Inorg. Chem. **2004**, *43*, 57–71

Inorganic Chemistry
Article

Reactions of the Tetrahedral Clusters $[MCo_3(CO)_{12}]^-$ (M = Ru, Fe) with Functional Mono- and Diynes

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Received July 16, 2003

The tetrahedral cluster $[RuCo_3(CO)_{12}]^-$ reacts with various alkynes, including the new $PhC{\equiv}CC(O)NHCH_2C{\equiv}CH$ (**L^1**), to afford the butterfly clusters $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}RC_2R')]^-$ (**1,** R = R′ = C(O)OMe; **2**, R = H, R′ = Ph; **3**, R = H, R′ = $MeC{=}CH_2$; **4**, R = H, R′ = $CH_2OCH_2C{\equiv}CH$; **5**, R = H, R′ = $CH_2NHC(O)C{\equiv}CPh$), in which the ruthenium atom occupies a hinge position and the alkyne is coordinated in a μ_4-η^2 fashion. Reaction of the anions **1**–**3** with $[Cu(NCMe)_4]BF_4$ led to selective loss of the 12e fragment $Co(CO)^-$ to form $[RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}RC_2R')]$ (**6,** R = R′ = C(O)OMe; **7,** R = H, R′ = Ph; **8**, R = H, R′ = $MeC{=}CH_2$). To prepare functionalized $RuCo_3$ or $FeCo_3$ clusters that could be subsequently condensed with a silica matrix via the sol–gel method, we reacted $[MCo_3(CO)_{12}]^-$ (M = Ru, Fe) with the alkyne $PhC{\equiv}CC(O)NH(CH_2)_3Si(OMe)_3$ (**L^2**) and obtained the butterfly clusters $[MCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC_2C(O)NH(CH_2)_3Si(OMe)_3)]^-$ **9** and **10**, respectively. Air-stable $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]^-$ (**11**) was obtained from 1,4-bis(trimethylsilyl)butadiyne and reacted with $[Cu(NCMe)_4]BF_4$ to give $[RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2C{\equiv}CSiMe_3)]$ (**12**), owing to partial ligand proto-desilylation, and not the expected $[RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$. Reaction of **11** with [NO]BF$_4$ afforded, in addition to **12**, $[RuCo_3(CO)_9(NO)(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]$ (**13**) owing to selective CO substitution on a wing-tip cobalt atom with NO. The thermal reaction of **11** with $[AuCl(PPh_3)]$ led to replacement of a CO on Ru by the PPh_3 originating from $[AuCl(PPh_3)]$ and afforded $[RuCo_3(CO)_9(PPh_3)(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)]^-$ (**14**), also obtained directly by reaction of **11** with one equivalent of PPh_3. Proto-desilylation of **11** using TBAF/THF–H_2O afforded $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)]^-$ (**15**) which, by Sonogashira coupling with 1,4-diiodobenzene, yielded the dicluster complex $[\{[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}C)]\}_2C_6H_4]^{2-}$ (**16**). The crystal structures of NEt_4·**3a**, NEt_4·**4a**, **6**, NEt_4·**11b**, NEt_4·**14**, and $[N(n\text{-}Bu)_4]$·**15a** have been determined by X-ray diffraction. Preliminary results indicate the potential of silica-tethered alkyne mixed-metal clusters, obtained by the sol–gel method, as precursors to bimetallic particles.

Introduction

We are currently interested in the selective incorporation of functional alkynes into metal carbonyl clusters in order to obtain low oxidation state molecular precursors to surface-anchored metal clusters that could lead to nanomaterials of controlled properties.[1,2] A covalent linkage between the metal cluster and the required functionality should enable a better control of the anchoring process and prevent the metal leaching often associated with the presence of dative bonds between the ligand and the metal(s). Although the reactions of simpler alkynes with carbonyl clusters have long been investigated, the factors governing their selectivity are not fully understood.[3] Various isomeric structures can be envisaged for the reaction products, and ways to chemically differentiate in the precursor cluster the various metal−metal bonds, which are reactive sites, include the use of bridging ligands, as recently explored with $[Co_4(CO)_{10}(\mu\text{-dppy})]$ (dppy

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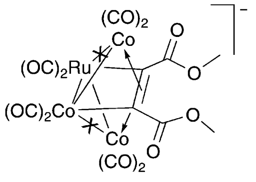
10.1021/ic034832k CCC: $27.50

= $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PNHPPh_2$ (dppa), or $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ (dppaSi)).[4] An extension of these studies to related isoelectronic mixed-metal systems was felt particularly desirable,[5] and we report here on the reactions of the tetrahedral clusters $[MCo_3(CO)_{12}]^-$ (M = Ru, Fe) with functional alkynes and compare the results with those obtained with $[Co_4(CO)_{12}]$ and its derivatives. Some of the resulting alkyne clusters were reacted with electrophilic reagents, such as $[Cu(NCMe)_4]BF_4$ or $[NO]BF_4$, to give neutral derivatives with higher solubility.

Furthermore, clusters linked through π-delocalized backbones have come under considerable scrutiny, owing to expectations that new structural, redox, and conductivity properties may result. The vast majority of such studies have involved the linking of identical homometallic cores,[6−14] and since only few examples of heterometallic clusters linked by unsaturated bridges have been reported,[15−17] we have used diynes to realize such a connection between $RuCo_3$ clusters.

Results and Discussion

The reaction between $[RuCo_3(CO)_{12}]^-$ and excess MeOC(O)C≡CC(O)OMe (dmad) in refluxing THF afforded the butterfly cluster **1** resulting from insertion of the alkyne into a Co−Co bond. A similar structure has been previously reported with PhC≡CPh.[18] When unsymmetrical alkynes of the type HC≡CR were reacted with $[RuCo_3(CO)_{12}]^-$, two isomers **a** and **b** were often obtained (Scheme 1) which differ in the orientation of the alkyne with respect to the Co−Ru vector. Surprisingly, no reaction was observed when R = $-CH_2Cl$ or $-(CH_2)_3C{\equiv}CH$ nor with PhC≡CC(O)Cl.



