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Reactions of Diphosphine-Stabilized Tetracobalt Carbonyl Clusters with $-Si(OR)_3$-Functionalized Alkynes

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Short-bite ligand cluster stabilization is achieved in the tetrahedral clusters $[Co_4(\mu\text{-}CO)_3(CO)_7(\mu\text{-dppy})]$ (**1a**−**c**), obtained in high yields by reactions of $[Co_4(CO)_{12}]$ with 1 equiv of the diphosphine ligands dppy, $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PNHPPh_2$ (dppa), or $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ (dppaSi), respectively. The structure of **1a** has been determined by X-ray diffraction, and the P atoms occupy axial positions on the basal face, transoid to a Co−Co bond. Clusters **1a**−**c** were reacted with phenylacetylene to afford the corresponding butterfly clusters $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppy})(\mu_4\text{-}\eta^2\text{-}PhC_2H)]$ (**2a**−**c**) by insertion of the alkyne into a Co−Co bond of the precursor. This was established by an X-ray diffraction study of $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})(\mu_4\text{-}\eta^2\text{-}PhC_2H)]$ (**2a**). In an alternative synthetic procedure, the alkyne cluster $[Co_4(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC_2H)]$ (**3**), prepared from $[Co_4(CO)_{12}]$ and phenylacetylene, was reacted with the diphosphines dppy. This led in good yields to butterfly clusters, isomeric with **2a**−**c** in terms of the position of the bridging carbonyls, as revealed by an X-ray diffraction study of the dppa derivative **2′b**·$0.5CH_2Cl_2$. To obtain suitable cluster precursors to sol−gel materials, we have reacted **1a**,**b** with the new trialkoxysilyl alkyne $PhC{\equiv}CC(O)NH(CH_2)_3Si(OMe)_3$ (**L**^{1}) and isolated the corresponding functionalized butterfly clusters $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppy})\{\mu_4\text{-}\eta^2\text{-}PhC_2C(O)NH(CH_2)_3Si(OMe)_3\}]$ (**4a**,**b**), respectively. Similar reactions between **1a**,**b** and the alkyne $HC{\equiv}CCH_2NHC(O)NH(CH_2)_3Si(OEt)_3$ (**L**^{2}) afforded the related clusters $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppy})\{\mu_4\text{-}\eta^2\text{-}HC_2CH_2NHC(O)NH(CH_2)_3Si(OEt)_3\}]$ (**5a**,**b**). The cluster $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})\{\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3\}]$ (**6a**) was obtained by reaction of **1a** with $HC{\equiv}C(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3$ (**L**^{3}). Reaction of $[Co_4(CO)_{12}]$ with **L**^{1} led to the formation of the dinuclear complex $[Co_2(CO)_6\{\mu\text{-}\eta^2\text{-}PhC_2C(O)NH(CH_2)_3Si(OMe)_3\}]$ (**7**), which was also prepared by reaction of $[Co_2(CO)_8]$ with **L**^{1}. Reaction of **1a** with dppaSi afforded the mixed-diphosphine cluster $[Co_4(\mu\text{-}CO)_3(CO)_5(\mu\text{-dppm})(\mu\text{-dppaSi})]$ (**8**), which was characterized by X-ray diffraction. In the course of attempts at linking two molecules of **2a** with 1,4-diodobenzene under Sonogashira conditions, the dinuclear complex $[Co_2(CO)_4(\mu\text{-dppm})\{\mu\text{-}\eta^2\text{-}PhC_2H\}]$ (**9**) was isolated instead. Reaction of 1,4-bis(trimethylsilyl)butadiyne (**L**^{4}) with $[Co_4(CO)_{12}]$ afforded the known complex $[\{Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}Me_3SiC_2\text{-})\}_2]$ (**10**) and with **1a** yielded the desired product $[Co_4(CO)_8(\mu\text{-dppm})(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$ (**12**), in addition to the known complex $[Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$ (**13**). Proto-desilylation of **12** using TBAF/THF−H_2O occurred unexpectedly at the cluster core-bound alkyne carbon to afford $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})(\mu_4\text{-}\eta^2\text{-}HC_2C{\equiv}CSiMe_3)]$ (**16**), instead of the anticipated cluster $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)]$. The crystal structure of **16** has been determined by X-ray diffraction.

Introduction

The confinement of molecular clusters in the cavities of meso- or nanoporous inorganic matrixes, followed by thermal activation under inert atmosphere, has considerable potential for the stabilization of highly dispersed metal particles whose coalescence into larger, ill-defined aggregates can thus be prevented. This approach has obvious relevance to the fabrication of microelectronic devices[1] and to the preparation of new catalyts whose selectivity will critically depend on the size and dispersion of the metal particles and also on the shape of the

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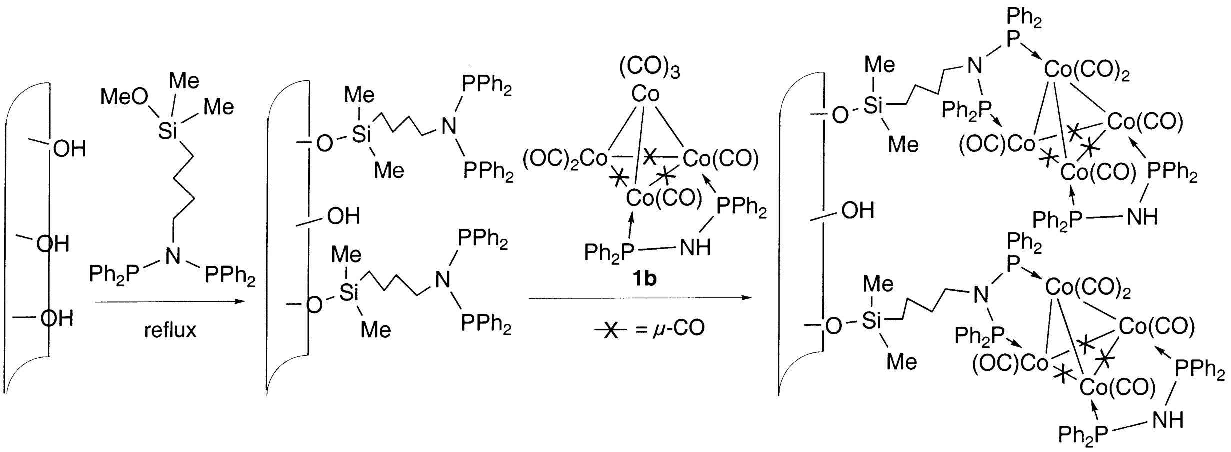
Scheme 1. Anchoring of a Co_4 Cluster into Funtionalized Alumina Membranes[7]



cavity in which they are embedded.[2,3] We have shown that impregnation of a mesoporous xerogel or of MCM-41 with an organic solution of the heterometallic cluster $[NEt_4][Co_3Ru(CO)_{12}]$ and subsequent thermal treatment lead to highly dispersed magnetic nanoparticles under milder conditions than when conventional metal salts are used as precursors.[4]

In addition to the impregnation method, and since the nature of the interactions between the metal cluster and the host matrix plays a very important role, in particular but not solely in controling the quantity of metal incorporated, it appears attractive to develop anchoring methods that consist in the grafting of molecular metal clusters into the pores of the matrix[5] by using a bifunctional ligand that would provide a stronger link between the molecular precursor and the host.[6] This ligand should also lead to a stable molecular species in order to minimize the risk of breaking the metal–ligand interaction and thus avoid leaching of the metal complex. We have begun to explore general approaches to this aim, by attaching first one end of the ligand to the inorganic matrix and then reacting the other functional end with the molecular cluster, or first preparing the functionalized cluster and reacting it with the host matrix to generate the covalent linkage.[7] We have prepared the short-bite alkoxysilyl-functionalized diphosphine ligands $(Ph_2P)_2N(CH_2)_3Si(OMe)_3$, $(Ph_2P)_2N(CH_2)_4SiMe_2(OMe)$, and $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$[7,8] and used them to derivatize the pore walls of nanoporous alumina membranes.[7] The covalent attachment of the diphosphine ligands by Si–O bond formation provides a molecular anchor that allowed subsequent reaction with the derivative $[Co_4(CO)_{10}(\mu\text{-dppa})]$ (dppa = $Ph_2PNHPPh_2$), **1b**,[9] which has a more selective substitution chemistry than the parent $[Co_4(CO)_{12}]$ (Scheme 1).[7]

We have also used an ordered mesoporous silica of the type SBA-15 as matrix,[10] with $(Ph_2P)_2N(CH_2)_3Si(OMe)_3$ as anchoring ligand.[7] The molecular cluster to be tethered was again $[Co_4(CO)_{10}(\mu\text{-dppa})]$, and subsequent thermal treatment of the organometallic hybrid mesoporous silica led to pure nanocrystalline Co_2P particles that were more regular in spatial repartition, size, and shape than when a silica xerogel, obtained by the sol–gel process, was used.[11]

In such systems, the dative bonding between the functional ligand and the cluster results from donation of the phosphorus lone pair to the metal and the improved stability of the diphosphine system compared to a monophosphine linkage result from the formation of a stable $\overline{\text{MPNPM}'}$ five-membered ring. Generating a *covalent* linkage between the metal complex and the host matrix represents an attractive extension, and we have already applied the sol–gel process to incorporate mono- and bimetallic species into an inorganic matrix by condensation of alkoxysilyl-substituted metal alkyl complexes with TEOS.[12] We became interested in developing other ligand systems that would form strong, covalent bonds with the metal cluster and could be amenable to condensation with an inorganic matrix or its precursor (e.g., TEOS). Functional alkynes appeared to us suitable candidates since interaction of their

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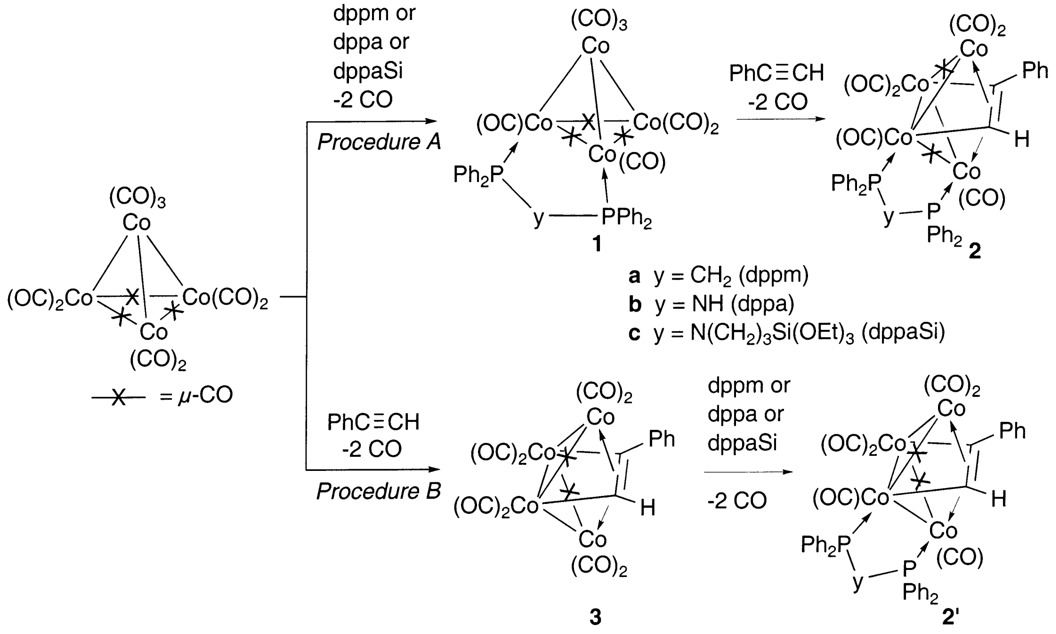
Scheme 2. Synthetic Routes to Butterfly Clusters 2a–c and Their Isomers 2′a–c



carbon–carbon triple bond with two or more metal centers can lead to the formation of strong, covalent metal–carbon σ bonds,[13] and we have recently reported our first results in this direction.[14] In this context, we have focused the present work on the preparation and characterization of molecular precursors based on tetranuclear cobalt carbonyl clusters, which could give rise to interesting magnetic materials.[4] The cluster [$Co_4(CO)_{12}$] has a rich substitution chemistry,[15–18] and its reactions with suitably functionalized alkynes may afford convenient precursors for subsequent anchoring processes upon condensation reaction between this function and surface OH groups. However [$Co_4(CO)_{10}(\mu_4$-η^2-alkyne)] clusters, of which the first example reported in the literature was [$Co_4(CO)_{10}(\mu_4$-η^2-EtC_2Et)],[19] are often prone to decomposition, giving [$Co_2(CO)_6(\mu$-η^2-alkyne)] complexes,[15b,20] which is consistent with the greater reactivity of [$Co_4(CO)_{10}(\mu_4$-η^2-alkyne)] clusters compared to the corresponding dicobalt complexes [$Co_2(CO)_6(\mu$-η^2-alkyne)].[21] Stabilization of these clusters against fragmentation with bi- or polydentate phosphines is therefore desirable.[22]

It was also hoped that this metal core stabilization would lead to improved yield and selectivity of reactions between the metal clusters and alkynes. We have focused on short-bite diphosphine ligands such as $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PNHPPh_2$ (dppa), and the functionalized diphosphine $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ (dppaSi) known to be suitable for supporting a metal–metal bond and increasing cluster stability.[23] By combining the beneficial basicity of phosphine donors and the bridging ability of these diphosphine ligands that results in five-membered rings, we hoped to obtain functional alkyne-substituted clusters more stable than when starting from [$Co_4(CO)_{12}$].

