCH_2N$), 5.48 (br t, $^3J(HH) = 5.8$ Hz, 1H, CH_2CH_2NH), 5.64 (br t, $^3J(HH) = 5.8$ Hz, 1H, $\equiv CCH_2NH$). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ 7.62 (s, $SiCH_2$), 18.10 (s, CH_3), 23.26 (s, $CH_2CH_2CH_2$), 29.92 ($\equiv CCH_2N$), 42.90 (s, NCH_2CH_2), 58.61 (s, OCH_2), 70.79 (s, $HC\equiv$), 81.13 (s, $HC\equiv C-$), 158.3 (C=O). $^{29}Si\{^1H\}$ NMR (79.48 MHz, $CDCl_3$): δ −45.5. Anal. Calcd for $C_{13}H_{26}N_2O_4Si$: C, 51.63; H, 8.66; N, 9.26. Found: C, 50.95; H, 8.66; N, 9.24.

Synthesis of $HC\equiv CCH_2NHC(O)NHC_6H_4SMe$ (L^3). A solution of 4-(methylthio)phenylisocyanate (0.93 mL, 6.65 mmol) in 15 mL of CH_2Cl_2 was added dropwise to a solution of propargylamine (0.50 mL, 7.32 mmol) in 15 mL of CH_2Cl_2 placed at 0 °C. The solution was stirred at room temperature overnight, and the product was obtained quantitatively as a white powder that is scarcely soluble in CH_2Cl_2 (1.46 g, 6.65 mmol). IR (KBr, cm^{-1}): 3320 (s, $\nu_{\equiv CH}$), 1629 (vs, $\nu_{C=O}$) and 1586 (vs, δ_{NH}). ^1H NMR (acetone-d_6): δ 2.40 (s, 3H, CH_3), 2.61 (t, $^4J(HH) = 2.55$ Hz, 1H, $\equiv CH$), 3.98 (dd, $^4J(HH) = 2.55$ Hz, $^3J(HH) = 7$ Hz, 2H, CH_2N), 6.04 (m, 1H, CH_2NH), 7.17 and 7.44 (AA′BB′ spin system, 4H, C_6H_4), 8.05 (br s, 1H, C_6H_4NH). $^{13}C\{^1H\}$ NMR (75.48 MHz, acetone-d_6): δ 16.06 (s, CH_3), 29.16 (s, $\equiv CCH_2N$), 70.87 (s, $HC\equiv$), 81.0 (s, $HC\equiv C-$), 118.92 and 128.24 (2s, CH of C_6H_4), 131.0 and 138.0 (2s, C_{quater} of C_6H_4), 158.0 (s, C=O). Anal. Calcd for $C_{11}H_{12}N_2OS$: C, 59.98; H, 5.49; N, 12.72; S, 14.55. Found: C, 59.61; H, 5.41; N, 12.83; S, 14.53.

$[NEt_4][RuCo_3(CO)_{10}\{\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3\}]$ ($NEt_4{\cdot}2$). Procedure A: Reaction of $[NEt_4][RuCo_3(CO)_{12}]$ with $HC\equiv C(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3$. A solution of $NEt_4{\cdot}$**1** (0.174 g, 0.235 mmol) and **L^1** (0.092 g, 0.282 mmol) was refluxed in 40 mL of THF for 6 h. The solution was filtered and the solvent was removed under vacuum. Violet crystals of $NEt_4{\cdot}$**2** (0.158 g, 0.157 mmol, 67%) were obtained by recrystallization of the product from CH_2Cl_2/pentane. IR (CH_2Cl_2, cm^{-1}): 2048 (mw), 2002 (vs), 1970 (sh), 1814 (m) $\nu_{C\equiv O}$, 1720 (m, $\nu_{C=O}$). ^1H NMR ($CDCl_3$): δ 0.60 (m, 2H, $SiCH_2$), 1.21 (m, 12H, NCH_2CH_3), 1.33 (m, 9H, OCH_2CH_3), 1.54 (m, 2H, $CH_2CH_2CH_2$), 2.74 (m, 2H, HC_2CH_2), 3.20 (m, 10H, NCH_2CH_3 and $HNCH_2$), 3.90 (m, 8H, OCH_2CH_3 and CH_2CH_2O), 4.81 (br, NH), 8.27 (br s, 0.40H, HC_2 of one isomer), 8.74 (br s, 0.60H, HC_2 of the other isomer). Anal. Calcd for $C_{32}H_{47}Co_3N_2O_{15}RuSi$: C, 38.22; H, 4.71; N, 2.79. Found: C, 37.59; H, 4.55; N, 2.73.