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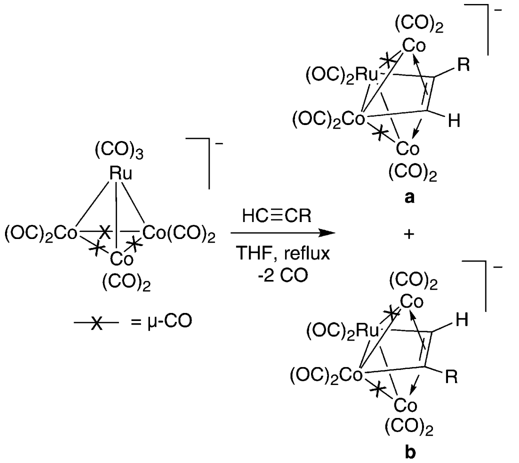
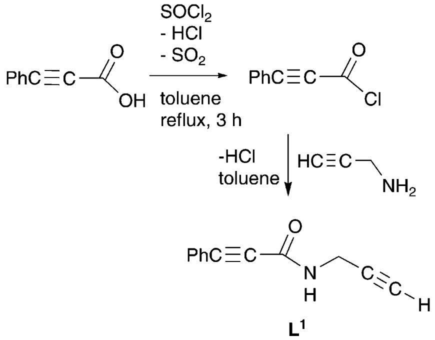
Scheme 1. Reaction of the Cluster $[RuCo_3(CO)_{12}]^-$ with Terminal Alkynes



2 R = Ph
3 R = MeC=CH_2
4 R = $CH_2OCH_2C{\equiv}CH$
5 R = $CH_2N(H)C(O)C{\equiv}CPh$

All reactions proceeded either in refluxing THF or acetone for a few hours and were monitored by IR spectroscopy while the color of the solution changed from red to violet. Recrystallization afforded clusters of the type $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2R)]^-$ (R = Ph (**2**), MeC=CH_2 (**3**), $CH_2OCH_2C{\equiv}CH$ (**4**), $CH_2N(H)C(O)C{\equiv}CPh$ (**5**)) in excellent yields (73−95%). The products have been characterized by IR and ^1H NMR spectroscopic methods, elemental analysis, and, in the case of **3a** and **4a**, by X-ray diffraction.

The new diyne ligand PhC≡CC(O)NHCH$_2$C≡CH ($\mathbf{L}^1$), which contains internal and terminal carbon−carbon triple bonds, was prepared in two steps by the method outlined in eq 1 which involved treatment of phenylpropynoic acid with thionyl chloride, followed by the addition of propargylamine. The ligand was characterized by ^1H, ^{13}C NMR, IR spectroscopy, and elemental analysis. The reactivity of internal alkynes is lower than that of terminal alkynes, which in turn



(1)

$\mathbf{L}^1$

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Table 1. Selected Bond Distances [Å] and Bond Angles [deg] for the Anion **3a** with Estimated Standard Deviations in Parentheses