In this paper, we describe the synthesis and X-ray diffraction studies of diphosphine derivatives of [$Co_4(CO)_{12}$] and of two isomers of Co_4-alkyne diphosphine clusters and report an investigation on the substitution reactions of diphosphine derivatives of [$Co_4(CO)_{12}$] with new alkynes containing alkoxysilyl functions suitable to form sol–gel materials. We also undertook an investigation of the reactions of [$Co_4(CO)_{12}$] and its diphosphine derivatives with the conjugated, protected diyne 1,4-bis(trimethylsilyl)butadiyne. Only a few reactions of [$Co_4(CO)_{12}$] with diynes have been reported.[13a,15b,24] Subsequent functionalization of these clusters should be possible, and studies with nonprotected diynes have shown that they behave toward the cluster effectively as two separate alkyne units. Recently, the first example of tetracobalt metalloligated (or “spiked”) triangular cluster containing an acetylide ligand, [$Co_4(CO)_{10}(\mu$-CO)-{$H_2C{=}CC(Me)_2N(Me)C(Me)C(\mu_4$-C)}], was prepared by

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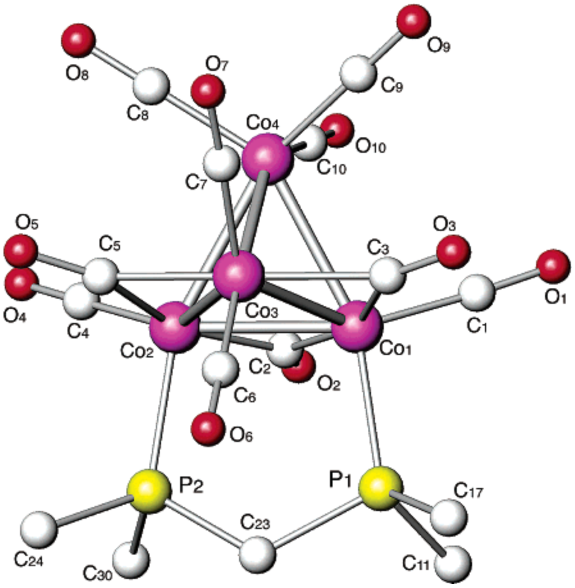

Figure 1. View of the molecular structure of cluster **1a.** Only the ipso carbons of the phenyl groups are shown, and the hydrogen atoms have been omitted for clarity.

reaction of $[Co_4(CO)_{12}]$ with the diacetylenic amine $N(Me)(HC{\equiv}CCMe_2)_2$.[25]

Results and Discussion

Synthesis and Characterization of the Clusters $[Co_4(\mu\text{-}CO)_3(CO)_7(\mu\text{-}dppy)]$ (1a−c). Reaction of $[Co_4(CO)_{12}]$ with 1 equiv of dppm, dppa, or dppaSi in CH_2Cl_2 or in hexane at room temperature afforded rapidly the tetrahedral clusters **1a**−**c**, in which the diphosphine ligand has substituted two carbonyl ligands and bridges two basal cobalt atoms (Scheme 2). This has been previously reported in the case of **1b**.[9] The structure of **1a** has now been determined by X-ray diffraction to provide more comparative data. A view of the structure is shown in Figure 1, and selected bond distances and angles are given in Table 1.

The molecular structure of **1a** contains a slightly distorted tetrahedral Co_4 cluster. There is almost a mirror plane passing through the cluster, which contains the atoms Co(3), Co(4), C(6), C(7), C(10), and C(23). The basal face Co(1)−Co(3) has three edge-bridging carbonyl groups, and the P substituents occupy axial positions at Co(1) and Co(2) with P(1)−Co(1)−Co(4) and P(2)−Co(2)−Co(4) angles of 159.56(4)° and 157.70(4)°, respectively. The Co−Co edge bridged by the dppm ligand (Co(1)−Co(2) = 2.4268(8) Å) is shorter than the other two (Co(1)−Co(3) = 2.4565(7) Å and Co(2)−Co(3) = 2.4540(8) Å). The remaining seven carbonyl ligands are essentially linear (Co−C−O = 177.0(4)−179.2(4)°). The Co−P bond lengths (Co(1)−P(1) = 2.190(1) Å and Co(2)−P(2) = 2.194(1) Å) are within the range of those observed in phosphine and phosphite derivatives of $[Co_4(CO)_{12}]$.[26,27] The five-membered ring Co_2P_2C adopts an envelope conformation with the CH_2 group at the flap.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 1a (estimated standard deviations in parentheses)

Co(1)−Co(2)	2.4268(8)	Co(2)−C(5)	1.920(4)
Co(1)−Co(3)	2.4565(7)	Co(3)−Co(4)	2.528(1)
Co(1)−Co(4)	2.5014(7)	Co(3)−C(3)	1.957(4)
Co(1)−P(1)	2.190(1)	Co(3)−C(5)	1.945(4)
Co(1)−C(1)	1.759(5)	Co(3)−C(6)	1.789(5)
Co(1)−C(2)	1.932(5)	Co(3)−C(7)	1.779(5)
Co(1)−C(3)	1.929(4)	Co(4)−C(8)	1.809(5)
Co(2)−Co(3)	2.4540(8)	Co(4)−C(9)	1.830(6)
Co(2)−Co(4)	2.5348(8)	Co(4)−C(10)	1.791(5)
Co(2)−P(2)	2.194(1)	P(1)−C(23)	1.855(4)
Co(2)−C(2)	1.923(4)	P(2)−C(23)	1.843(4)
Co(2)−C(4)	1.767(5)		

Co(2)−Co(1)−Co(3)	60.33(2)	Co(2)−Co(4)−Co(3)	57.98(2)
Co(2)−Co(1)−Co(4)	61.89(2)	P(1)−C(23)−P(2)	114.5(2)
Co(2)−Co(1)−P(1)	99.71(4)	C(23)−P(1)−Co(1)	110.5(1)
Co(3)−Co(1)−Co(4)	61.32(3)	C(23)−P(2)−Co(2)	111.3(1)
Co(3)−Co(1)−P(1)	102.84(4)	Co(1)−C(1)−O(1)	177.0(4)
Co(4)−Co(1)−P(1)	159.56(4)	Co(1)−C(2)−O(2)	142.1(4)
Co(1)−Co(2)−Co(3)	60.43(2)	Co(2)−C(2)−O(2)	139.9(4)
Co(1)−Co(2)−Co(4)	60.50(2)	Co(1)−C(3)−O(3)	143.0(3)
Co(1)−Co(2)−P(2)	98.22(4)	Co(3)−C(3)−O(3)	138.5(3)
Co(3)−Co(2)−Co(4)	60.88(2)	Co(2)−C(4)−O(4)	179.2(4)
Co(3)−Co(2)−P(2)	104.17(4)	Co(2)−C(5)−O(5)	143.6(4)
Co(4)−Co(2)−P(2)	157.70(4)	Co(3)−C(5)−O(5)	137.5(4)
Co(1)−Co(3)−Co(2)	59.23(2)	Co(3)−C(6)−O(6)	179.2(4)
Co(1)−Co(3)−Co(4)	60.22(2)	Co(3)−C(7)−O(7)	177.9(4)
Co(2)−Co(3)−Co(4)	61.14(2)	Co(4)−C(8)−O(8)	178.1(5)
Co(1)−Co(4)−Co(2)	57.61(2)	Co(4)−C(9)−O(9)	179.1(5)
Co(1)−Co(4)−Co(3)	58.47(2)	Co(4)−C(10)−O(10)	178.4(5)

The P(1)−C(23)−P(2) angle of 114.5(2)° is larger than in $[Co_4(CO)_8\{\mu\text{-}Me_2PCH_2PMe_2\}_2]$ (107.5(4)° and 110.7(4)°) taken for comparison in the absence of a dppm analogue.[28a] The P−C−P angle in dppm complexes is generally smaller than the P−N−P angle in the corresponding dppa complexes, with typical values of ca. 107° and 119°, respectively.[23c,d] A notable exception was found in the rectangular cluster $[Pd_4(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2(\mu\text{-}dppa)_2]^{2+}$, which displays P−C−P and P−N−P angles of 118.9(2)° and 113.5(2)°, respectively.[23b] In the free ligands, the P−C−P and P−N−P angles in dppm and dppa are 106.2(3)°[28b] and 118.9(2)°, respectively.[28c,d]

The structural similarity between clusters **1a**−**c** is supported by the pattern of the $\nu(CO)$ absorptions in the IR spectrum and the singlet in the $^{31}P\{^1H\}$ NMR spectrum for the two equivalent P nuclei. The broadening of the $^{31}P\{^1H\}$ NMR signals for all complexes is consistent with the rapid relaxation[29] induced by the quadrupolar Co nuclei ($I = 7/2$). Best yields of **1a** were obtained with very short reaction times since this molecule progressively transforms to give the green, tetrasubstituted cluster $[Co_4(CO)_8(\mu\text{-}dppm)_2]$. This latter cluster is also obtained by reaction of excess dppm with $[Co_4(CO)_{12}]$ or by thermal treatment of $[Co_2(CO)_6(\mu\text{-}dppm)]$.[30] Since it did not react with $PhC{\equiv}CH$, even when Me_3NO was used as CO activator, it was not further investigated.

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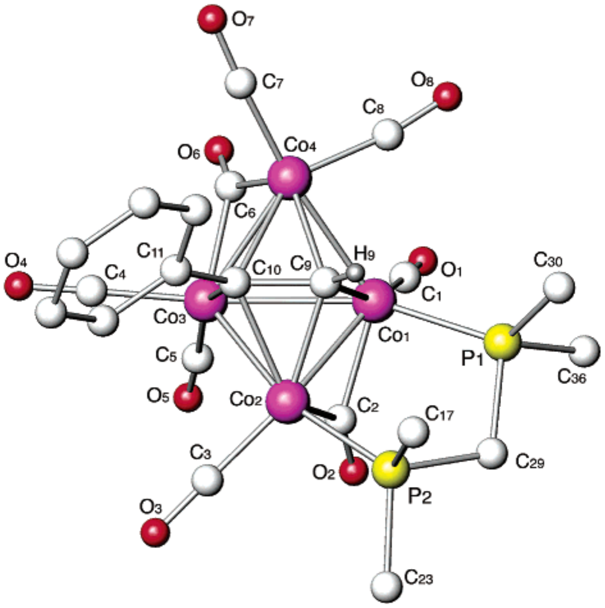

Figure 2. View of the molecular structure of cluster **2a.** Only the ipso carbons of the phenyl groups of the phosphine ligand are shown, and the hydrogen atoms have been omitted for clarity.

Synthesis and Characterization of the Clusters [$Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppy})(\mu_4\text{-}\eta^2\text{-}PhC_2H)$] (2a−c). Clusters **1a**−**c** were reacted with excess phenylacetylene to afford the green butterfly clusters **2a**−**c** in high yield (Scheme 2). This was established by an X-ray diffraction study of **2a**, and a view of the structure is shown in Figure 2. Selected bond distances and angles are given in Table 2 and discussed below. Insertion of the alkyne into a Co−Co bond of the precursor has occurred between one of the phosphine-substituted Co centers of **1a** and, most likely, the apical Co atom since it should be easier to break a Co−Co bond not supported by a bridging CO ligand. However, the related isoelectronic cluster [$RuCo_3(CO)_{12}$]$^-$, which has an apical $Ru(CO)_3$ fragment, also reacted with alkynes to afford butterfly clusters in which a Co−Ru bond forms the hinge of the butterfly,[31] implying that in this case a CO-bridged Co−Co bond was the site of alkyne insertion.