Procedure B: Reaction of $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2OH)]$ ($NEt_4{\cdot}3$) (see below) with $OCN(CH_2)_3Si(OEt)_3$. To a solution of $NEt_4{\cdot}$**3** (0.100 g, 0.132 mmol) in 15 mL CH_2Cl_2 was added dropwise 3-(triethoxysilyl)propylisocyanate (0.148 mmol, 0.037 mL). The mixture was stirred at room temperature for 2 days. The solution was filtered through Celite and concentrated. Violet crystals of $NEt_4{\cdot}$**2** (0.065 g, 0.065 mmol, 48%) were obtained after recrystallizing twice the product from CH_2Cl_2/pentane. When this procedure was followed, the ratio between isomers **2a** and **2b** was 5:1.

Synthesis of $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2OH)]$ ($NEt_4{\cdot}3$). Using a procedure similar to that described for $NEt_4{\cdot}$**2**, $NEt_4{\cdot}$**1** (0.223 g, 0.301 mmol) and 3-butyn-1-ol (0.105 g, 1.50 mmol, 0.114 mL) were refluxed in 50 mL of THF for 5 h. After workup, $NEt_4{\cdot}$**3** (0.200 g, 0.264 mmol, 87%) was obtained as dark violet crystals by recrystallization from CH_2Cl_2/hexane. IR (CH_2Cl_2, ν(CO), cm^{-1}): 2049 (m), 2003 (vs), 1970 (sh), 1819 (m). ^1H NMR ($CDCl_3$): δ 1.37 (m, 12H, CH_3), 1.51 (br, OH), 2.72 (m, 2H, HC_2CH_2), 3.26 (m, 8H, NCH_2), 3.44 (m, 2H, OCH_2), 8.25 (br s, 0.16H, HC_2 of one isomer), 8.74 (br s, 0.84H, HC_2 of the other isomer). Anal. Calcd for $C_{22}H_{26}Co_3NO_{11}Ru{\cdot}1/2H_2O$: C, 33.75; H, 3.40; N, 1.75, Found: C, 33.57; H, 3.41; N, 1.75.

Synthesis of $[Co_2(CO)_6\{\mu_2\text{-}\eta^2\text{-}HC_2(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3\}]$ (4). Procedure A: Reaction of $[Co_2(CO)_8]$ with L^1. A solution of $[Co_2(CO)_8]$ (0.387 g, 1.140 mmol) in 30 mL of CH_2Cl_2 and **L^1** (0.522 g, 1.60 mmol) was stirred at room temperature for 3 h. Completion of the reaction was revealed from TLC by the disappearance of $[Co_2(CO)_8]$. The solvent was then removed under vacuum. Extraction with hexane afforded red viscous compound **4** (0.626 g, 1.04 mmol, 91%). IR (hexane, cm^{-1}): 2098 (vs), 2063 (vs), 2029 (vs), 1979 (w), ν(C≡O) and 1740 (vs), ν(C=O). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.61 (m, 2H, $SiCH_2$), 1.21 (t, $^3J(HH) = 7.5$ Hz, 9H, CH_3), 1.63 (m, 2H, $CH_2CH_2CH_2$), 3.16 (m, 4H, $HNCH_2CH_2$ and HC_2CH_2,), 3.81 (q, $^3J(HH) = 7.5$ Hz, 6H, OCH_2CH_3), 4.12 (t, $^3J(HH) = 6.15$ Hz, 2H, OCH_2CH_2), 4.89 (br, NH), 6.02 (s, 1H, H−C−Co). In benzene-d_6, the ^1H NMR signals for $HNCH_2CH_2$ and HC_2CH_2 were separated: 2.74 (HC_2CH_2), 3.16 ($HNCH_2CH_2$).

Procedure B: Reaction of $[Co_2(CO)_6\{\mu_2\text{-}\eta^2\text{-}HC_2(CH_2)_2OH\}]$ (5) (see below) with $OCN(CH_2)_3Si(OEt)_3$. Synthesis of $[Co_2(CO)_6\{\mu_2\text{-}\eta^2\text{-}HC_2(CH_2)_2OH\}]$ (5). A solution of $[Co_2(CO)_8]$ (0.325 g, 0.954 mmol) in 25 mL of CH_2Cl_2 and 3-butyn-1-ol (0.079 mL, 1.05 mmol) was stirred at room temperature for 2 h. Completion of the reaction was revealed from TLC by the disappearance of $[Co_2(CO)_8]$. The solvent was then removed under vacuum. Extraction with hexane afforded red viscous compound **5** (0.304 g, 0.854 mmol, 89%). IR (hexane, ν(CO), cm^{-1}): 2098 (vs), 2053 (vs), 2029 (vs), 1980 (w). ^1H NMR ($CDCl_3$): δ 1.58 (br, OH), 3.11 (t, $^3J(HH) = 6.5$ Hz, 2H, HC_2CH_2), 3.90 (m, 2H, OCH_2), 6.02 (s, 1H, H−C−Co).