Molecule A							
Ru(1)−Co(1)	2.751(1)	Co(1)−Co(2)	2.462(2)	Co(2)−C(4)	1.78(1)	Co(3)−C(8)	1.83(1)
Ru(1)−Co(2)	2.541(2)	Co(1)−Co(3)	2.464(2)	Co(2)−C(5)	1.74(1)	Co(3)−C(11)	2.070(8)
Ru(1)−Co(3)	2.545(2)	Co(1)−C(1)	1.78(1)	Co(2)−C(6)	1.84(1)	Co(3)−C(12)	2.070(8)
Ru(1)−C(6)	2.17(1)	Co(1)−C(2)	1.74(1)	Co(2)−C(11)	2.067(8)	C(11)−C(12)	1.39(1)
Ru(1)−C(8)	2.17(1)	Co(1)−C(3)	2.35(1)	Co(2)−C(12)	2.121(9)	C(12)−C(13)	1.49(1)
Ru(1)−C(9)	1.87(1)	Co(1)−C(4)	2.32(1)	Co(3)−C(3)	1.78(1)	C(13)−C(14)	1.52(2)
Ru(1)−C(10)	1.88(1)	Co(1)−C(11)	1.97(9)	Co(3)−C(7)	1.74(1)	C(13)−C(15)	1.30(1)
Ru(1)−C(12)	2.216(9)						
C(12)−Ru(1)−Co(2)	52.4(2)	C(11)−Co(2)−C(12)	38.8(3)	O(3)−C(3)−Co(1)	126.9(9)	Co(1)−C(11)−Co(2)	75.2(3)
C(12)−Ru(1)−Co(3)	51.0(2)	C(11)−Co(2)−Co(1)	50.5(3)	O(3)−C(3)−Co(3)	161.0(1)	C(12)−C(11)−Co(3)	70.4(5)
Co(2)−Ru(1)−Co(3)	87.95(4)	C(12)−Co(2)−Ru(1)	55.9(2)	O(4)−C(4)−Co(1)	128.3(9)	Co(1)−C(11)−Co(3)	75.2(3)
C(12)−Ru(1)−Co(1)	68.2(2)	Co(1)−Co(2)−Ru(1)	66.69(4)	O(4)−C(4)−Co(2)	159.0(1)	Co(2)−C(11)−Co(3)	117.2(4)
Co(2)−Ru(1)−Co(1)	55.28(4)	C(11)−Co(3)−C(12)	39.3(3)	O(5)−C(5)−Co(2)	178.6(11)	C(11)−C(12)−C(13)	125.4(8)
Co(3)−Ru(1)−Co(1)	55.29(4)	C(11)−Co(3)−Co(1)	50.5(3)	O(6)−C(6)−Co(2)	145.9(9)	C(11)−C(12)−Co(3)	70.4(5)
C(11)−Co(1)−Co(2)	54.3(2)	C(12)−Co(3)−Ru(1)	56.3(3)	O(6)−C(6)−Ru(1)	135.6(8)	C(11)−C(12)−Co(2)	68.5(5)
C(11)−Co(1)−Co(3)	54.3(2)	Co(1)−Co(3)−Ru(1)	66.61(4)	O(7)−C(7)−Co(3)	175.0(13)	C(13)−C(12)−Co(2)	119.7(6)
Co(2)−Co(1)−Co(3)	91.59(6)	O(1)−C(1)−Co(1)	177.8(10)	O(8)−C(8)−Co(3)	144.6(9)	Co(3)−C(12)−Co(2)	114.8(4)
C(11)−Co(1)−Ru(1)	73.8(2)	O(2)−C(2)−Co(1)	177.1(12)	O(8)−C(8)−Ru(1)	136.9(8)	C(11)−C(12)−Ru(1)	104.8(6)
Co(2)−Co(1)−Ru(1)	58.03(4)	O(10)−C(10)−Ru(1)	178.4(9)	O(9)−C(9)−Ru(1)	179.0(1)	Co(3)−C(12)−Ru(1)	72.8(3)
Co(3)−Co(1)−Ru(1)	58.10(4)	C(12)−C(11)−Co(1)	113.2(6)	C(12)−C(11)−Co(2)	72.7(5)	Co(2)−C(12)−Ru(1)	71.7(3)
Molecule B							
Ru(2)−Co(4)	2.724(2)	Ru(2)−C(35)	2.174(8)	Co(5)−C(27)	1.81(1)	Co(6)−C(31)	1.79(1)
Ru(2)−Co(5)	2.573(2)	Co(4)−Co(5)	2.487(2)	Co(5)−C(28)	1.72(1)	Co(6)−C(34)	2.071(9)
Ru(2)−Co(6)	2.542(1)	Co(4)−Co(6)	2.433(2)	Co(5)−C(29)	1.93(1)	Co(6)−C(35)	2.121(8)
Ru(2)−C(29)	2.11(1)	Co(4)−C(24)	1.80(1)	Co(5)−C(34)	2.081(9)	C(34)−C(35)	1.45(1)
Ru(2)−C(31)	2.28(1)	Co(4)−C(25)	1.78(1)	Co(5)−C(35)	2.056(8)	C(35)−C(36)	1.48(1)
Ru(2)−C(32)	1.85(1)	Co(4)−C(26)	2.02(1)	Co(6)−C(26)	1.83(1)	C(36)−C(37)	1.44(1)
Ru(2)−C(33)	1.90(1)	Co(4)−C(34)	1.947(8)	Co(6)−C(30)	1.75(1)	C(36)−C(38)	1.32(1)
C(35)−Ru(2)−Co(6)	52.7(2)	Co(6)−Co(4)−Co(5)	92.06(6)	O(28)−C(28)−Co(5)	172.7(10)	Co(4)−C(34)−Co(5)	76.2(3)
C(35)−Ru(2)−Co(5)	50.5(2)	C(34)−Co(4)−Ru(2)	75.5(2)	O(29)−C(29)−Co(5)	140.0(9)	Co(6)−C(34)−Co(5)	117.1(3)
Co(6)−Ru(2)−Co(5)	87.63(5)	Co(6)−Co(4)−Ru(2)	58.74(4)	O(29)−C(29)−Ru(2)	141.2(9)	C(34)−C(35)−C(36)	123.5(8)
C(35)−Ru(2)−Co(4)	68.7(2)	Co(5)−Co(4)−Ru(2)	58.96(4)	O(30)−C(30)−Co(6)	176.1(11)	C(34)−C(35)−Co(5)	70.3(5)
Co(6)−Ru(2)−Co(4)	54.90(4)	C(34)−Co(5)−Co(4)	49.5(2)	O(31)−C(31)−Co(6)	150.9(9)	C(34)−C(35)−Co(6)	67.9(5)
Co(5)−Ru(2)−Co(4)	55.92(5)	C(35)−Co(5)−Ru(2)	54.7(2)	O(31)−C(31)−Ru(2)	132.8(8)	Co(5)−C(35)−Co(6)	116.0(4)
C(34)−Co(6)−C(35)	40.6(3)	Co(4)−Co(5)−Ru(2)	65.12(5)	O(32)−C(32)−Ru(2)	173.9(11)	C(34)−C(35)−Ru(2)	105.7(5)
C(34)−Co(6)−Co(4)	50.4(2)	O(24)−C(24)−Co(4)	176.8(10)	O(33)−C(33)−Ru(2)	179.0(11)	C(36)−C(35)−Ru(2)	130.5(7)
C(35)−Co(6)−Ru(2)	54.7(2)	O(25)−C(25)−Co(4)	178.3(13)	C(35)−C(34)−Co(6)	71.5(5)	Co(5)−C(35)−Ru(2)	74.9(3)
Co(4)−Co(6)−Ru(2)	66.36(5)	O(26)−C(26)−Co(4)	133.6(8)	C(35)−C(34)−Co(4)	110.0(5)	Co(6)−C(35)−Ru(2)	72.6(3)
C(34)−Co(4)−Co(6)	55.1(3)	O(26)−C(26)−Co(6)	148.4(9)	Co(4)−C(34)−Co(6)	74.5(3)		
C(34)−Co(4)−Co(5)	54.3(3)	O(27)−C(27)−Co(5)	174.8(12)	C(35)−C(34)−Co(5)	68.5(5)		

are less reactive than acetylene.[19] Thus, as expected, the diyne $\mathbf{L^1}$ reacted with $[RuCo_3(CO)_{12}]^-$ selectively through its C≡CH triple bond. This was established by ^{1}H NMR spectroscopy of **5** (see Scheme 1 and below).

The IR spectra of clusters **2**−**5** display a similar pattern despite the diversity of alkynes used. Strong terminal carbonyl absorption bands are found between 2059 and 1970 cm^{-1} while the bridging carbonyls absorb between 1833 and 1817 cm^{-1}. In the IR spectra of NEt_4·**1** and NEt_4·**5**, an additional absorption band at 1712 or 1646 cm^{-1} is characteristic of the ester or amide carbonyl, respectively. The ^{1}H NMR spectra of clusters NEt_4·**1**−NEt_4·**5** show, in addition to the signals for the NEt_4^+ cation, typical resonances for the hydrogen atoms of the alkyne-derived ligand. The hydrogen atoms in the $CH^AH^B{=}C(CH_3)$ moiety of **3** are chemically different and present an ABX_3 spin system, like in the free alkyne, but the resolution of the signals did not allow extraction of the coupling constants. The singlets around δ 8.17−8.84 in the ^{1}H NMR spectra of NEt_4·**2**−NEt_4·**5** are assigned to the acetylenic protons. Their downfield shift is typical of hydrogen atoms bound to carbons interacting in a σ or π manner with metals.[3e,5] In addition, two singlets in this range are observed in the case of the anionic clusters **2** and **3**, which correspond to the formation of two isomers **a** and **b**, respectively (Scheme 1). These could not be separated by column chromatography. However, crystals of NEt_4·**3** with two different morphologies were obtained, which correspond to the two isomers **3a** and **3b**. ^{1}H NMR experiments carried out on two manually separated samples show that the more deshielded ^{1}H NMR signal should be assigned to the Co-bound CH proton. The isomer identified by X-ray diffraction was **3a**, and crystals of **3b** were not suitable for X-ray diffraction. Clusters NEt_4·**2a**,**b** were also isolated from the reaction of $[RuCo_3(CO)_{12}]^-$ with PhC≡CC(O)OH owing to decarboxylation of this alkyne under reflux. For NEt_4·**4** and NEt_4·**5**, only one isomer was observed and the cluster identified by X-ray diffraction, NEt_4·**4a**, has the CH group attached to Co, not to Ru, whereas, for NEt_4·**5**, we cannot state which isomer was formed.