Whereas the ^1H NMR spectrum of **1a** in $CDCl_3$ showed a broad resonance at 2.85 ppm for the CH_2 protons, they appeared as an ABXY spin system ($CH^AC H^BP_2$) in **2a**, as expected from the loss of symmetry in **2**. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum of **2b** contains two broad resonances at δ 81.2 and 87.4 ppm for the two chemically different P nuclei, in contrast to **2a** and **2c**, for which only one broad resonance was observed, at 28.3 and 81.0 ppm, respectively. We verified for **2a** that at 0 °C this resonance splits into two broad signals with a 1:1 intensity. The J(PP) coupling could not be resolved owing to the broadness of the signals. We assume that **2b**,**c** have a structure analogous to that of **2a**. We have no evidence for the formation of isomeric structures corresponding to an opposite orientation of the alkyne in the cluster; the latter would be disfavored for steric reasons, owing to repulsion between the phenyl groups.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2a (estimated standard deviations in parentheses)

Co(1)−Co(2)	2.410(1)	Co(3)−C(4)	1.791(4)
Co(1)−Co(3)	2.620(1)	Co(3)−C(5)	1.790(4)
Co(1)−Co(4)	2.411(1)	Co(3)−C(6)	1.967(4)
Co(1)−P(1)	2.218(1)	Co(3)−C(10)	2.007(3)
Co(1)−C(1)	1.782(4)	Co(4)−C(6)	1.895(4)
Co(1)−C(2)	1.965(3)	Co(4)−C(7)	1.763(4)
Co(1)−C(9)	1.988(3)	Co(4)−C(8)	1.756(4)
Co(2)−Co(3)	2.480(1)	Co(4)−C(9)	2.057(3)
Co(2)−P(2)	2.200(1)	Co(4)−C(10)	2.118(3)
Co(2)−C(2)	1.845(3)	P(1)−C(29)	1.856(4)
Co(2)−C(3)	1.746(4)	P(2)−C(29)	1.840(3)
Co(2)−C(9)	2.026(3)	C(9)−C(10)	1.405(4)
Co(2)−C(10)	2.091(3)	C(10)−C(11)	1.484(4)
Co(3)−Co(4)	2.455(1)		

Co(2)−Co(1)−Co(3)	58.90(3)	Co(1)−Co(4)−C(10)	75.91(9)
Co(2)−Co(1)−Co(4)	93.80(4)	Co(3)−Co(4)−C(9)	74.31(9)
Co(2)−Co(1)−P(1)	98.01(4)	Co(3)−Co(4)−C(10)	51.42(8)
Co(2)−Co(1)−C(9)	53.8(1)	C(9)−Co(4)−C(10)	39.3(1)
Co(3)−Co(1)−Co(4)	58.24(3)	P(1)−C(29)−P(2)	112.6(1)
Co(3)−Co(1)−P(1)	156.89(4)	Co(1)−P(1)−C(29)	108.0(1)
Co(3)−Co(1)−C(9)	71.6(1)	Co(2)−P(2)−C(29)	107.7(1)
Co(4)−Co(1)−P(1)	128.80(4)	Co(1)−C(9)−Co(2)	73.8(1)
Co(4)−Co(1)−C(9)	54.8(1)	Co(1)−C(9)−Co(4)	73.1(1)
P(1)−Co(1)−C(9)	94.7(1)	Co(1)−C(9)−C(10)	109.7(2)
Co(1)−Co(2)−Co(3)	64.78(4)	Co(2)−C(9)−Co(4)	119.1(2)
Co(1)−Co(2)−P(2)	99.32(5)	Co(2)−C(9)−C(10)	72.5(2)
Co(1)−Co(2)−C(9)	52.4(1)	Co(2)−C(10)−Co(3)	74.4(1)
Co(1)−Co(2)−C(10)	76.4(1)	Co(2)−C(10)−Co(4)	113.5(1)
Co(3)−Co(2)−P(2)	164.03(3)	Co(2)−C(10)−C(9)	67.6(2)
Co(3)−Co(2)−C(9)	74.2(1)	Co(3)−C(10)−Co(4)	73.0(1)
Co(3)−Co(2)−C(10)	51.23(8)	Co(4)−C(10)−C(9)	68.0(2)
P(2)−Co(2)−C(9)	95.1(1)	Co(1)−C(1)−O(1)	178.5(3)
P(2)−Co(2)−C(10)	126.17(9)	Co(1)−C(2)−O(2)	136.9(3)
C(9)−Co(2)−C(10)	39.9(1)	Co(2)−C(2)−O(2)	144.7(3)
Co(1)−Co(3)−Co(2)	56.32(3)	Co(2)−C(3)−O(3)	178.8(3)
Co(1)−Co(3)−Co(4)	56.61(2)	Co(3)−C(4)−O(4)	178.4(3)
Co(1)−Co(3)−C(10)	72.97(9)	Co(3)−C(5)−O(5)	175.8(4)
Co(2)−Co(3)−Co(4)	91.00(3)	Co(3)−C(6)−O(6)	138.6(3)
Co(2)−Co(3)−C(10)	54.31(9)	Co(4)−C(6)−O(6)	142.3(3)
Co(4)−Co(3)−C(10)	55.6(1)	Co(4)−C(7)−O(7)	175.8(4)
Co(1)−Co(4)−Co(3)	65.16(2)	Co(4)−C(8)−O(8)	171.6(4)
Co(1)−Co(4)−C(9)	52.11(9)		

Synthesis and Characterization of the Isomeric Clusters [$Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppy})(\mu_4\text{-}\eta^2\text{-}PhC_2H)$] (2′a−c). In an alternative synthetic procedure, we reacted the alkyne cluster **3**, derived from [$Co_4(CO)_{12}$] and phenylacetylene,[20] with the diphosphines dppy (Scheme 2, procedure B). Although this led to the expected carbonyl substitution at the butterfly cluster in good yields, an X-ray diffraction study of the dppa derivative **2′b**·$0.5CH_2Cl_2$ revealed that an isomer of **2b** has formed. A view of the structure of **2′b** is shown in Figure 3, and selected bond distances and angles are given in Table 3. Like in **2b**, a Co−Co bond connecting a wing-tip and a hinge atom is supported by the diphosphine, and the alkyne phenyl group is in a remote position with respect to the PPh_2 group. However, disubstitution of CO in **3** by dppa has occurred regiospecifically on an unbridged Co−Co edge, and the two bridging carbonyls do not span the same Co−Co bonds as established in **2a** and assumed in **2b**. Clusters **2b** and **2′b** are not mirror images of each other. Their IR spectra are however very similar. Disubstitution of CO in [$Co_4(CO)_{10}(\mu_4\text{-}\eta^2\text{-alkyne})$] clusters by monophosphines has been reported to occur regiospecifically on the wing-tip atoms,[32] which is of course impossible with diphosphines such as dppy. As was observed for **2b**, the

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[31] Braunstein, P.; Rosé, J.; Bars, O. *J. Organomet. Chem.* **1983**, *252*, C101.

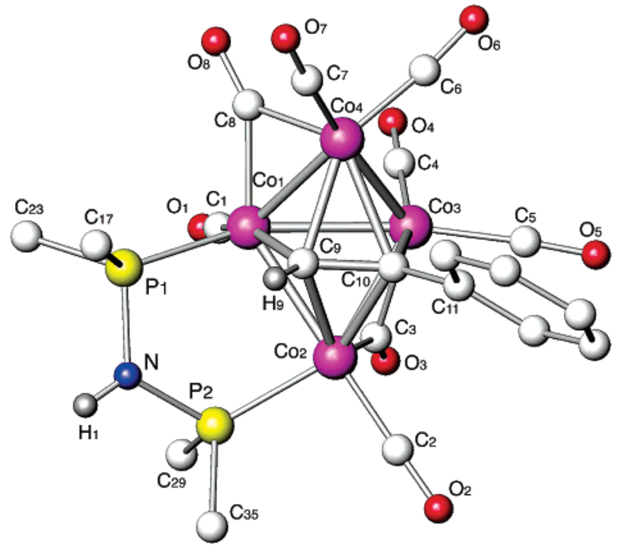


Figure 3. View of the molecular structure of the cluster **2′b** in **2′b**·0.5CH$_2$Cl$_2$. Only the ipso carbons of the phenyl groups of the phosphine ligand are shown, and the solvent and hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 2′b·0.5CH$_2$Cl$_2$ (estimated standard deviations in parentheses)

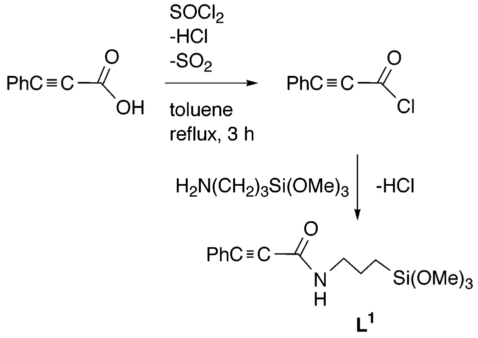
Co(1)−Co(2)	2.456(1)	Co(3)−C(3)	2.055(3)
Co(1)−Co(3)	2.543(1)	Co(3)−C(4)	1.795(3)
Co(1)−Co(4)	2.419(1)	Co(3)−C(5)	1.800(3)
Co(1)−P(1)	2.172(1)	Co(3)−C(10)	2.009(3)
Co(1)−C(1)	1.785(3)	Co(4)−C(6)	1.759(3)
Co(1)−C(8)	1.914(3)	Co(4)−C(7)	1.776(3)
Co(1)−C(9)	1.983(3)	Co(4)−C(8)	1.935(3)
Co(2)−Co(3)	2.448(1)	Co(4)−C(9)	2.050(3)
Co(2)−P(2)	2.168(1)	Co(4)−C(10)	2.142(3)
Co(2)−C(2)	1.777(3)	P(1)−N	1.683(3)
Co(2)−C(3)	1.833(3)	P(2)−N	1.694(3)
Co(2)−C(9)	2.072(3)	C(9)−C(10)	1.409(4)
Co(2)−C(10)	2.050(3)	C(10)−C(11)	1.498(4)
Co(3)−Co(4)	2.456(1)		
Co(2)−Co(1)−Co(3)	58.61(3)	Co(3)−Co(4)−C(10)	51.27(8)
Co(2)−Co(1)−Co(4)	93.60(2)	C(9)−Co(4)−C(10)	39.2(1)
Co(2)−Co(1)−P(1)	101.73(3)	P(1)−N−P(2)	119.9(1)
Co(2)−Co(1)−C(9)	54.40(9)	C(17)−P(1)−C(23)	102.5(1)
Co(3)−Co(1)−Co(4)	59.28(2)	Co(1)−P(1)−N	104.5(1)
Co(3)−Co(1)−P(1)	159.14(3)	C(29)−P(1)−C(35)	104.8(1)
Co(3)−Co(1)−C(9)	72.89(9)	Co(2)−P(2)−N	114.6(1)
Co(4)−Co(1)−P(1)	120.41(3)	Co(1)−C(9)−Co(4)	73.7(1)
Co(4)−Co(1)−C(9)	54.44(9)	Co(1)−C(9)−Co(2)	74.5(1)
P(1)−Co(1)−C(9)	90.19(9)	Co(1)−C(9)−C(10)	108.6(2)
Co(1)−Co(2)−Co(3)	62.48(2)	Co(2)−C(9)−Co(4)	119.1(1)
Co(1)−Co(2)−P(2)	85.22(3)	Co(2)−C(9)−C(10)	69.2(2)
Co(1)−Co(2)−C(9)	5 1.10(8)	Co(4)−C(9)−C(10)	73.9(2)
Co(1)−Co(2)-C(10)	75.43(9)	Co(2)−C(10)-Co(3)	74.2(1)
Co(3)−Co(2)−P(2)	141.59(3)	Co(2)−C(10)−Co(4)	115.9(1)
Co(3)−Co(2)−C(9)	73.66(9)	Co(2)−C(10)−C(9)	70.8(2)
Co(3)−Co(2)−C(10)	52.15(8)	Co(3)−C(10)−Co(4)	72.5(1)
P(2)−Co(2)−C(9)	102.89(9)	Co(3)−C(10)−C(9)	104.4(2)
P(2)−Co(2)−C(10)	141.94(9)	Co(4)−C(10)−C(9)	66.9(2)
C(9)−Co(2)−C(10)	40.0(1)	C(9)−C(10)−C(11)	125.9(3)
Co(1)−Co(3)−Co(2)	58.90(2)	Co(1)−C(1)−O(1)	178.7(4)
Co(1)−Co(3)−Co(4)	57.84(2)	Co(2)−C(2)−O(2)	179.1(3)
Co(1)−Co(3)−C(10)	74.06(9)	Co(2)−C(3)−O(3)	149.4(3)
Co(2)−Co(3)−Co(4)	92.86(2)	Co(3)−C(3)−O(3)	132.7(3)
Co(2)−Co(3)−C(10)	53.67(8)	Co(3)−C(4)−O(4)	179.0(3)
Co(4)−Co(3)−C(10)	56.25(9)	Co(3)−C(5)−O(5)	175.6(4)
Co(1)−Co(4)−Co(3)	62.89(2)	Co(4)−C(6)−O(6)	173.4(4)
Co(1)−Co(4)−C(9)	51.89(8)	Co(4)−C(7)−O(7)	176.3(3)
Co(1)−Co(4)−C(10)	74.68(8)	Co(1)−C(8)−O(8)	144.3(3)
Co(3)−Co(4)−C(9)	73.84(9)	Co(4)−C(8)−O(8)	137.8(3)

^{31}P{^{1}H} NMR spectrum of **2′b** shows two signals, at δ 79.7 and 87.6 ppm.

The alkyne C(9)−C(10) bonds of 1.405(4) Å in **2a** and 1.409(4) Å in **2′b**·0.5CH$_2$Cl$_2$ are significantly elongated when compared to the free alkyne (1.19 Å), consistent with their 2σ, 2π bonding.[13a] The Co−Co distances range from 2.410(1) to 2.620(1) Å in **2a** and from 2.419(1) to 2.543(1) Å in **2′b**·0.5CH$_2$Cl$_2$, the shorter bonds being those supported by the bridging ligands and the longer being the hinge of the butterfly Co(1)−Co(3). The differences in Co−C(9) and Co−C(10) distances reflect the presence of the phenyl group at C(10) and of the dppy ligand. The dihedral angles between the butterfly wings of 121.7° in **2a** and 117° in **2′b** lead to nonbonding Co(2)···Co(4) distances of 3.52 and 3.55 Å, respectively. The alkyne hydrogen at C(9) was not detected by ^{1}H NMR spectroscopy (masked by aryl protons), but it was located by X-ray diffraction in both structures. In the butterfly cluster [Co$_4$(CO)$_8$(PPh$_3$)$_2$(μ_4-η^2-HC$_2$H)], the C−H ^{1}H NMR resonance was observed as a triplet at 7.82 ppm.[33] We assume that clusters **2′a**−**c** have a similar structure, although spectroscopic data in solution would not allow the identification of minor structural changes.