To a solution of **5** (0.092 g, 0.258 mmol) was then added dropwise 3-(triethoxysilyl)propylisocyanate (0.071 mL, 0.284 mmol). The solution was stirred at room temperature for 11 h. Completion of the reaction was revealed from TLC by the disappearance of **5** (eluent CH_2Cl_2). The solvent was removed under vacuum. Extraction with hexane afforded red viscous compound **4** (0.144 g, 0.240 mmol, 93%).

Synthesis of $[NEt_4][RuCo_3(CO)_{10}\{\mu_4\text{-}\eta^2\text{-}HC_2CH_2NHC(O)NH(CH_2)_3Si(OEt)_3\}]$ ($NEt_4{\cdot}6$). Procedure A: Reaction of $[NEt_4][RuCo_3(CO)_{12}]$ with $HC\equiv CCH_2NHC(O)NH(CH_2)_3Si(OEt)_3$. A solution of $NEt_4{\cdot}$**1** (0.253 g, 0.341 mmol) and **L^2** (0.114 g, 0.377 mmol) was refluxed in 50 mL of THF for 6 h. The solution was filtered and the solvent was removed under reduced pressure. The product was recrystallized twice from CH_2Cl_2/pentane to afford a violet powder of $NEt_4{\cdot}$**6** (0.277 g, 0.279 mmol, 82%). IR (CH_2Cl_2, ν(CO), cm^{-1}): 2050 (m), 2005 (vs), 1970 (s), 1820 (m), 1671 (m, C=O). ^1H NMR ($CDCl_3$): δ 0.63 (m, 2H, $SiCH_2$), 1.22 (m, 21H, OCH_2CH_3 and NCH_2CH_3), 1.60 (m, 2H, $CH_2CH_2CH_2$), 3.13 (m, 2H, $HNCH_2CH_2$), 3.8 (m, 16H, OCH_2CH_3, NCH_2CH_3 and $HNCH_2C_2H$), 4.41 (m, 1H, NH), 4.64 (m, 1H, NH), 8.24 (br s, 0.16H, HC_2- of one isomer), 8.67 (br s, 0.84H, HC_2- of the second isomer). Anal. Calcd for $C_{31}H_{46}Co_3N_3O_{14}RuSi-2CH_2Cl_2$: C, 34.15; H, 4.34; N, 3.62. Found: C, 33.85; H, 4.43; N, 3.99.

Procedure B: Reaction of $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2CH_2NH_2)]$ with $OCN(CH_2)_3Si(OEt)_3$. To a solution of NEt_4·**8**, prepared by reaction of NEt_4·**1** (0.140 g, 0.188 mmol) with propargylamine (0.052 mL, 0.756 mmol) in 35 mL of CH_2Cl_2 at 0 °C, was added dropwise 0.053 mL (0.215 mmol) of 3-(triethoxysilyl)propylisocyanate. The solution was stirred at room temperature for 24 h, filtered, and concentrated, and the product was recrystallized from CH_2Cl_2/hexane to give NEt_4·**6** (0.069 g, 0.070 mmol, 37% based on NEt_4·**1**). When this procedure was followed, the ratio between isomers **6a** and **6b** was 1:2.