Molecular Structures of NEt_4·3a and NEt_4·4a. Selected bond distances and angles are listed in Tables 1 and 2 and views of the molecular structures are shown in Figures 1 and 2, respectively. These clusters possess a $RuCo_3$ butterfly core with the ruthenium atom in a hinge position. In contrast,

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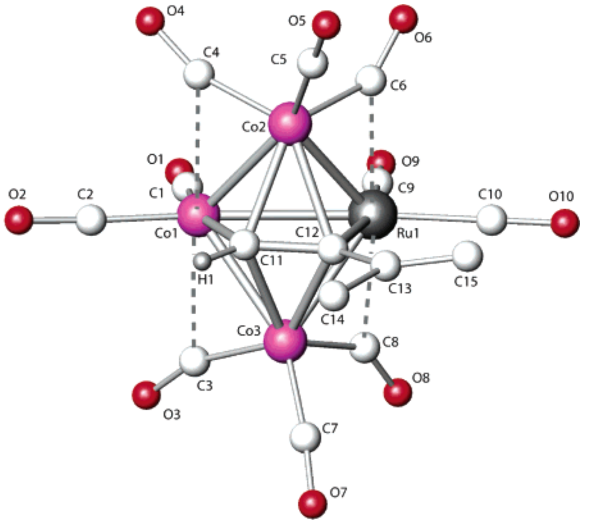

Figure 1. View of the molecular structure of the anionic cluster in **3a**. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances [Å] and Bond Angles [deg] for the Anion **4a** with Estimated Standard Deviations in Parentheses

Ru(1)−Co(1)	2.754(1)	Co(2)−C(4)	1.745(3)
Ru(1)−Co(2)	2.570(1)	Co(2)−C(5)	1.793(3)
Ru(1)−Co(3)	2.531(1)	Co(2)−C(6)	1.889(3)
Ru(1)−C(6)	2.100(3)	Co(2)−C(11)	2.073(2)
Ru(1)−C(8)	2.222(3)	Co(2)−C(12)	2.047(2)
Ru(1)−C(9)	1.909(3)	Co(3)−C(3)	1.817(3)
Ru(1)−C(10)	1.880(3)	Co(3)−C(7)	1.755(3)
Ru(1)−C(12)	2.171(3)	Co(3)−C(8)	1.824(3)
Co(1)−Co(2)	2.4935(9)	Co(3)−C(11)	2.098(2)
Co(1)−Co(3)	2.435(1)	Co(3)−C(12)	2.134(2)
Co(1)−C(1)	1.788(3)	C(11)−C12	1.404(3)
Co(1)−C(2)	1.778(3)	C(12)−C(13)	1.501(3)
Co(1)−C(3)	2.052(3)	C(14)−C(15)	1.469(4)
Co(1)−C(11)	1.961(3)	C(15)−C(16)	1.173(4)
C(12)−Ru(1)−Co(2)	50.29(6)	O(3)−C(3)−Co(3)	149.0(2)
C(12)−Ru(1)−Co(3)	53.31(6)	O(4)−C(4)−Co(2)	174.0(3)
Co(2)−Ru(1)−Co(3)	88.33(1)	O(5)−C(5)−Co(2)	177.5(3)
C(12)−Ru(1)−Co(1)	67.75(6)	O(6)−C(6)−Co(2)	140.0(2)
Co(2)−Ru(1)−Co(1)	55.73(1)	O(6)−C(6)−Ru(1)	139.9(2)
Co(3)−Ru(1)−Co(1)	54.66(2)	O(7)−C(7)−Co(3)	178.8(3)
C(11)−Co(1)−Co(2)	53.87(7)	O(8)−C(8)−Co(3)	149.3(2)
C(11)−Co(1)−Co(3)	55.77(6)	O(8)−C(8)−Ru(1)	133.8(2)
Co(2)−Co(1)−Co(3)	92.30(4)	O(9)−C(9)−Ru(1)	179.0(3)
C(11)−Co(1)−Ru(1)	74.23(7)	O(10)−C(10)−Ru(1)	179.2(2)
Co(2)−Co(1)−Ru(1)	58.39(3)	C(12)−C(11)−Co(1)	110.8(2)
Co(3)−Co(1)−Ru(1)	58.01(1)	C(12)−C(11)−Co(2)	69.0(1)
C(11)−Co(2)−C(12)	39.86(9)	Co(1)−C(11)−Co(2)	76.32(8)
C(11)−Co(2)−Co(1)	49.82(7)	C(12)−C(11)−Co(3)	72.0(1)
C(11)−Co(2)−Ru(1)	76.93(6)	Co(1)−C(11)−Co(3)	73.63(7)
C(12)−Co(2)−Ru(1)	54.70(6)	Co(2)−C(11)−Co(3)	116.9(1)
Co(1)−Co(2)−Ru(1)	65.88(3)	C(11)−C(12)−C(13)	123.1(2)
C(11)−Co(3)−C(12)	38.74(9)	C(11)−C(12)−Co(3)	69.2(1)
C(11)−Co(3)−Co(1)	50.59(6)	C(13)−C(12)−Co(3)	118.9(2)
C(12)−Co(3)−Co(1)	74.87(6)	C(11)−C(12)−Co(2)	71.1(1)
C(11)−Co(3)−Ru(1)	77.39(6)	C(13)−C(12)−Co(2)	124.1(2)
C(12)−Co(3)−Ru(1)	54.66(6)	Co(3)−C(12)−Co(2)	116.4(1)
Co(1)−Co(3)−Ru(1)	67.33(1)	C(11)−C(12)−Ru(1)	107.2(2)
O(1)−C(1)−Co(1)	179.3(3)	C(13)−C(12)−Ru(1)	129.3(2)
O(2)−C(2)−Co(1)	179.5(3)	Co(3)−C(12)−Ru(1)	72.02(7)
O(3)−C(3)−Co(1)	133.2(2)	Co(2)−C(12)−Ru(1)	75.01(8)