Attempts to functionalize clusters **2b** and **2′b** by deprotonation of the NH group using DBU or KH as a base followed by addition of Cl(CH$_2$)$_3$Si(OEt)$_3$ or O=C=N(CH$_2$)$_3$Si(OMe)$_3$ failed. Other approaches were therefore attempted (see below).

Synthesis of Alkoxysilyl-Functionalized Alkyne Clusters. With the objective to incorporate in a Co$_4$ cluster a functional alkyne that could be subsequently condensed with a silica matrix via the sol−gel method, we decided to take advantage of the stabilizing effect of dppm or dppa on the Co$_4$ core to react **1a**,**b** with the new alkyne PhC≡CC(O)NH(CH$_2$)$_3$Si(OMe)$_3$ (**L^1**) and the recently reported alkynes HC≡CCH$_2$NHC(O)NH(CH$_2$)$_3$-Si(OEt)$_3$ (**L^2**) and HC≡C(CH$_2$)$_2$OC(O)NH(CH$_2$)$_3$Si(OEt)$_3$ (**L^3**).[14] Alkyne **L^1** was prepared in two steps by the method outlined in eq 1, which involved treatment of 3-phenylpropiolic acid with thionyl chloride followed by addition of 3-aminopropyl trimethoxysilane. The ligand was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectroscopy. The infrared spectrum in dichloromethane contains a strong absorption band at 2220 cm^{-1} for the C≡C triple bond.



(1)

The reactions of **1a**,**b** with **L^1** and **L^2** afforded the clusters **4a**,**b** and **5a**,**b**, respectively, and **6a** was obtained by reaction of **1a** with **L^3**. The analytical and

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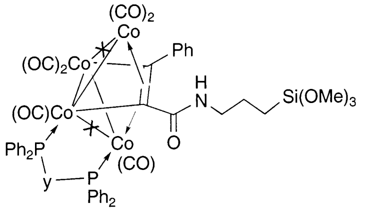
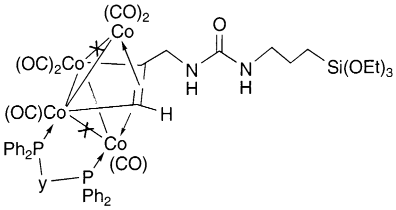
(32) Raithby, P. R. In *Transition Metal Clusters;* Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 2.

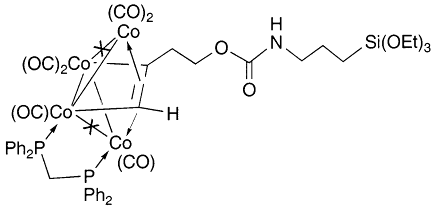
spectroscopic data confirmed the presence of both the functional alkyne and the diphosphine in the clusters. The structures shown for these compounds were deduced from their spectroscopic properties and by analogy with those established by X-ray diffraction for **2a** and **2b**.



4a y = CH_2
4b y = NH



5a y = CH_2
5b y = NH

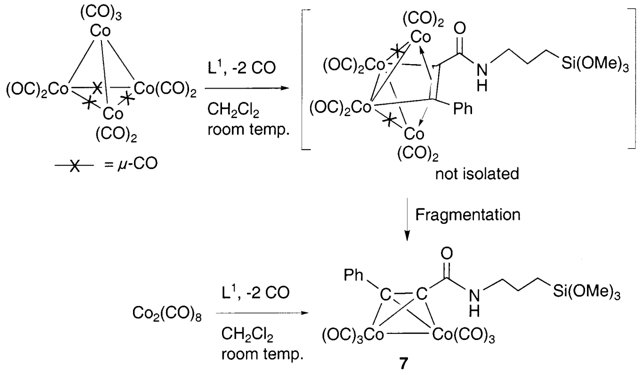


6a

Like in the case of **2b**, two broad $^{31}P\{^1H\}$ NMR resonances are observed for **4b** and **5b** at δ 91.1, 103.5 and 78.3, 89.0 ppm, respectively, but only one broad signal was observed for **4a**, **5a**, and **6a**, like for **2a**. The IR spectrum of all clusters show a characteristic ν(C=O) band for the amide function in the region 1646–1720 cm^{-1} in addition to those for the Co-bound carbonyls. All these clusters were obtained in the form of a paste, which is difficult to purify since column chromatography cannot be applied (presence of the alkoxysilyl groups). Residual alkyne often contaminates the samples.

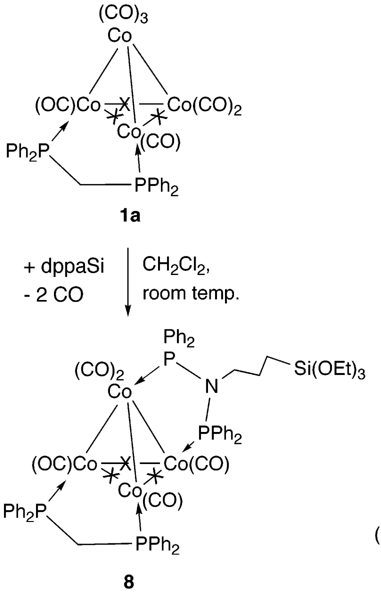
It was not possible to prepare the clusters **4a**,**b**, **5a**,**b**, and **6a** by first reacting $[Co_4(CO)_{12}]$ with the corresponding alkynes followed by the addition of the diphosphines because the blue $[Co_4(CO)_{10}(\mu_4\text{-}\eta^2\text{-alkyne})]$ clusters rapidly fragment in solution to give i.a. the red $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-alkyne})]$ complexes. The latter can be obtained directly by reaction of $[Co_2(CO)_8]$ with the corresponding alkyne (in the case of **L^1**, see Scheme 3).[20] Complex **7** was characterized by IR and NMR ^{1}H spectroscopy and elemental analysis. These observations clearly illustrate the advantage of using a diphosphine-stabilized precursor cluster for subsequent reactions with functional alkynes.

Scheme 3



Nevertheless, complexes of the type $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-alkyne})]$ may be useful synthons for the subsequent synthesis of tri- and tetranuclear clusters.[34] We are currently evaluating complex **7** with its $Si(OMe)_3$ function as a precursor to the synthesis of Co-containing materials by the sol–gel route.

Synthesis of $[Co_4(\mu\text{-}CO)_3(CO)_5(\mu\text{-dppm})(\mu\text{-dppa-Si})]$ (8). To broaden the scope of possibilities of attachment of a functional Co_4 cluster to a silica matrix, we also examined the incorporation of dppaSi in **1a** (eq 2). This reaction afforded the mixed-diphosphine cluster **8**, which was characterized by X-ray diffraction. A view of the structure is shown in Figure 4, and selected bond distances and angles are given in Table 4.



(2)

The molecular structure of **8** can be derived from that of the parent cluster **1a** by substituting an apical and an equatorial carbonyl group on Co(3) and Co(4), respectively, with the dppaSi ligand. The two different diphosphine ligands bridge opposite edges of a distorted Co_4 tetrahedron, and each Co is thus substituted by a P donor. The structure is similar to those of $[Co_4(CO)_8(\mu\text{-dmpm})_2]$[28a] and $[Rh_4(CO)_8(\mu\text{-dppm})_2]$.[35] The Co–Co bond lengths are in the range 2.434(1)–2.543(1) Å and are comparable with those found in the literature for

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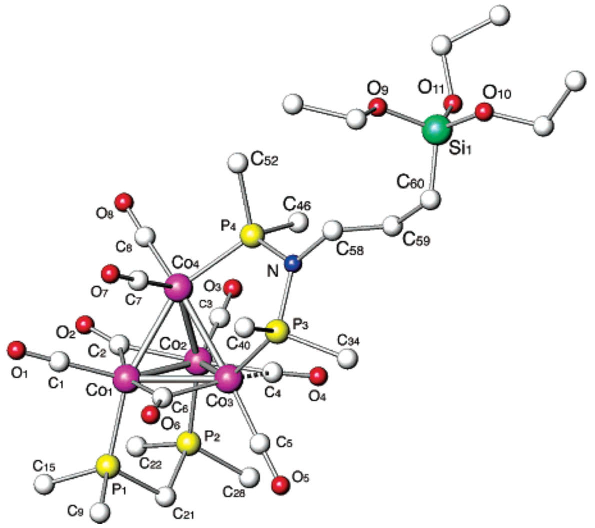


Figure 4. View of the molecular structure of cluster **8.** Only the ipso carbons of the phenyl groups are shown, and the hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for 8 (estimated standard deviations in parentheses)

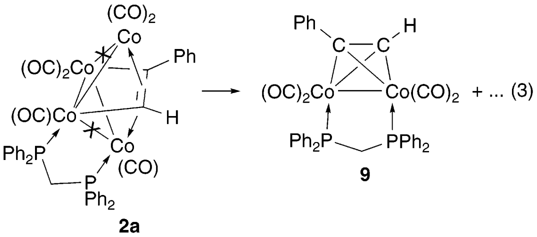
Co(1)−Co(2)	2.434(1)	Co(3)−Co(4)	2.535(1)
Co(1)−Co(3)	2.507(1)	Co(3)−P(3)	2.183(1)
Co(1)−Co(4)	2.490(1)	Co(3)−C(4)	1.981(4)
Co(1)−P(1)	2.184(1)	Co(3)−C(5)	1.757(5)
Co(1)−C(1)	1.773(5)	Co(3)−C(6)	1.941(4)
Co(1)−C(2)	1.921(4)	Co(4)−P(4)	2.188(1)
Co(1)−C(6)	1.936(4)	Co(4)−C(7)	1.775(5)
Co(2)−Co(3)	2.477(1)	Co(4)−C(8)	1.793(5)
Co(2)−Co(4)	2.543(1)	P(1)−C(21)	1.847(4)
Co(2)−P(2)	2.219(1)	P(2)−C(21)	1.847(4)
Co(2)−C(2)	1.920(4)	P(3)−N	1.706(4)
Co(2)−C(3)	1.763(4)	P(4)−N	1.697(4)
Co(2)−C(4)	1.897(5)		

Co(2)−Co(1)−Co(3)	60.18(2)	Co(2)−Co(4)−Co(3)	58.40(2)
Co(2)−Co(1)−Co(4)	62.20(2)	Co(2)−Co(4)−P(4)	111.56(4)
Co(2)−Co(1)−P(1)	98.41(4)	Co(3)−Co(4)−P(4)	94.04(4)
Co(3)−Co(1)−Co(4)	60.98(2)	P(1)−C(21)−P(2)	108.5(2)
Co(3)−Co(1)−P(1)	104.75(4)	C(21)−P(1)−Co(1)	110.1(1)
Co(4)−Co(1)−P(1)	159.51(4)	C(21)−P(2)−Co(2)	108.6(1)
Co(1)−Co(2)−Co(3)	61.37(2)	N−P(3)−Co(3)	116.5(1)
Co(1)−Co(2)−Co(4)	59.98(2)	N−P(4)−Co(4)	111.0(1)
Co(1)−Co(2)−P(2)	96.08(4)	P(3)−N−P(4)	114.9(2)
Co(3)−Co(2)−Co(4)	60.63(2)	Co(1)−C(1)−O(1)	178.8(4)
Co(3)−Co(2)−P(2)	109.01(4)	Co(1)−C(2)−O(2)	140.4(3)
Co(4)−Co(2)−P(2)	156.04(4)	Co(2)−C(2)−O(2)	140.9(3)
Co(1)−Co(3)−Co(2)	58.45(2)	Co(2)−C(3)−O(3)	178.9(4)
Co(1)−Co(3)−Co(4)	59.18(2)	Co(2)−C(4)−O(4)	141.2(4)
Co(1)−Co(3)−P(3)	133.11(4)	Co(3)−C(4)−O(4)	139.3(4)
Co(2)−Co(3)−Co(4)	60.97(2)	Co(3)−C(5)−O(5)	177.7(4)
Co(2)−Co(3)−P(3)	134.51(4)	Co(1)−C(6)−O(6)	139.8(3)
Co(4)−Co(3)−P(3)	87.34(4)	Co(3)−C(6)−O(6)	139.4(3)
Co(1)−Co(4)−Co(2)	57.82(2)	Co(4)−C(7)−O(7)	177.1(4)
Co(1)−Co(4)−Co(3)	59.84(2)	Co(4)−C(8)−O(8)	177.2(4)
Co(1)−Co(4)−P(4)	153.84(4)		

similar structures.[27,28a,36] The five terminal carbonyls display Co−C−O angles between 177.1(4)° and 178.9(4)°. The Co−C distances range from 1.757(5) to 1.793(5) Å and are substantially shorter than the Co−(μ-C) distances involving the bridging carbonyls C(2)O(2) and C(6)O(6) (1.920(4)−1.941(4) Å). The Co(2)−C(4) distance of 1.897(5) Å is considerably shorter than the Co(3)−C(4) distance of 1.981(4) Å, which suggests that C(4)O(4) is a bent semibridging carbonyl.[37] The refinement of the X-ray data shows that the CSi(OEt)$_3$ group is disordered over two positions with occupancy factors of 2/3 and 1/3. The Si−O, C−O, and C−C distances have been fixed at values of 1.6, 1.45, and 1.55 Å, respectively.