Synthesis of $[NEt_4][RuCo_3(CO)_{10}\{\mu_4\text{-}\eta^2\text{-}HC_2CH_2NHC(O)NHC_6H_4SMe\}]$ (NEt_4·7). Procedure A: Reaction of $[NEt_4][RuCo_3(CO)_{12}]$ with $HC{\equiv}CCH_2NHC(O)NHC_6H_4SMe$. A solution of NEt_4·**1** (0.146 g, 0.197 mmol) and **L^3** (0.173 g, 0.787 mmol) was refluxed in 35 mL of THF for 5 h. After filtration through Celite, evaporation to dryness, extraction of the product with CH_2Cl_2, and recrystallization from CH_2Cl_2/hexane afforded NEt_4·**7** (0.168 g, 0.185 mmol, 94%) as a violet powder. IR (CH_2Cl_2, ν(CO), cm^{-1}): 2051 (m), 2006 (vs), 1972 (s), 1820 (m), 1702 (m, $\nu_{C=O}$). ^{1}H NMR (acetone-d_6): δ 1.32 (m, 12H, $CH_2C\mathit{H}_3$), 2.39 (s, 3H, SCH_3), 3.34 (m, 8H, $C\mathit{H}_2CH_3$), 3.91 (s, 2H, $C\mathit{H}_2NH$), 5.45 (m, 1H, $CH_2N\mathit{H}$), 5.60 (m, 1H, $C_6H_4N\mathit{H}$), 7.16 and 7.42 (AA′BB′ spin system, 4H, C_6H_4), 8.08 (br s, 0.33H, HC_2− of one isomer), 8.75 (br s, 0.66H, HC_2− of the second isomer). Anal. Calcd for $C_{33}H_{32}Co_3N_3O_{11}RuS$: C, 41.44; H, 3.37; N, 4.39; S, 3.35. Found: C, 41.74; H, 3.84; N, 4.76; S, 3.84.

Procedure B: Reaction of $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2CH_2NH_2)]$ with $OCNC_6H_4SMe$. To a CH_2Cl_2 solution of NEt_4·**8** prepared by reaction of NEt_4·**1** (0.111 g, 0.150 mmol) with propargylamine (0.041 mL, 0.6 mmol) was added dropwise at 0 °C 0.15 mmol (0.021 mL) of $OCNC_6H_4SMe$. After stirring for 24 h at room temperature, the solution was filtered through Celite, concentrated, and recrystallized from CH_2Cl_2/hexane to give violet crystals of NEt_4·**7** (0.057 g, 0.063 mmol, 42% based on NEt_4·**1**).

Synthesis of $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2CH_2NH_2)]$ (NEt_4·8). Propargylamine (1.286 mmol, 0.088 mL) was added to a solution of $[NEt_4][RuCo_3(CO)_{12}]$ (0.238 g, 0.321 mmol) in 50 mL of THF. The mixture was heated under reflux for 5 h. After cooling, the solution was filtered and the solvent and the propargylamine in excess were evaporated under vacuum. Extraction with CH_2Cl_2 afforded NEt_4·**8** (0.210 g, 0.282 mmol, 88%). This cluster decomposes even under N_2 and should be used immediately. IR (CH_2Cl_2, ν(CO), cm^{-1}): 2048 (m), 2002 (vs), 1969 (s), 1889 (m, $Co(CO)_4^-$ resulting from decomposition), 1819 (m). ^{1}H NMR (CD_2Cl_2): δ 1.32 (m, 12H, CH_3), 1.67 (m, 2H, NH_2), 2.33 (m, 2H, $C\mathit{H}_2NH_2$), 3.20 (m, 8H, $NC\mathit{H}_2CH_3$), 8.41 (br s, 0.33H, HC_2) of one isomer), 8.72 (br s, 0.66H, HC_2 of the second isomer).

Synthesis of $[Co_2(CO)_6\{\mu_2\text{-}\eta^2\text{-}HC_2CH_2NHC(O)NH(CH_2)_3Si(OEt)_3\}]$ (9). A mixture of $[Co_2(CO)_8]$ (0.350 g, 1.028 mmol) and **L^2** (0.342 g, 1.131 mmol) in 35 mL of CH_2Cl_2 was allowed to react at room temperature for 2 h. A color change from brown to red was observed, and monitoring by TLC showed the disappearance of the starting complex. After filtration, the solvent was removed and the product was extracted with a mixture of hexane/CH_2Cl_2 (90:10) and placed at −20 °C to give red prismatic crystals (0.54 g, 0.918 mmol, 90%). IR (CH_2Cl_2, ν(CO), cm^{-1}): 2094 (vs), 2052 (vs), 2026 (vs), 1679 (m, $\nu_{C=O}$). ^{1}H NMR ($CDCl_3$): δ 0.62 (m, $SiCH_2$), 1.21 (t, ^3J(HH) = 7 Hz, 9H, CH_3), 1.61 (quint, ^3J(HH) = 7.4 Hz, 2H, $CH_2C\mathit{H}_2CH_2$), 3.16 (q, ^3J(HH) = 6.82 Hz, 2H, $NC\mathit{H}_2CH_2$), 3.82 (q, ^3J(HH) = 7 Hz, 6H, OCH_2), 4.54 (d, ^3J(HH) = 6 Hz, 2H, $\equiv CC\mathit{H}_2N$), 4.63 (br t, ^3J(HH) ≈ 6 Hz, 1H, NH), 4.76 (br t, ^3J(HH) ≈ 6 Hz, 1H, NH), 6.06 (s, 1H, HC−Co). Anal. Calcd for $C_{19}H_{26}Co_2N_2O_{10}Si$: C, 38.79; H,4.45; N, 4.76, Found: C, 38.49; H, 4.30; N,4.61.