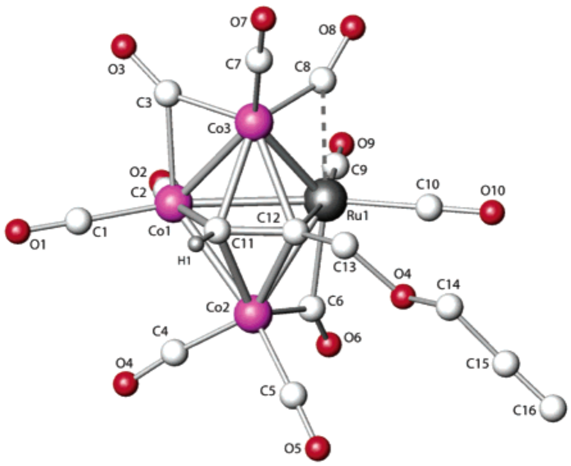

Figure 2. View of the molecular structure of the anionic cluster in **4a**. Hydrogen atoms have been omitted for clarity.

the cobalt atom occupies a wingtip position in the related cluster $[Ru_3Co(CO)_{11}(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)]^-$.[20] In other mixed-metal anionic clusters with butterfly core structures, such as $[Ru_3M(CO)_{10}Cp(\mu_4\text{-}\eta^2\text{-}MeC_2Me)]^-$ (M = W, Mo), the metal atom M always occupies a hinge position,[21] as found in **1**−**5**. The alkyne ligand bridges all four metals in a μ_4-η^2 fashion, lying parallel to the Ru−Co(1) bond. This arrangement completes an octahedral core structure consisting of the four metals and the two acetylenic carbon atoms. With an electron count of 60e, clusters **1**−**5** appear electron deficient, since an M_4 butterfly cluster obeying the EAN rule would require 62 electrons. However, considering **1**−**5** as octahedral $RuCo_3C_2$ clusters, their electron count is consistent with Wade's rules which predict a *closo* structure.[22] The nonbonding distances between the cobalt atoms Co(2) and Co(3) in **3a** and **4a** are 3.53 and 3.55 Å and the dihedral angles between the butterfly wings are 115.3° and 120.4°, respectively. The acetylenic protons have been located in both cases.

Bond lengths within the metal framework are typical of butterfly structures involving these metals. The Ru(1)−Co(1) distance is the longest of the Ru−Co distances, a general feature for metal−metal distances involving the metals in the hinge. There are two different, almost identical molecules, **A** and **B**, in the asymmetric unit of NEt_4·**3a**. The carbonyl ligands C(3)O(3), C(4)O(4), C(6)O(6), and C(8)O(8) in molecule **3aA** conform to the semibridging category of Crabtree−Lavin, and the other carbonyls are terminal, whereas in **4**, C(3)O(3) and C(6)O(6) are bridging between Co(1), Co(3) and Ru(1), Co(2), respectively while C(8)O(8) is semibridging between Ru(1) and Co(3).[23] Owing to disorder or high thermal agitation, the NEt_4 group in molecule **3aB** has been idealized and the distances N−C and C−C have been fixed at 1.53 and 1.58 Å, respectively.

Synthesis of the Neutral Trinuclear Clusters 6−8 from the Anionic Clusters 1−3. In contrast to $[RuCo_3(CO)_{12}]^-$, the anionic clusters **1**−**3** did not lead to cluster expansion upon reaction with $[Cu(NCMe)_4]BF_4$ but rather to selective fragmentation with loss of the 12e fragment $Co(CO)^-$ to give the trinuclear alkyne-clusters **6**−**8**, as established by an X-ray

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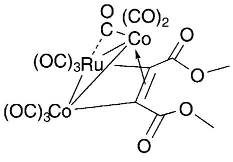
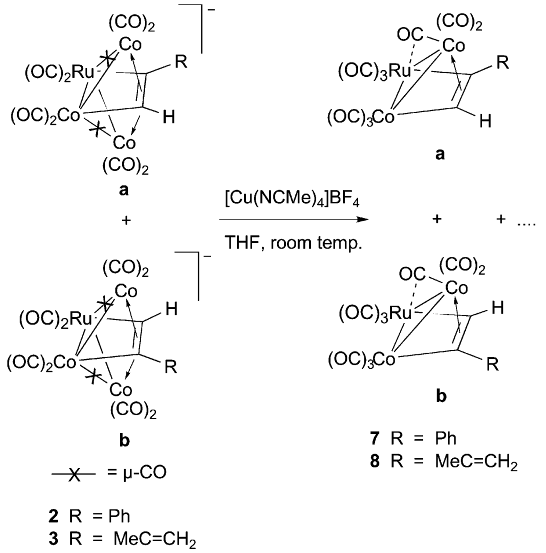


6

diffraction study of **6**.[18,24] In contrast to **6**, where the alkyne substituents are identical, two isomers of clusters **7** and **8** were obtained which differ by the orientation of the alkyne (Scheme 2). The infrared spectrum of **6** contains, in addition to the terminal and bridging carbonyl absorption bands, an absorption at 1720 cm^{-1} characteristic of the ester function. The ^{1}H NMR spectrum of **6** reveals two singlets for the chemically different methyl groups of the dmad ligand. In the case of **7** and **8**, the ^{1}H NMR spectra contain two singlets for the acetylenic hydrogen at 7.97, 9.59 and 7.83, 9.36 ppm, respectively. These singlets suggest the presence of isomers **a** and **b** (Scheme 2). For the MeC=CH_2 moiety in **8**, two resonances are observed for the methyl group (two isomers), and four resonances for the olefinic hydrogen atoms (ABX_3 spin system). These two isomers could not be separated.

Scheme 2



In each of the compounds **1**, **2**−**6** and **8** an organic function remains available which could be used for the subsequent functionalization of the coordinated ligands. Unfortunately, attempts to hydrosilylate the C=C or a C=O double bond of **3** and **6**, respectively, with $HSi(OMe)_3$[25] or $HSiCl_3$[26] in the presence of H_2PtCl_6 or [Rh(diphos)(NBD)]BF_4, as catalysts, have not yet been successful.