At room temperature, the ^{31}P{^{1}H} NMR spectrum contains only two broad resonances at 28.1 and 100.5 ppm, corresponding to the dppm and dppaSi ligands, respectively, which is not surprising for such clusters.[28a]

Formation of [Co$_2$(CO)$_4$(μ-dppm){μ-η^2-PhC$_2$H}] (9) from [Co$_4$(μ-CO)$_2$(CO)$_6$(μ-dppm)(μ_4-η^2-PhC$_2$H)] (2a). We attempted the linking of two molecules of **2a** with 1,4-diodobenzene under Sonogashira conditions.[38] Unfortunately, no coupling reaction was observed, and instead, fragmentation of **2a** afforded the red dinuclear complex **9** (eq 3).[39] Cluster fragmentation was probably triggered by the base which is necessary for the reaction. Similar behavior was recently observed with other alkyne-substituted clusters.[14]



Compound **9** was identified by its ^{1}H NMR data, and the Co$_2$C$_2$H proton was observed as a triplet at 5.79 ppm (^3J(PH) = 7.5 Hz), which is in agreement with literature values for related clusters.[40] Compounds of the type [Co$_2$(CO)$_4$(μ-dppm)(μ-η^2-alkyne)] are generally prepared by reaction of the appropriate alkyne with [Co$_2$(CO)$_6$-(μ-dppm)][40] or by reaction of dppm with the dinuclear complexes [Co$_2$(CO)$_6$(μ-η^2-alkyne)].[41]

Reaction of Co$_4$ Clusters with a Protected Diyne. With the objective of introducing protected functionalities in [Co$_4$(CO)$_{12}$], we explored its reactivity with 1,4-bis(trimethylsilyl)butadiyne Me$_3$SiC≡CC≡CSiMe$_3$ (**L^4**), also because reactions of diynes with this cluster have been very little investigated.[24] The reaction was performed in hexane or in dichloromethane. TLC indicated the formation of a blue intermediate, which rapidly transforms in solution to give the known, green product [{Co$_2$(CO)$_6$(μ-η^2-Me$_3$SiC$_2$−)}$_2$] (**10**) in 21% yield (Scheme 4). We assume that initial coordination of one of the triple bonds to [Co$_4$(CO)$_{12}$] yielded an intermediate of the type [Co$_4$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡CSiMe$_3$)]. The presence of a second triple bond was suggested to facilitate further rearrangements and fragmentation into two Co$_2$ units.[24]

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[39] Spectroscopic data for **9**: IR (hexane, ν_{CO}): 2028 (s), 2000 (vs), 1976 (vs), 1957 (w). ^{1}H NMR (300.13 MHz, CDCl$_3$) δ: 3.09 (m, 1H, PCH^AH^{B}P, part of an ABX$_2$ spin system), 3.58 (m, 1H, PCH^AH^BP, part of an ABX$_2$ spin system), 5.79 (t, 1H, ^3J(HP) = 7.5 Hz), 7.20−7.87 (m, 20H, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$) δ: 44.0 (br, $w_{1/2}$ = 133 Hz). Anal. Calcd for C$_{37}$H$_{28}$Co$_2$O$_4$P$_2$·1/5 hexane: C, 62.54; H, 4.23. Found: C, 62.55; H, 4.09.

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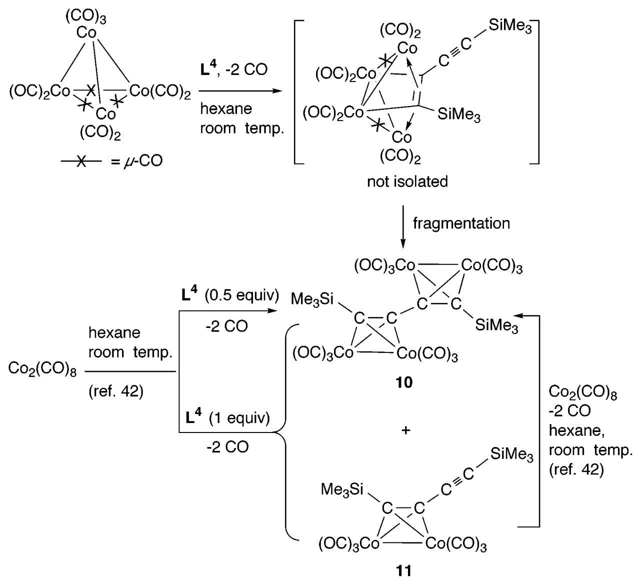
Scheme 4



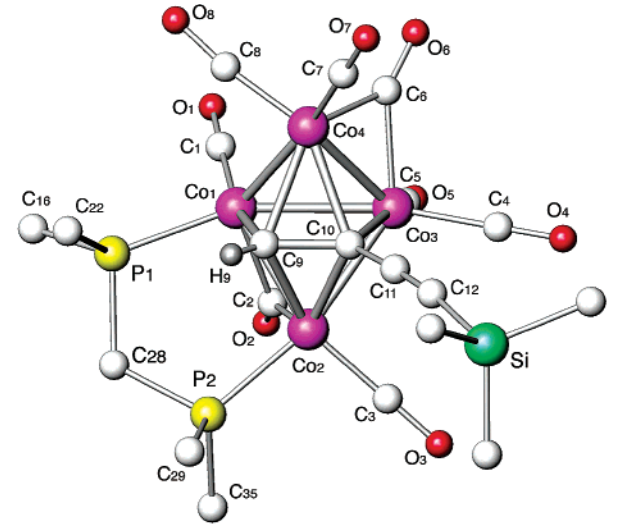


Figure 5. View of the molecular structure of cluster **16.** Only the ipso carbons of the phenyl groups are shown, and the hydrogen atoms have been omitted for clarity.

Complex **10** was obtained directly by reaction of $[Co_2(CO)_8]$ with $\mathbf{L^4}$, in addition to $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}Me_3SiC_2\text{-}C{\equiv}CSiMe_3)]$ (**11**),[42] or by reaction of the latter with $[Co_2(CO)_8]$[42] (Scheme 4). Complexes **10** and **11** also form by deprotonation of $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}Me_3SiC_2H)]$, itself prepared by reaction of $[Co_2(CO)_8]$ with $Me_3SiC{\equiv}CH$, followed by intermolecular C−C coupling between two molecules of the resulting complex.[43] Complex **10** has recently been isolated (in 6% yield) from the reaction of $[Mo_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(CO)_4Cp_2]$ with $[Co_2(CO)_8]$.[44] Preliminary experiments have indicated that **10** exhibits electrical conductivity.[43]

We then turned again to the diphosphine-stabilized cluster **1a** and reacted it with $\mathbf{L^4}$. Heating the reaction mixture in dichloromethane for ca. 3 days afforded the desired product $[Co_4(CO)_8(\mu\text{-dppm})(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2\text{-}C{\equiv}CSiMe_3)]$ (**12**) in addition to the known, red complex $[Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$ (**13**) and other unidentified products (Scheme 5). No reaction was detected at room temperature. Complex **13**, which results from fragmentation of **12** during reaction, has also been obtained directly by reaction of $[Co_2(CO)_6\text{-}(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$ with dppm.[45,46] In hexane at 80 °C, **1a** rapidly reacted with $\mathbf{L^4}$, but **12** was obtained in very low yield, whereas **13** was the major product. Increasing the reaction temperature favors the transformation of **12** to **13**. When **12** was exposed to air, it also transformed to **13**.

Both complexes **12** and **13** were identified by their IR and NMR spectra and elemental analyses. Their ^1H NMR spectra are very similar, with two different signals for the $-SiMe_3$ groups. Their PCH_2P protons appear as an ABXY or ABX_2 ($X = Y = P$) spin system, respectively. The identity of **12** was deduced by comparison with related $[Co_4(CO)_8(\mu\text{-dppm})(\mu_4\text{-}\eta^2\text{-alkyne})]$ clusters discussed above. The $\nu(C{\equiv}C)$ absorption was not observed for **12**, whereas it appears at 2115 cm^{-1} for **13**.[46]

The complex **13** was deprotected at the alkynyl group using Bu_4NF to give **14** (Scheme 5). When stronger proto-desilylation conditions were used (TBAF, moist THF, room temperature), complex **15** was obtained rapidly in high yield.[46] The proto-desilylation of **12** using $TBAF/THF-H_2O$ was monitored by TLC and necessitates a few hours to afford a green, air-sensitive product. We did not observe by ^1H NMR the CH resonance of the expected product $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)]$. The product **16** was characterized by ^1H NMR and IR spectroscopy, and its structure could be established by X-ray diffraction and shown to be, surprisingly, that of $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})(\mu_4\text{-}\eta^2\text{-}HC_2C{\equiv}CSiMe_3)]$. A view of the molecule is shown in Figure 5, and selected bond distances and angles are given in Table 5. Unexpectedly, desilylation occurred at the $Co-C-SiMe_3$ group and not at the alkynyl carbon. The formation of **16** thus contrasts with that of the mixed-metal cluster $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2\text{-}C{\equiv}CH)]^-$, which is obtained rapidly by proto-desilylation of $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]^-$.[47]

The molecular structure of **16** is thus similar to that of **2a**. The nonbonding Co(2)···Co(4) distance is 3.52 Å, and the dihedral angle between the wings is 117.8°. The orientation of the C(9)−C(10) bond, which is parallel to the Co(1)−Co(3) hinge of the metal butterfly, is again consistent with a minimization of the steric repulsions with the dppm ligand. To achieve a C−C coupling analogous to the oxidative coupling of **14** or of $[Co_2(CO)_4\text{-}(\mu\text{-dppm})(HC{\equiv}CC_2C{\equiv}CH)]$ under standard Eglinton-Glaser conditions $(Cu(OAc)_2$, pyridine), which afforded the dimer $[Co_2(CO)_4(dppm)(Me_3SiC_2C{\equiv}C-)]_2$[45] and the trimer $[Co_2(CO)_4(\mu\text{-dppm})(-C{\equiv}CC_2C{\equiv}C-)]_3$,[46] respectively, and with the aim of forming clusters linked through π-delocalized backbones, the isolated cluster **16** was reacted with TBAF, but deprotection at the alkynyl group was unsuccessful.

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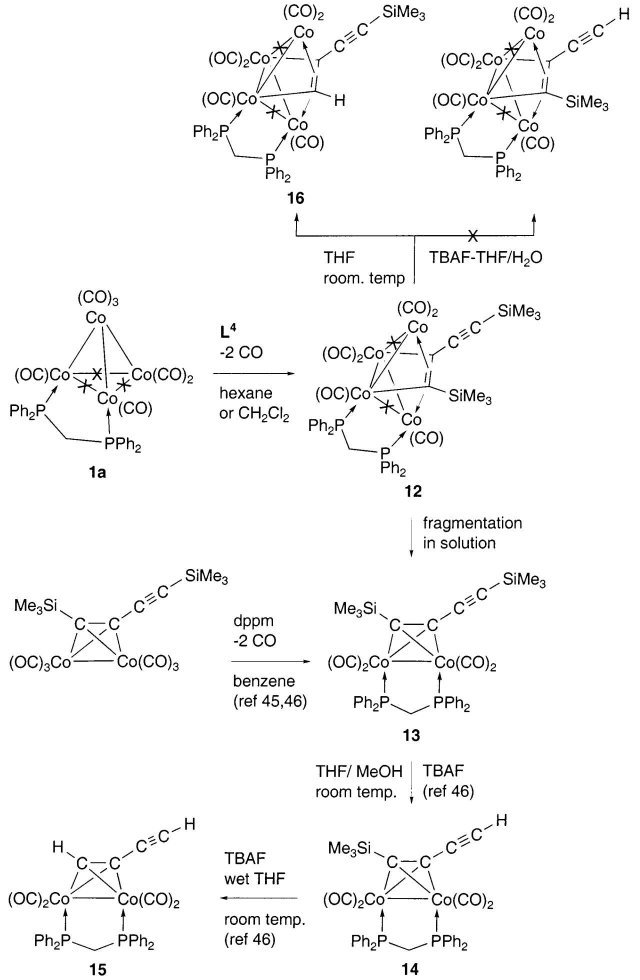
Scheme 5



In conclusion, we have shown that prior stabilization of the Co_4 core of $[Co_4(CO)_{12}]$ by the short-bite diphosphine ligands $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PNHPPh_2$ (dppa), or $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ (dppaSi) is beneficial and the stabilized tetrahedral clusters **1a**−**c** have been fully characterized. The butterfly clusters $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-}dppy)(\mu_4\text{-}\eta^2\text{-}PhC_2H)]$ (**2a**−**c**) were isolated in excellent yield by insertion of the alkyne into a Co−Co bond of the diphosphine-stabilized precursor or by reaction of $[Co_4(CO)_{12}]$ with phenylacetylene followed by CO substitution with the diphosphines dppy. Isomers were obtained that differ by the position of the bridging carbonyls, as established by an X-ray diffraction study on **2a** and **2′b**. Reaction of the new alkyne $PhC{\equiv}CC(O)NH(CH_2)_3Si(OMe)_3$ (**L**^{1}) with **1a**,**b** afforded the butterfly clusters $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-}dppy)\{\mu_4\text{-}\eta^2\text{-}PhC_2C(O)NH(CH_2)_3Si(OMe)_3\}]$ (**4a**,**b**), respectively. Similar reactions with the alkyne $HC{\equiv}CCH_2NHC(O)NH(CH_2)_3Si(OEt)_3$ (**L**^{2}) led to $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-}dppy)\{\mu_4\text{-}\eta^2\text{-}HC_2CH_2NHC(O)NH(CH_2)_3Si(OEt)_3\}]$ (**5a**,**b**). Cluster $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-}dppm)\{\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3\}]$ (**6a**) was obtained by reaction of **1a** with $HC{\equiv}C(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3$ (**L**^{3}). Reaction of $[Co_4(CO)_{12}]$ with **L**^{1} led to the formation of $[Co_2(CO)_6\{\mu\text{-}\eta^2\text{-}PhC_2C(O)NH(CH_2)_3\ Si(OMe)_3\}]$ (**7**), which was also prepared by reaction of $[Co_2(CO)_8]$ with **L**^{1}. Reaction of **1a** with dppaSi afforded the mixed-diphosphine cluster $[Co_4(\mu\text{-}CO)_3(CO)_5(\mu\text{-}dppm)(\mu\text{-}dppaSi)]$ (**8**). The 1,4-bis(trimethylsilyl) butadiyne (**L**^{4}) afforded with $[Co_4(CO)_{12}]$ the known complex $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}Me_3SiC_2{-})\}_2]$ (**10**) and with **1a** gave the desired product $[Co_4(CO)_8(\mu\text{-}dppm)(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$ (**12**), in addition to the known complex $[Co_2(CO)_4(\mu\text{-}dppm)(\mu_2\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$ (**13**). Proto-desilylation of **12** using TBAF/THF−H_2O occurred unexpectedly at the cluster core-bound alkyne carbon to afford the structurally characterized $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-}dppm)(\mu_4\text{-}\eta^2\text{-}HC_2C{\equiv}CSiMe_3)]$ (**16**), instead of the expected cluster $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-}dppm)(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)]$.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for 16 (estimated standard deviations in parentheses)