Synthesis of $[Co_2(CO)_6\{\mu_2\text{-}\eta^2\text{-}HC_2CH_2NHC(O)NHC_6H_4\text{-}SMe)\}]$ (10). The ligand **L^3** (0.152 g, 0.688 mmol) was reacted with $[Co_2(CO)_8]$ (0.190 g, 0.555 mmol) in 30 mL of CH_2Cl_2 at room temperature. After being stirred for 2 h, the solution was filtered through Celite and the solvent was removed under reduced pressure. The product was extracted with CH_2Cl_2/hexane (80:20), and the solution was concentrated and placed at −20 °C for 1 week to give orange microcrystals (0.177 g, 0.41 mmol, 65%). IR (CH_2Cl_2, ν(CO), cm^{-1}): 2095 (s), 2055 (vs), 2026 (vs), 1676 (m, $\nu_{C=O}$). ^{1}H NMR ($CDCl_3$): δ 2.45 (s, 3H, CH_3), 4.59 (d, ^3J(HH) = 6.26 Hz, 2H, CH_2N), 5.08 (br t, ^3J(HH) = 6.26 Hz, 1H, $CH_2N\mathit{H}$), 6.07 (s, 1H, HC−Co), 6.38 (br s, 1H, $C_6H_4N\mathit{H}$), 7.23 (m, 4H, C_6H_4). Anal. Calcd for $C_{17}H_{12}Co_2N_2O_7S$: C, 40.34; H, 2.39; N, 5.53; S, 6.33. Found: C, 40.41; H, 2.39; N, 5.47; S, 6.05.

X-ray Structural Analysis of $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3]$ (NEt_4·2) and $[Co_2(CO)_6\{\mu_2\text{-}\eta^2\text{-}HC_2CH_2NHC(O)NH(CH_2)_3Si(OEt)_3\}]$ (9). Single crystals were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo Kα, λ = 0.71073 Å). The complete conditions of data collection (Denzo software) and structure refinements are given below. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SIR97) and refined against F^2 using the SHELXL97 software.[14,15] The absorption was corrected empirically [with Sortav]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.

Crystal data and structure refinement details for NEt_4·**2**: $C_{32}H_{47}Co_3N_2O_{15}RuSi$, M = 1005.67, violet crystals, triclinic, space group $P\bar{1}$, a = 7.501(2) Å, b = 13.762(2) Å, c = 21.544(2) Å, α = 97.07(5)°, β = 93.91(5)°, γ = 97.82(5)°, V = 2178.4(7) Å^3, Z = 2, ρ_{calcd} = 1.533 g cm^{-3}, μ(Mo Kα) = 1.552 mm^{-1}. Intensity measurements were performed by $\omega-2\theta$ scans in the range 5.18° < 2θ < 60.24° at 173 K; 81 459 independent reflections with 5324 having $I > 2\sigma(I)$, F^2 refinement, 446 parameters, R1 = 0.1156, wR2 = 0.1530 and GOF = 0.965. CCDC 204010.

Crystal data and structure refinement details for **9**: $C_{19}H_{26}Co_2N_2O_{10}Si$, M = 588.37 g mol^{-1}, red crystal, monoclinic, space groupe $P2_1/a$, a = 9.099(3) Å, b = 19.989(5) Å, c = 14.404(4) Å, β = 93.20(2)°, Z = 4, ρ_{calcd} = 1.494 g cm^{-3}, μ(Mo Kα) = 1.365 mm^{-1}; a total of 22 545 reflections. Intensity measurements were performed by $\omega-2\theta$ scans in the range 2.46° < θ < 30.05° at 173 K; 7620 independent reflections with 2753 having $I > 2\sigma(I)$, F^2 refinement, 272 parameters, R1 = 0.010; wR2 = 0.020 and GOF = 1.145. Owing to the large thermal parameters of the atoms in the group $-Si(OEt)_3$ (thermal motion and/or disorder), the C−C and C−O distances have been fixed at values of 1.5 and 1.35 Å, respectively. CCDC 197184.

Additional material has also been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-197184 & 204010. 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.

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Supporting Information Available: Tables of atomic coordinates (S-1, S-5), thermal parameters (S-2, S-6), bond distances (S-3, S-7), and angles (S-4, S-8) for NEt_4·**2** and **9**, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020965M

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