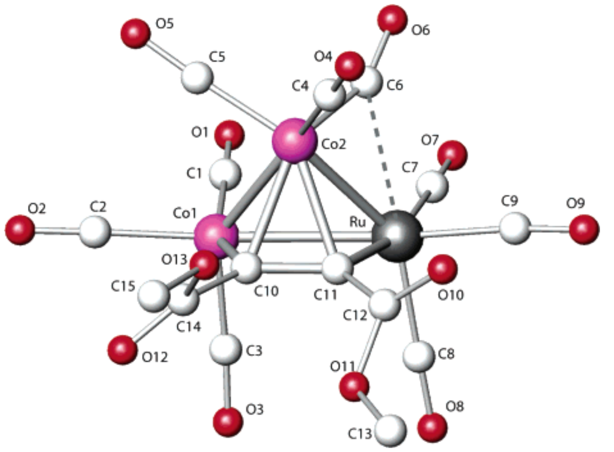


Figure 3. View of the molecular structure of the cluster **6**. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Distances [Å] and Bond Angles [deg] for **6** with Estimated Standard Deviations in Parentheses

Co(1)−Co(2)	2.495(1)	Co(2)−C(10)	2.040(5)
Co(1)−C(1)	1.828(7)	Co(2)−C(11)	2.039(6)
Co(1)−C(2)	1.842(7)	Ru···C(6)	2.386(7)
Co(1)−C(3)	1.788(7)	Ru−C(7)	1.971(7)
Co(1)−C(10)	1.942(6)	Ru−C(8)	1.906(7)
Co(1)−Ru	2.726(1)	Ru−C(9)	1.921(7)
Co(2)−Ru	2.585(1)	Ru−C(11)	2.084(6)
Co(2)−C(4)	1.809(8)	C(10)−C(11)	1.372(8)
Co(2)−C(5)	1.766(8)	C(11)−C(12)	1.502(9)
Co(2)−C(6)	1.815(7)	C(14)−C(10)	1.492(8)

Co(2)−Co(1)−Ru	59.16(3)	O(6)−C(6)−Ru	130.7(5)
Co(2)−Co1−C(10)	53.0(2)	O(7)−C(7)−Ru	177.8(6)
Ru−Co(1)−C(10)	73.2(2)	O(8)−C(8)−Ru	179.2(6)
Co(1)−Co(2)−Ru	64.88(3)	O(9)−C(9)−Ru	175.2(6)
C(10)−Co(2)−Co(1)	49.5(2)	C(11)−C(10)−C14	124.1(6)
C(11)−Co(2)−Co(1)	73.1(2)	C(11)−C(10)−Co(1)	109.5(4)
C(10)−Co(2)−Ru	75.2(2)	C(14)−C(10)−Co1	125.7(4)
C(11)−Co(2)−Ru	51.9(2)	C(11)−C(10)−Co(2)	70.3(3)
Co(2)−Ru−Co(1)	55.95(3)	C(14)−C(10)−Co(2)	125.6(4)
C(11)−Ru−Co(1)	67.5(2)	Co(1)−C(10)−Co(2)	77.5(2)
C(11)−Ru−Co(2)	50.4(2)	C(10)−C(11)−C(12)	124.0(5)
O(1)−C(1)−Co(1)	178.9(7)	C(10)−C(11)−Co(2)	70.3(3)
O(2)−C(2)−Co(1)	176.6(7)	C(12)−C(11)−Co(2)	127.8(4)
O(3)−C(3)−Co1	175.9(6)	C(10)−C(11)−Ru	109.7(4)
O(4)−C(4)−Co(2)	179.0(8)	C(12)−C(11)−Ru	125.3(4)
O(5)−C(5)−Co(2)	176.6(6)	Co(2)−C(11)−Ru	77.6(2)
O(6)−C(6)−Co(2)	154.5(6)		

Molecular Structure of $[RuCo_2(CO)_9\{\mu_3\text{-}\eta^2\text{-}MeOC(O)C_2C(O)OMe\}]$ (6). Crystals suitable for X-ray structure analysis were obtained by recrystallization from hexane at −30 °C. A view of the molecular structure is depicted in Figure 3. Selected bond lengths and angles are presented in Table 3. The ruthenium and cobalt atoms form a triangle in which all the metal−metal distances are different but within the range of typical Ru−Co and Co−Co single bonds. The carbonyl C(6)O(6) is the only one to be semibridging, namely, between Ru and Co(2): Co(2)−C(6) = 1.815(7) Å, Co(2)−C(6)−O(6) = 154.5(6)°, Ru···C(6) = 2.386(7) Å. The alkyne ligand is coordinated in a classical μ_3-η^2 fashion over the metal triangle, as observed in $[RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]$[18] and $[Ru_2Ir(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)]^-$.[27] The C(10)−C(11) bond is almost parallel to the Ru−Co(1) edge [C(10)−Co(1)−Ru−C(11) = 0.1(3)°]. Interestingly, in the related $[FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}EtC_2Et)]$ cluster, the alkyne is also bonded in a μ_3-η^2 mode but in contrast to **6** it is parallel to

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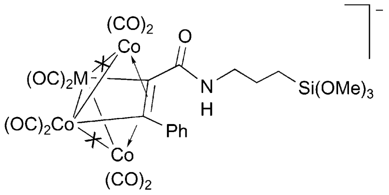
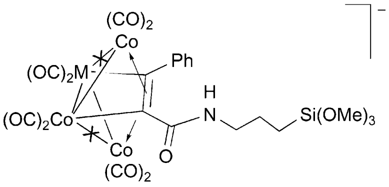
the Co−Co vector.[28] The alkyne carbon−carbon bond length of 1.372(8) Å compares with that in [$RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$] (1.370(3) Å)[18] and in [$Ru_2Ir(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$]$^-$ (1.363(11) Å).[27] Cluster **6** has the expected electron count of 48e for trinuclear clusters which obey the EAN rule. It also corresponds to a 7 skeletal electron pair *nido*-octahedral cluster (square-based pyramid) constituted by the metals and C(10) and C(11).[22]

Reactions of the Tetrahedral $RuCo_3$ and $FeCo_3$ Clusters with Alkoxysilyl-Functionalized Alkynes. With the aim of incorporating a functional alkyne in a $RuCo_3$ or $FeCo_3$ cluster that could be subsequently condensed in a silica matrix via the sol−gel method, we reacted clusters [$RuCo_3(CO)_{12}$]$^-$ and [$FeCo_3(CO)_{12}$]$^-$ with the recently prepared alkyne $PhC{\equiv}CC(O)NH(CH_2)_3Si(OMe)_3$ (**L**^{2}).[4] This afforded the anionic clusters **9** and **10**, respectively, which were identified by their IR and NMR spectra and elemental analysis. Their ^1H NMR spectra are similar and show two sets of signals in a 1:1 ratio, which correspond to the formation of two isomers which could not be separated but are reasonably assumed to correspond to the two possible orientations of the alkyne with respect to the Co−M edge, as indicated with **9a**,**b** and **10a**,**b**. The structure of these compounds was deduced from their spectroscopic properties and by analogy with the structurally characterized clusters **3** and **4** and the analogous cluster [$FeCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$]$^-$.[29] The IR spectra of **9** and **10** contain, besides the terminal and bridged carbonyl absorption bands, an absorption band at 1612 and 1637 cm^{-1}, respectively, which is characteristic of the amide carbonyl. We are currently evaluating these $Si(OMe)_3$-containing clusters as precursors to sol−gel materials.