Co(1)−Co(2)	2.406(1)	Co(3)−C(4)	1.809(4)
Co(1)−Co(3)	2.594(1)	Co(3)−C(5)	1.785(4)
Co(1)−Co(4)	2.442(1)	Co(3)−C(6)	1.963(4)
Co(1)−P(1)	2.219(1)	Co(3)−C(10)	1.988(3)
Co(1)−C(1)	1.776(4)	Co(4)−C(6)	1.888(3)
Co(1)−C(2)	2.015(4)	Co(4)−C(7)	1.780(4)
Co(1)−C(9)	1.973(3)	Co(4)−C(8)	1.760(4)
Co(2)−Co(3)	2.483(1)	Co(4)−C(9)	2.069(3)
Co(2)−P(2)	2.184(1)	Co(4)−C(10)	2.074(3)
Co(2)−C(2)	1.844(3)	P(1)−C(28)	1.847(3)
Co(2)−C(3)	1.751(4)	P(2)−C(28)	1.848(3)
Co(2)−C(9)	2.020(3)	C(9)−C(10)	1.413(5)
Co(2)−C(10)	2.071(3)	C(10)−C(11)	1.437(5)
Co(3)−Co(4)	2.441(1)	C(11)−C(12)	1.203(5)
Co(2)−Co(1)−Co(3)	59.41(3)	Co(1)−Co(4)−C(10)	74.75(9)
Co(2)−Co(1)−Co(4)	93.09(3)	Co(3)−Co(4)−C(9)	74.7(1)
Co(2)−Co(1)−P(1)	97.56(3)	Co(3)−Co(4)−C(10)	51.46(9)
Co(2)−Co(1)−C(9)	53.8(1)	C(9)−Co(4)−C(10)	39.9(1)
Co(3)−Co(1)−Co(4)	57.89(3)	P(1)−C(28)−P(2)	115.8(2)
Co(3)−Co(1)−P(1)	155.77(3)	Co(1)−P(1)−C(28)	108.3(1)
Co(3)−Co(1)−C(9)	72.7(1)	Co(2)−P(2)−C(28)	108.6(1)
Co(4)−Co(1)−P(1)	121.67(4)	Co(1)−C(9)−Co(2)	74.1(1)
Co(4)−Co(1)−C(9)	54.6(1)	Co(1)−C(9)−Co(4)	74.3(1)
P(1)−Co(1)−C(9)	87.9(1)	Co(1)−C(9)−C(10)	107.9(2)
Co(1)−Co(2)−Co(3)	64.05(2)	Co(2)−C(9)−Co(4)	118.8(2)
Co(1)−Co(2)−P(2)	101.04(3)	Co(2)−C(9)−C(10)	71.7(2)
Co(1)−Co(2)−C(9)	52.04(9)	Co(2)−C(10)−Co(3)	75.4(1)
Co(1)−Co(2)−C(10)	75.62(9)	Co(2)−C(10)−Co(4)	116.2(1)
Co(3)−Co(2)−P(2)	165.09(3)	Co(2)−C(10)−C(9)	67.9(2)
Co(3)−Co(2)−C(9)	74.5(1)	Co(3)−C(10)−Co(4)	73.8(1)
Co(3)−Co(2)−C(10)	50.8(1)	Co(4)−C(10)−C(9)	69.8(2)
P(2)−Co(2)−C(9)	96.4(1)	C(10)−C(11)−C(12)	176.8(4)
P(2)−Co(2)−C(10)	128.0(1)	Co(1)−C(1)−O(1)	178.5(4)
C(9)−Co(2)−C(10)	40.4(1)	Co(1)−C(2)−O(2)	136.4(3)
Co(1)−Co(3)−Co(2)	56.54(3)	Co(2)−C(2)−O(2)	146.5(3)
Co(1)−Co(3)−Co(4)	57.95(3)	Co(2)−C(3)−O(3)	178.2(4)
Co(1)−Co(3)−C(10)	72.6(1)	Co(3)−C(4)−O(4)	179.7(5)
Co(2)−Co(3)−Co(4)	91.27(2)	Co(3)−C(5)−O(5)	179.7(4)
Co(2)−Co(3)−C(10)	53.81(9)	Co(3)−C(6)−O(6)	138.1(3)
Co(4)−Co(3)−C(10)	54.71(9)	Co(4)−C(6)−O(6)	143.2(3)
Co(1)−Co(4)−Co(3)	64.16(2)	Co(4)−C(7)−O(7)	178.5(4)
Co(1)−Co(4)−C(9)	51.04(9)	Co(4)−C(8)−O(8)	171.7(4)

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: toluene over sodium, tetrahydrofuran, hexane, and pentane over sodium-benzophenone, dichloromethane over phosphorus pentoxide. Nitrogen (Air liquide, R-grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. The ligands $Ph_2PCH_2PPh_2$ (dppm),[48] $Ph_2PNHPPh_2$ (dppa),[49] and $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ (dppaSi)[8] and the clusters $[Co_4(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC_2H)]$[20] and $[Co_4(CO)_{10}(\mu\text{-}dppa)]$[9] were synthesized by literature methods. Elemental C, H, and N analyses

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Table 6. Crystal Data and Data Collection Parameters for 1a, 2a, 2′b·0.5CH$_2$Cl$_2$, 8, and 16

	1a	**2a**	**2′b**·0.5CH$_2$Cl$_2$	**8**	**16**
formula	$C_{35}H_{22}Co_4O_{10}P_2$	$C_{41}H_{28}Co_4O_8P_2$	$C_{40}H_{27}Co_4NO_8P_2$ $\cdot 0.5CH_2Cl_2$	$C_{66}H_{63}Co_4NO_{11}P_4Si$	$C_{40}H_{32}Co_4O_8P_2Si$
fw	900.19	946.29	989.75	1433.86	966.41
cryst color	red	green	green	green	green
cryst syst	triclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.2475(3)	11.139(5)	22.045(5)	11.6370(2)	10.807(5)
b (Å)	11.6675(4)	11.258(5)	17.711(5)	17.9680(3)	12.078(5)
c (Å)	16.3918(7)	17.036(5)	21.797(5)	18.6170(3)	17.196(5)
α (deg)	74.4260(10)	83.81(2)	90.000(5)	70.6790(9)	79.490(5)
β (deg)	89.2080(10)	77.82(2)	110.557(5)	77.3030(9)	74.334(5)
γ (deg)	72.497(2)	65.28(2)	90.000(5)	73.4500(7)	68.537(5)
V (Å^3)	1795.70(11)	1896.5(13)	7968(3)	3487.19(10)	2002.5(14)
Z	2	2	4	2	2
D_{calcd} (g·cm^{-3})	1.665	1.657	1.652	1.366	1.603
wavelength (Å)	0.71069	0.71069	0.71069	0.71069	0.71069
μ (mm^{-1})	1.960	1.857	1.837	1.099	1.789
temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)
hkl limits	−14.14/−16.15/−20.23	0.14/−12.14/−21.22	−32.30/0.26/0.32	−11.15/−21.23/0.24	−14.15/−16.16/0.20
F(000)	900	952	3976	1472	976
θ limits (deg)	2.50−29.98	1.22−27.54	2.51−32.05	1.84−27.46	2.2−30.0
no. of data measd	12 946	8657	13 817	15 787	11 653
no. of data ($I > 2\sigma(I)$)	7210	6342	7360	12 392	7930
R^a	0.1014	0.0388	0.0559	0.0693	0.0552
$R_w{}^a$	0.1181	0.1154	0.1224	0.1978	0.1409
GOF	1.172	1.039	0.819	1.289	0.89
largest peak in final diff (e Å^{-3})	0.953	0.500	0.492	1.948	0.62

were performed by the Service de Microanalyses du CNRS (ULP Strasbourg). Infrared spectra (cm^{-1}) were recorded on a IFS-66 FTIR Bruker or a Perkin-Elmer 1600 series FTIR spectrometers. The ^{1}H NMR spectra were recorded at 200.13 or 300.13 MHz, ^{31}P{^{1}H} NMR spectra at 121.5, 161.97, or 202.46 MHz, and ^{29}Si{^{1}H} NMR spectra at 79.48 on Bruker AC200, AC300, AVANCE 300, AVANCE 400, or AVANCE 500 instruments.

Synthesis of [Co$_4$(μ-CO)$_3$(CO)$_7$(μ-dppm)] (1a). To a solution of [Co$_4$(CO)$_{12}$] (0.350 g, 0.612 mmol) in 50 mL of CH$_2$Cl$_2$ was added with stirring a solution of dppm (0.235 g, 0.612 mmol) in 10 mL of CH$_2$Cl$_2$ at room temperature. The color of the solution changed immediately from black to dark red. Analytical TLC (CH$_2$Cl$_2$/hexane, 40/60) indicated the formation of two products. The solvent was immediately evaporated under reduced pressure, and the residue was chromatographed on a SiO$_2$ column, with CH$_2$Cl$_2$/hexane (40/60) as eluent, yielding the green tetrasubstituted [Co$_4$(CO)$_8$(μ-dppm)$_2$] (0.097 g, 0.079 mmol, 13%) and the dark red product **1a** (0.380 g, 0.422 mmol, 70%). Recrystallization from hexane afforded after one week single crystals suitable for X-ray diffraction. IR (hexane, ν_{CO}): 2068 (vs), 2027 (vs), 2019 (vs), 1996 (w), 1989 (m), 1979 (w), 1845 (m), 1830 (sh), 1802 (sh), 1795 (w). ^{1}H NMR (200.13 MHz, CDCl$_3$) δ: 2.85 (br, 2H, CH$_2$), 7.12−7.45 (m, 20H, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$) δ: 27.8 (br, $w_{1/2}$ = 84 Hz). Anal. Calcd for $C_{35}H_{22}Co_4O_{10}P_2$: C, 46.7; H, 2.46. Found: C, 46.99; H, 2.53.

Synthesis of [Co$_4$(μ-CO)$_3$(CO)$_7$(μ-dppaSi)] (1c). A solution of dppaSi (0.083 g, 0.140 mmol) in 10 mL of CH$_2$Cl$_2$ was added to a solution of [Co$_4$(CO)$_{12}$] (0.080 g, 0.140 mmol) in 20 mL of the same solvent. The color of the solution changed in a few minutes from black to dark red, and analytical TLC (hexane) indicated that all starting material was consumed. The solution was filtered, the solvent was evaporated under reduced pressure, and extraction of the product with hexane followed by recrystallization from hexane afforded **1c** (0.097 g, 0.088 mmol, 63%). IR (hexane, ν_{CO}): 2068 (vs), 2024 (vs), 2018 (vs), 1999 (sh), 1994 (m), 1980 (sh), 1839 (m), 1793 (m), 1782 (m). ^{1}H NMR (300.13 MHz, CDCl$_3$) δ: −0.45 (m, 2H, SiCH$_2$), 0.12 (m, 2H, CH$_2$CH_2CH$_2$), 0.98 (t, ^3J(HH) = 7.14 Hz, 9H, CH$_3$), 2.54 (m, 2H, NCH$_2$), 3.38 (q, ^3J(HH) = 7.14 Hz, 6H, OCH$_2$), 7.48−7.81 (m, 20H, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$) δ: 92.8 (br, $w_{1/2}$ = 166 Hz). Anal. Calcd for $C_{43}H_{41}Co_4NO_{13}P_2Si$: C, 46.72; H, 3.74; N, 1.27. Found: C, 46.05; H, 3.68; N, 1.23.

Synthesis of [Co$_4$(μ-CO)$_2$(CO)$_6$(μ-dppm)(μ_4-η^2-PhC$_2$H)] (2a/2′a). Reaction of [Co$_4$(μ-CO)$_3$(CO)$_7$(μ-dppm)] (1a) with PhC≡CH. A solution of phenylacetylene (1.11 mL, 10.11 mmol) was added to a solution of **1a** (0.471 g, 0.523 mmol) in 80 mL of hexane. The mixture was stirred at room temperature for 10 days (or 3 h at 80 °C). The reaction was monitored by TLC (CH$_2$Cl$_2$/hexane, 50/50), which indicated the progressive formation of a green compound. The solution was filtered, and the solid was collected, washed with hexane, and recrystallized from CH$_2$Cl$_2$/hexane at −30 °C to give green, single crystals of **2a** (0.410 g, 0.433 mmol, 83%). IR (CH$_2$Cl$_2$, ν_{CO}): 2049 (s), 2007 (vs), 1977 (sh), 1839 (mw), 1785 (sh). IR (KBr, ν_{CO}): 2042 (s), 1999 (vs), 1979 (vs), 1847 (m), 1785 (m). ^{1}H NMR (200.13 MHz, CDCl$_3$) δ: 3.32 (m, 1H, CH^ACH^{B}P$_2$, part of an ABXY spin system), 3.93 (m, 1H, CH^{A}CH^BP$_2$, part of an ABXY spin system), 6.96−7.55 (m, 25H, Ph), HC$_2$ masked by aryl protons. ^{31}P{^{1}H} NMR (202.46 MHz, CDCl$_3$) δ: (25 °C) 28.3 (br, $w_{1/2}$ = 422 Hz); (0 °C) 27.9 (br), 29.0 (br). Anal. Calcd for $C_{41}H_{28}Co_4O_8P_2$: C, 52.04; H, 2.98. Found: C, 51.81; H, 3.01.

Reaction of [Co$_4$(CO)$_{10}$(μ_4-η^2-PhC$_2$H)] (3) with dppm. A solution of dppm (0.093 g, 0.243 mmol) in 25 mL of CH$_2$Cl$_2$ was added to a solution of **3** (0.150 g, 0.243 mmol) in 25 mL of CH$_2$Cl$_2$. The mixture was stirred at room temperature, and the color of the solution changed instantaneously from blue to green. TLC with CH$_2$Cl$_2$/hexane (50/50) as eluent indicated the formation of only one product and some decomposition. The residue was chromatographed on a SiO$_2$ column with CH$_2$Cl$_2$/hexane (50/50) as eluent. Recrystallization of the product from CH$_2$Cl$_2$/hexane at −30 °C afforded a green powder of **2′a** (0.168 g, 0.177 mmol, 73%). IR (CH$_2$Cl$_2$, ν_{CO}): 2049 (vs), 2007 (vs), 1983 (vs), 1836 (mw), 1784 (w). IR (KBr, ν_{CO}): 2045 (s), 1998 (vs, br), 1828 (m), 1737 (w). Anal. Calcd for $C_{41}H_{28}Co_4O_8P_2$: C, 52.04; H, 2.98. Found: C, 51.91; H, 3.11. The ^{1}H and ^{31}P NMR data are the same as for **2a**.

Synthesis of [Co$_4$(μ-CO)$_2$(CO)$_6$(μ-dppa)(μ_4-η^2-PhC$_2$H)] (2b/2′b). Reaction of [Co$_4$(μ-CO)$_3$(CO)$_7$(μ-dppa)] (1b) with PhC≡CH. A solution of phenylacetylene (0.37 mL, 3.37 mmol) was added to a solution of **1b** (0.224 g, 0.248 mmol) in 60 mL of hexane. The mixture was heated to 80 °C for 3 h, and the reaction was monitored by TLC (CH_2Cl_2/hexane, 40/60), which indicated the progressive formation of a green compound. This latter was treated like **2a**, and green crystals of **2b** were obtained after recrystallization for 10 days (0.220 g, 0.232 mmol, 94%). IR (CH_2Cl_2, ν_{CO}): 2050 (vs), 2005 (vs), 1971 (sh), 1832 (m). IR (KBr, ν_{CO}): 2041 (vs), 2005 (s), 1990 (vs), 1972 (vs), 1947 (m), 1840 (m), 1810 (m). ^{1}H NMR (300.13 MHz, $CDCl_3$) δ: 4.11 (br, NH), 6.40−7.68 (m, 25H, Ph), HC_2 masked by aryl protons. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 81.2 br, 87.4 br. Anal. Calcd for $C_{40}H_{27}Co_4NO_8P_2{\cdot}1/3C_6H_{14}$: C, 51.68; H, 3.27; N, 1.44. Found: C, 51.67; H, 3.36; N, 1.57.

Reaction of [$Co_4(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC_2H)$] (3) with dppa. Similarly to the synthesis of **2′a**, reaction of **3** (0.250 g, 0.405 mmol) with dppa (0.156 g, 0.405 mmol) was monitored by TLC, which indicated the formation of the desired product and some decomposition. Recrystallization of the product gave green single crystals of **2′b** (0.360 g, 0.379 mmol, 94%), suitable for X-ray diffraction (see text). IR (CH_2Cl_2, ν_{CO}): 2048 (vs), 2003 (vs), 1987 (sh), 1827 (m). IR (KBr, ν_{CO}): 2046 (vs), 2005 (s), 1993 (sh), 1985 (vs), 1922 (m), 1841 (mw), 1819 (m). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 79.7 br, 87.6 br. Anal. Calcd for $C_{40}H_{27}Co_4NO_8P_2{\cdot}1/2CH_2Cl_2$: C, 50.04; H, 2.90; N, 1.44. Found: C, 50.42; H, 3.12; N, 1.58. The ^{1}H NMR spectrum is the same as that for **2b** (see above).

Synthesis of [$Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppaSi})(\mu_4\text{-}\eta^2\text{-}PhC_2H)$] (2c/2′c). Reaction of [$Co_4(\mu\text{-}CO)_3(CO)_7(\mu\text{-dppaSi})$] (1c) with PhC≡CH. Cluster **1c** (0.100 g, 0.090 mmol) and phenylacetylene (0.098 mL, 0.892 mmol) were refluxed in 20 mL of CH_2Cl_2 for 3 h. The color of the solution changed from dark red to green. The solution was filtered, the solvent was evaporated, and the residue was recrystallized from CH_2Cl_2/hexane to give a green powder of **2c** (0.091 g, 0.079 mmol, 88%). IR (CH_2Cl_2, ν_{CO}): 2048 (s), 2000 (vs), 1971 (vs), 1831 (m), 1789 (w). IR (KBr, ν_{CO}): 2041 (s), 1997 (vs), 1969 (vs), 1830 (m). ^{1}H NMR (300.13 MHz, $CDCl_3$) δ: −0.045 (m, 2H, $SiCH_2$), 0.94 (m, 11H, $CH_2CH_2CH_2$ and CH_3), 3.35 (m, 2H, NCH_2), 3.47 (m, 6H, OCH_2), 6.81−7.71 (m, 25H, Ph), HC_2 masked by aryl protons. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 81.0 (br, $w_{1/2}$ = 337 Hz). Anal. Calcd for $C_{49}H_{47}Co_4NO_{11}P_2Si{\cdot}1/3C_6H_{14}$: C, 51.89; H, 4.41; N, 1.19. Found: C, 51.71; H, 4.77; N, 1.43.

Reaction of [$Co_4(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC_2H)$] (3) with dppaSi. By a procedure similar to that detailed for **2′b**, the product **2′c** was synthesized by reaction of **3** (0.252 g, 0.408 mmol) with dppaSi (0.242 g, 0.408 mmol) in CH_2Cl_2. TLC indicated that the reaction was instantaneous. Yield of **2′c**: 0.422 g, 0.367 mmol, 90%. IR (CH_2Cl_2, ν_{CO}): 2050 (vs), 2001 (vs), 1970 (s), 1834 (m), 1783 (w). IR (KBr, ν_{CO}): 2045 (vs), 1995 (vs), 1962 (s), 1839 (m), 1823 (m). Anal. Calcd for $C_{49}H_{47}Co_4NO_{11}P_2Si{\cdot}1/3C_6H_{14}$: C, 51.89; H, 4.41; N, 1.19. Found: C, 51.93; H, 5.07; N, 1.64. The ^{1}H and $^{31}P\{^1H\}$ NMR data are the same as for **2c**.

Synthesis of PhC≡CC(O)NH(CH_2)$_3$Si(OMe)$_3$ (L^1). A mixture of 3-phenylpropiolic acid (2.00 g, 13.70 mmol) and thionyl chloride (1.95 g, 1.20 mL, 16.44 mmol) in 50 mL of toluene was stirred and heated to reflux for 3 h. The orange reaction mixture was allowed to cool to room temperature, and the solvent was evaporated to dryness. It was dissolved in 25 mL of freshly distilled toluene, and the mixture was cooled in an ice bath. A solution of 3-aminopropyltrimethoxysilane (4.82 mL, 27.40 mmol) in 25 mL of toluene was then added dropwise. After the addition was complete, the ice bath was removed and the mixture stirred at room temperature for 1 h and then poured into 100 mL of cold water. The mixture was filtered, and the solid was discarded. The aqueous phase was separated and extracted with 50 mL of ethyl acetate, and this extract was combined with the organic phase. The organic fraction was dried over $MgSO_4$, and evaporation of the solvent afforded a viscous, yellow liquid of **L**^{1} (1.84 g, 5.97 mmol, 44% (based on acid)). IR (CH_2Cl_2): 2220 (s, $\nu_{C\equiv C}$), 1654 (s, $\nu_{C=O}$), 1514 (vs, δ_{NH}). ^{1}H NMR (300.13 MHz, $CDCl_3$) δ: 0.69 (m, 2H, $SiCH_2$), 1.70 (m, 2H, $CH_2CH_2CH_2$), 3.34 (m, 2H, NCH_2), 3.51 (s, 9H, CH_3), 6.26 (br, NH), 7.31−7.56 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$) δ: 6.18 (s, $SiCH_2$), 22.06 (s, $CH_2CH_2CH_2$), 42.13 (s, NCH_2), 50.28 (s, CH_3), 83.18 and 84.22 (2s, C≡C), 120.28 (s, C_{ipso} of C_6H_5), 128.46, 129.44, and 132.33 (3s, CH of C_6H_5), 153.40 (s, C=O). $^{29}Si\{^1H\}$ NMR (79.48 MHz, $CDCl_3$) δ: − 42.7.

Synthesis of [$Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})\{\mu_4\text{-}\eta^2\text{-}PhC_2C(O)NH(CH_2)_3Si(OMe)_3\}$] (4a). A solution of PhC≡CC(O)NH(CH_2)$_3$Si(OMe)$_3$ (**L**^{1}) (1.256 g, 4.080 mmol) in 5 mL of CH_2Cl_2 was added to a solution of **1a** (0.370 g, 0.411 mmol) in 40 mL of CH_2Cl_2. The mixture was heated to reflux, and the reaction was monitored by TLC (CH_2Cl_2/hexane, 40/60) and followed the disappearance of **1a**. A green product progressively formed which did not migrate on the TLC plate, and after 4 h formation of an other green, unidentified product was observed, which migrates immediately after the precursor. The reaction was stopped after 7 h. The solution was filtered, and the solvent was removed under reduced pressure. Purification from toluene/pentane at −20 °C gave viscous **4a** (0.333 g, 0.289 mmol, 71%). IR (CH_2Cl_2): 2061 (sh), 2054 (s), 2029 (m), 2002 (vs), 1976 (m), 1830 (w), $\nu_{C\equiv O}$, 1646 (vs, $\nu_{C=O}$). ^{1}H NMR (300.13 MHz, $CDCl_3$) δ: 0.68 (m, 2H, $SiCH_2$), 1.69 (m, 2H, $CH_2CH_2CH_2$), 3.35 (m, 2H, NCH_2), 3.57 (s, 9H, CH_3), 6.36 (br, 1H, NH), 7.03−8.35 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 39.8 (br, $w_{1/2}$ = 83 Hz).

Synthesis of [$Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppa})\{\mu_4\text{-}\eta^2\text{-}PhC_2C(O)NH(CH_2)_3Si(OMe)_3\}$] (4b). By a similar procedure, the reaction of **2b** (0.157 g, 0.166 mmol) with PhC≡CC(O)NH(CH_2)$_3$Si(OMe)$_3$ (**L**^{1}) (0.511 g, 1.66 mmol) in 25 mL of CH_2Cl_2 gave **4b** (0.132 g, 0.114 mmol, 69%). IR (CH_2Cl_2): 2054 (m), 2015 (s), 2000 (vs), 1970 (sh), 1832 (mbr), $\nu_{C\equiv O}$, 1646 (m, $\nu_{C=O}$). ^{1}H NMR (300.13 MHz, $CDCl_3$) δ: 0.42 (m, 2H, $SiCH_2$), 1.70 (m, 2H, $CH_2CH_2CH_2$), 3.11 (m, 2H, NCH_2), 3.46 (s, 9H, CH_3), 5.68 (br, NH), 6.53 (m, NH), 7.11−7.51 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 91.1 (br, $w_{1/2}$ = 81 Hz), 103.5 (br, $w_{1/2}$ = 648 Hz).