9a M = Ru
10a M = Fe



9b M = Ru
10b M = Fe

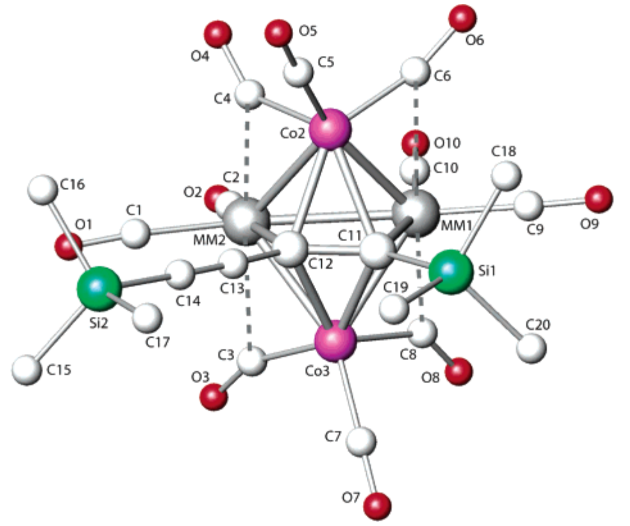
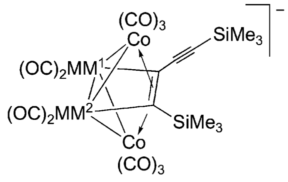
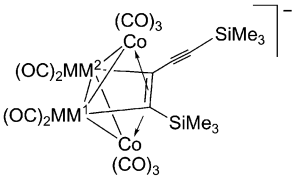


Figure 4. View of the molecular structure of the anionic cluster in **11b**. Hydrogen atoms have been omitted for clarity.

Reaction of $RuCo_3$ Clusters with a Protected Diyne. Reaction of [NEt_4][$RuCo_3(CO)_{12}$] with 1,4-bis(trimethylsilyl)butadiyne afforded in good yield the expected butterfly, air-stable cluster [NEt_4][$RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2\text{-}C{\equiv}CSiMe_3)$] ($NEt_4{\cdot}$**11**) in two isomeric forms **11a** and **11b**, in a 2:3 ratio. The identity of **11** was deduced from analytical and spectroscopic data and confirmed by a single-crystal X-ray diffraction study. The cluster contains an uncomplexed C≡C triple bond, but no IR absorption was found in the ν(C≡C) region. The ^1H NMR spectrum contained four resonances at δ 0.035, 0.094, 0.108, and 0.240 for the two $SiMe_3$ groups of the two isomers. The molecular structure of **11b**, shown in Figure 4, is similar to that of **3a** and **4a**. The nonbonding Co(2)⋯Co(3) distance is 3.54(1) Å, and the dihedral angle between the butterfly wings is 114.9(2)°. The refinement of the X-ray data led to consider the positions MM1 and MM2 as disordered, with occupancy factors of Ru 0.43, Co 0.57 and Ru 0.57, Co 0.43, respectively. The Co(2)−C(4), Co(2)−C(6), Co(3)−C(3), and Co(3)−C(8) distances of 1.87(1), 1.77(1), 1.79(1), and 1.88(1) Å, respectively, are considerably shorter than the MM2−C(4), MM1−C(6), MM2−C(3), and MM1−C(8) distances of 2.08(1), 2.48(1), 2.31(1), and 2.03(1), respectively, which suggests that C(3)O(3), C(4)O(4), C(6)O(6), and C(8)O(8) occupy semibridging positions (Table 4). The six remaining carbonyl ligands are terminal.



11a



11b

Complexation of [$Co_2(CO)_8$] or [$Pt(C_2H_4)(PPh_3)_2$] to the free C(13)≡C(14) triple bond of **11** could not be achieved, probably for steric reasons.

Reaction of $NEt_4{\cdot}$11 with [$Cu(NCMe)_4$]BF_4. This reaction yielded a red product, as observed with clusters **1**−**3** which afforded the triangular clusters **6**−**8**, respectively. We observed by ^1H NMR two $SiMe_3$ resonances at δ 0.15 and 0.19 in addition to two singlets at δ 8.02 and 9.48, characteristic of the hydrogen atoms bound to carbon atoms

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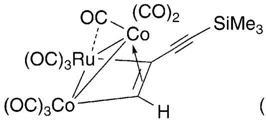
Table 4. Selected Bond Distances [Å] and Bond Angles [deg] for **11** with Estimated Standard Deviations in Parentheses

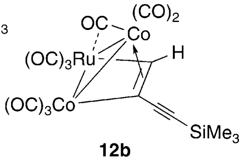
MM1−Co(2)	2.484(2)	Co(2)−C(4)	1.87(1)
MM1−Co(3)	2.512(2)	Co(2)−C(5)	1.73(2)
MM1−C(6)	2.48(1)	Co(2)−C(6)	1.77(1)
MM1−C(8)	2.03(1)	Co(2)−C(11)	2.128(9)
MM1−C(9)	1.84(1)	Co(2)−C(12)	2.065(9)
MM1−C(10)	1.81(1)	Co(3)−C(3)	1.79(1)
MM1−C(11)	2.11(1)	Co(3)−C(7)	1.77(1)
MM2−Co(2)	2.545(2)	Co(3)−C(8)	1.88(1)
MM2−Co(3)	2.487(2)	Co(3)−C(11)	2.069(9)
MM2−C(1)	1.856(9)	Co(3)−C(12)	2.101(9)
MM2−C(2)	1.81(1)	C(11)−C(12)	1.41(1)
MM2−C(3)	2.31(1)	C(12)−C(13)	1.45(1)
MM2−C(4)	2.08(1)	C(13)−C(14)	1.20(1)
MM2−C(12)	2.09(1)	C(11)−Si(1)	1.902(9)
		C(14)−Si(2)	1.827(10)