Synthesis of [$Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})\{\mu_4\text{-}\eta^2\text{-}HC_2CH_2NHC(O)NH(CH_2)_3\ Si(OEt)_3\}$] (5a). A solution of **1a** (0.134 g, 0.148 mmol) and HC≡CCH$_2$NHC(O)NH(CH_2)$_3$Si(OEt)$_3$ (0.445 g, 1.470 mmol) was refluxed in 35 mL of CH_2Cl_2 for 7 h. Completion of the reaction was monitored by TLC (CH_2Cl_2/hexane, 40/60) to follow the disappearance of **1a**. The solvent was then removed under vacuum, and the product was purified from toluene/pentane at −20 °C to afford green, viscous **5a** (0.141 g, 0.123 mmol, 83%). IR (CH_2Cl_2): 2052 (s), 1993 (vs), 1966 (m), 1831 (w) $\nu_{C\equiv O}$; 1679 (vs, $\nu_{C=O}$). ^{1}H NMR (300.13 MHz, $CDCl_3$) δ: 0.62 (m, 2H, $SiCH_2$), 1.21 (m, 9H, CH_3), 1.60 (m, 2H, $CH_2CH_2CH_2$), 2.19 (br, 1H, $CH^ACH^BP_2$, part of an ABXY spin system), 3.16 (br, 3H, $HNCH_2CH_2$ and $CH^ACH^BP_2$, part of an ABXY spin system), 3.79 (m, 6H, OCH_2), 3.96 (m, 2H, HC_2CH_2N), 5.14 (m, 2H, NH), 6.91−7.85 (m, 20H, Ph), HC_2 masked by aryl protons. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 26.4 (br, $w_{1/2}$ = 83 Hz).

Synthesis of [$Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppa})\{\mu_4\text{-}\eta^2\text{-}HC_2CH_2NHC(O)NH(CH_2)_3\ Si(OEt)_3\}$] (5b). By a similar procedure, refluxing a solution of **1b** (0.107 g, 0.118 mmol) with HC≡CCH$_2$NHC(O)NH(CH_2)$_3$Si(OEt)$_3$ (0.356 g, 1.184 mmol) in 30 mL of CH_2Cl_2 for 5 h gave **5b** (0.109 g, 0.095 mmol, 81%). IR (CH_2Cl_2): 2049 (vs), 1998 (vs), 1970 (sh), 1832 (m), $\nu_{C\equiv O}$; 1679 (vs, $\nu_{C=O}$). ^{1}H NMR (300.13 MHz, $CDCl_3$) δ: 0.62 (m, 2H, $SiCH_2$), 1.21 (m, 9H, CH_3), 1.42 (m, 2H, $CH_2CH_2CH_2$), 3.16 (m, 2H, $HNCH_2CH_2$), 3.82 (m, 6H, OCH_2), 3.95 (m, 2H, HC_2CH_2N), 4.83 (m, 2H, NH), 7.08−7.80 (m, 20H, Ph), H−C_2 and PNHP masked. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 78.3 (br, $w_{1/2}$ = 331 Hz), 89.0 (br, $w_{1/2}$ = 248 Hz).

Synthesis of [$Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})\{\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2OC(O)NH(CH_2)_3\ Si(OEt)_3\}$] (6a). A solution of **1a** (0.300 g, 0.333 mmol) and HC≡C(CH_2)$_2$OC(O)NH(CH_2)$_3$Si(OEt)$_3$ (1.05 g, 3.310 mmol) was refluxed in 40 mL of CH_2Cl_2 for 9 h. The solvent was removed under reduced pressure, and the viscous, green product was extracted with hexane. After keeping the extract for 3 days at −20 °C, the product precipitated, the solvent was discarded, and the residue was triturated with pentane to afford green **6a** (0.354 g, 0.304 mmol, 92%). IR (CH_2Cl_2): 2048 (vs), 2001 (vs), 1975 (sh), 1831 (w), $\nu_{C\equiv O}$; 1720 (m, $\nu_{C=O}$). ^1H NMR (300.13 MHz, $CDCl_3$) δ: 0.63 (m, 2H, $SiCH_2$), 1.22 (t, $^3J(HH) = 7.15$ Hz, 9H, CH_3), 1.61 (m, 2H, $CH_2CH_2CH_2$), 2.50 (m, 1H, $CH^ACH^BP_2$, part of an ABXY spin system), 3.07 (m, 1H, $CH^ACH^BP_2$, part of an ABXY spin system), 3.14 (m, 4H, HC_2CH_2 and $HNCH_2$), 3.85 (m, 8H, OCH_2CH_2 and OCH_2CH_3), 4.74 (br, NH). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 29.8 (br, $w_{1/2} = 249$ Hz).

Synthesis of $[Co_2(CO)_6\{\mu\text{-}\eta^2\text{-}PhC_2C(O)NH(CH_2)_3Si(OMe)_3\}]$ (7). A solution of $[Co_2(CO)_8]$ (0.320 g, 0.940 mmol) in 30 mL of CH_2Cl_2 and $PhC\equiv CC(O)NH(CH_2)_3Si(OMe)_3$ (**L^1**) (0.298 g, 0.968 mmol) was stirred at room temperature for 50 min. 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 **7** as red crystals (0.380 g, 0.640 mmol, 68%). This product was also obtained, in lower yield (26%), by reaction of **L^1** with $[Co_4(CO)_{12}]$. IR (hexane): 2096 (m), 2064 (vs), 2032 (vs), 1977 (w), $\nu_{C\equiv O}$; 1660 (m, $\nu_{C=O}$). ^1H NMR (300.13 MHz, $CDCl_3$) δ: 0.70 (m, 2H, $SiCH_2$), 1.74 (m, 2H, $CH_2CH_2CH_2$), 3.44 (m, 2H, NCH_2), 3.56 (s, 9H, CH_3), 6.17 (br, 1H, NH), 7.33−7.79 (m, 5H, Ph). Anal. Calcd for $C_{21}H_{21}Co_2NO_{10}Si$: C, 42.51; H, 3.57; N, 2.36. Found: C, 42.48; H, 3.51; N, 2.31.

Synthesis of $[Co_4(\mu\text{-}CO)_3(CO)_5(\mu\text{-}dppm)(\mu\text{-}dppaSi)]$ (8). $[Co_4(\mu\text{-}CO)_3(CO)_7(\mu\text{-}dppm)]$ (**1a**) (0.100 g, 0.111 mmol) and dppaSi (0.065 g, 0.111 mmol) in 30 mL of CH_2Cl_2 were mixed and stirred at room temperature. The reaction was stopped after ca. 3 h when all starting materials were consumed (TLC). Separation of the reaction mixture was performed by preparative TLC (CH_2Cl_2), giving three green bands. Immediate extraction with CH_2Cl_2 of the first and the third band afforded unidentified products and that of the second band $[Co_4(CO)_8(\mu\text{-}dppm)(\mu\text{-}dppaSi)]$ (**8**) (0.089 g, 0.062 mmol, 56%). Data for **8**: IR (CH_2Cl_2, ν_{CO}): 2054 (m), 2005 (s), 1971 (vs), 1955 (sh), 1820 (w), 1791 (m), 1765 (m). ^1H NMR (300.13 MHz, $CDCl_3$) δ: −0.39 (m, 2H, $SiCH_2$), 0.67 (m, 2H, $CH_2CH_2CH_2$), 0.94 (m, 9H, CH_3), 2.52 (br, 2H, PCH_2P), 3.43 (m, 8H, OCH_2 and NCH_2), 6.90−7.61 (m, 40H, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 28.1 (br, $w_{1/2} = 146$ Hz), 100.5 (br, $w_{1/2} = 219$ Hz). Anal. Calcd for $C_{66}H_{63}Co_4NO_{11}P_4Si$: C, 55.28; H, 4.43; N, 0.98. Found: C, 54.64; H, 4.43; N, 0.95.

Reaction of $[Co_4(CO)_{12}]$ with $Me_3SiC\equiv CC\equiv CSiMe_3$. To a solution of $[Co_4(CO)_{12}]$ (0.153 g, 0.268 mmol) in 25 mL of hexane was added a solution of 1,4-bis(trimethylsilyl)butadiyne (0.522 g, 2.680 mmol) in 2 mL of hexane. TLC with hexane as eluent indicated the formation of a blue product, which transforms rapidly to a green one, and other secondary products. The reaction was stopped after 24 h stirring at room temperature. Chromatographic separation on a SiO_2 column with hexane as eluent afforded green $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}Me_3SiC_2-)\}_2]$ (**10**) (0.042 g, 0.055 mmol, 21%). IR (hexane, ν_{CO}): 2094 (m), 2076 (s), 2055 (vs), 2027 (vs), 1979 (w). ^1H NMR (300.13 MHz, $CDCl_3$) δ: 0.12 (s, $SiMe_3$). Anal. Calcd for $C_{22}H_{18}Co_4O_{12}Si_2$: C, 34.48; H, 2.37. Found: C, 34.79; H, 1.93.

Reaction of 1a with $Me_3SiC\equiv CC\equiv CSiMe_3$. A solution of **1a** (0.235 g, 0.261 mmol) in 30 mL of CH_2Cl_2 and 1,4-bis(trimethylsilyl)butadiyne (0.453 g, 2.326 mmol) was heated at 55 °C for 3 days. The reaction was monitored by TLC, which indicated the formation of two major products (red and green) and other secondary unidentified products. The solvent was removed, and the mixture was separated by preparative TLC with hexane/CH_2Cl_2 (50/50) as eluent. The red band yielded $[Co_2(CO)_4(\mu\text{-}dppm)(\mu\text{-}\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)]$ (**13**) (0.045 g, 0.055 mmol, 21%) after recrystallization from hexane. IR (hexane, ν_{CO}): 2058 (w), 2030 (vs), 2008 (vs), 1982 (vs), 1960 (m). ^1H NMR (300.13 MHz, $CDCl_3$) δ: 0.23 (s, 9H, $SiMe_3$), 0.36 (s, 9H, $SiMe_3$), 3.33 (m, 1H, PCH^AH^BP, part of an ABX_2 spin system), 3.89 (m, 1H, PCH^AH^BP, part of an ABX_2 spin system), 7.02−7.47 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 37.6 (br, $w_{1/2} = 133$ Hz). Anal. Calcd for $C_{39}H_{40}Co_2O_4P_2Si_2$: C, 57.92; H, 4.99. Found: C, 57.37; H, 4.65.

The green band gave $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-}dppm)(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)]$ (**12**) (0.081 g, 0.078 mmol, 30%) by extraction with hexane. The product should be stored at −20 °C in the solid state. IR (hexane, ν_{CO}): 2050 (vs), 2005 (vs), 1994 (m), 1967 (w), 1843 (m), 1835 (m). ^1H NMR (300.13 MHz, $CDCl_3$) δ: −0.18 (s, 9H, $\equiv CSiMe_3$), 0.33 (s, 9H, $-C_2SiMe_3$), 4.23 (m, 1H, PCH^AH^BP, part of an ABXY spin system), 5.00 (m, 1H, PCH^AH^BP, part of an ABXY spin system), 7.15−7.94 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 25.0 (br, $w_{1/2} = 498$ Hz). Anal. Calcd for $C_{43}H_{40}Co_4O_8P_2Si_2$: C, 49.73; H, 3.88. Found: C, 50.12; H, 4.51.

Proto-desilylation of 12. To a solution of **12** (0.060 g, 0.057 mmol) in 10 mL of THF was added dropwise with stirring n-Bu_4NF (1.0 M in THF/5 wt % H_2O; 0.014 mmol, 0.014 mL). The mixture was stirred at room temperature for 8 h until TLC indicated complete consumption of the precursor. A minor, green fraction followed that of the desired product. The solvent was evaporated under vacuum, and the product was extracted with CH_2Cl_2 and filtered through Celite. Separation by preparative TLC with hexane/CH_2Cl_2 (50/50) as eluent afforded $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-}dppm)(\mu_4\text{-}\eta^2\text{-}HC_2C\equiv CSiMe_3)]$ (**16**) (0.028 g, 0.028 mmol, 50%). IR (hexane, ν_{CO}): 2057 (vs), 2022 (vs), 2016 (vs), 1988 (m), 1866 (m), 1838 (w). ^1H NMR (300.13 MHz, $CDCl_3$) δ: 0.15 (s, 9H, $SiMe_3$), 3.22 (m, 1H, PCH^AH^BP, part of an ABXY spin system), 3.95 (m, 1H, PCH^AH^BP, part of an ABXY spin system), 7.05−7.65 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ: 30.7 br. Anal. Calcd for $C_{40}H_{32}Co_4O_8P_2Si$: C, 49.71; H, 3.34. Found: C, 50.12; H, 3.55.

X-ray Structural Analyses of $[Co_4(\mu\text{-}CO)_3(CO)_7(\mu\text{-}dppm)]$ (1a), $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-}dppm)(\mu_4\text{-}\eta^2\text{-}PhC_2H)]$ (2a), $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-}dppa)(\mu_4\text{-}\eta^2\text{-}PhC_2H)]\cdot 0.5CH_2Cl_2$ (2′b·0.5CH$_2$Cl$_2$), $[Co_4(\mu\text{-}CO)_3(CO)_5(\mu\text{-}dppm)(\mu\text{-}dppaSi)]$ (8), and $[Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-}dppm)(\mu_4\text{-}\eta^2\text{-}HC_2C\equiv CSiMe_3)]$ (16). Single crystals were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo Kα, $\lambda = 0.71073$ Å). The complete conditions of data collection (Denzo software) and structure refinements are given in Table 6. 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.[50,51] The absorption was corrected empirically with Sortav. All non-hydrogen atoms except those of the disordered $CSi(OEt)_3$ group in **8** were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, bond distances, and angles for **1a**, **2a**, **2′b**·0.5CH$_2$Cl$_2$, **8**, and **16**, respectively. This material is available free of charge via the Internet at http://pubs.acs.org. This material has also been deposited in CIF format at http://pubs.acs.org and with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-214676-214680. 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).

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