Co(2)−MM1−Co(3)	90.34(5)	Co(3)−C(7)−O(7)	177.0(1)
Co(2)−MM1−C(11)	54.5(2)	MM1−C(8)−O(8)	138.7(9)
Co(3)−MM1−C11	52.3(2)	Co(3)−C(8)−O(8)	141.5(9)
Co(2)−MM2−Co(3)	89.52(5)	MM1−C(9)−O(9)	174.3(9)
Co(2)−MM2−C(12)	51.8(3)	MM1−C(10)−O10	178.8(1)
Co(3)−MM2−C(12)	53.8(2)	MM1−C(11)−Co(2)	71.8(3)
MM1−Co(2)−C(11)	53.7(3)	MM1−C(11)−Co(3)	74.0(3)
MM1−Co(2)−C(12)	76.8(3)	MM1−C(11)−C(12)	106.5(6)
MM2−Co(2)−C(11)	76.0(2)	Co(2)−C(11)−Co(3)	115.1(4)
MM2−Co(2)−C(12)	52.7(3)	Co(2)−C(11)−C(12)	67.9(5)
C(11)−Co(2)−C(12)	39.2(3)	Co(3)−C(11)−C(12)	71.5(5)
MM1−Co(3)−C(11)	53.7(3)	MM2−C(12)−Co(2)	75.5(3)
MM1−Co(3)−C(12)	75.6(3)	MM2−C(12)−Co(3)	72.8(3)
MM2−Co(3)−C(11)	78.4(2)	MM2−C(12)−C(11)	110.3(7)
MM2−Co(3)−C(12)	53.4(3)	MM2−C(12)−C(13)	121.0(7)
C(11)−Co(3)−C(12)	39.4(3)	Co2−C(12)−Co(3)	116.5(4)
MM2−C(1)−O(1)	175.6(9)	Co(2)−C(12)−MM2	75.5(3)
MM2−C(2)−O(2)	177.0(1)	Co(2)−C(12)−C(11)	72.9(5)
MM2−C3−O(3)	128.7(8)	Co(2)−C(12)−C(13)	118.4(6)
Co(3)−C(3)−O(3)	157.2(9)	Co(3)−C(12)−MM2	72.8(3)
MM2−C(4)−O(4)	138.3(9)	Co(3)−C(12)−C(11)	69.0(5)
Co(2)−C(4)−O(4)	141.7(10)	Co(3)−C(12)−C(13)	125.0(6)
Co(2)−C(5)−O(5)	178.5(16)	C(11)−C(12)−C(13)	128.7(9)
MM1−C(6)−O(6)	128.8(8)	C(12)−C(13)−C(14)	174.0(1)
Co(2)−C(6)−O(6)	161.9(10)		

interacting in a σ or π manner with metal centers. This suggests again the presence of two isomers of the cluster [$RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2C{\equiv}CSiMe_3)$] (**12**) and not of the expected cluster [$RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$]. By analogy with previous assignments on related clusters, the more deshielded ^1H NMR signal should be assigned to the Co-bound CH proton. The unexpected deprotection of the $SiMe_3$ group could be due to the presence of fluoride originating from [$Cu(NCMe)_4$]BF_4. Proto-desilylation occurred at the Co−C−$SiMe_3$ group rather than at the alkynyl carbon as might have been expected by analogy to [$Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$].[30] This was also observed in the case of the deprotection of [$Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$] with TBAF/THF−$H_2O$ which afforded [$Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})(\mu_4\text{-}\eta^2{-}HC_2C{\equiv}CSiMe_3)$] instead of the expected [$Co_4(\mu\text{-}CO)_2(CO)_6(\mu\text{-dppm})(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)$].[4] Cluster **12** was characterized by the usual methods, details of which are given in the Experimental Section. The low yield (22%) and difficulties in crystallizing the product precluded full characterization. However, the IR spectrum is very similar to those of the related clusters **6**−**8**. The $\nu(C{\equiv}C)$ absorption for the uncoordinated C≡C triple bond was not observed whereas it appears at 2108 cm^{-1} for the cluster [$Ru_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$].[31] The FAB mass spectrum shows the presence of the parent ion and the stepwise loss of carbonyl ligands.



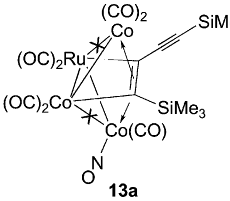
12a



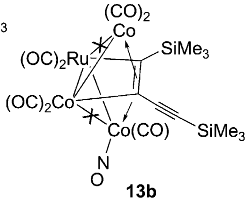
12b

Reaction of NEt_4·11 with [NO]BF_4. Cluster NEt_4·**11** reacts with [NO]BF_4 to afford the new neutral cluster [$RuCo_3(CO)_9(NO)(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$] (**13**) by selective substitution of a carbonyl ligand on a wing-tip cobalt atom with a nitrosyl group. The identity of **13** was deduced by comparaison with the known cluster [$RuCo_3(CO)_9(NO)(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)$] synthesized by reaction of [$RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)$]$^-$ with [NO]BF_4 or by reaction of [$RuCo_3(CO)_{11}(NO)$] with diphenylacetylene.[32] The nitrosyl group gives rise to an absorption band at 1805 cm^{-1}. The ^1H NMR spectrum contains two different signals for the two −$SiMe_3$ groups, which suggests the presence of only one isomer, in contrast to the situation in the precursor complex. However, we do not know which isomer was formed. The FAB mass spectrum contains a parent ion and shows stepwise loss of carbonyl groups.

The formation of **13** was accompanied by that of the partially deprotected cluster **12**. Similar decrease in nuclearity affording [$RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CPh)$] occurred during the reaction of [$RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)$]$^-$ with [NO]BF_4.[32] Deprotection leading to **12** is also due to the presence of fluoride ions originating from [NO]BF_4, and it is surprising that, under similar conditions, the remaining **13** was not deprotected. One of the objectives of the reactions of NEt_4·**11** with [$Cu(NCMe)_4$]BF_4 and [NO]BF_4 was the obtention of neutral clusters, which are often more soluble and easier to purify, but unfortunately, the yield was low in both cases.



13a



13b

Reaction of NEt_4·11 with [$AuCl(PPh_3)$] and PPh_3. With the object of introducing the $AuPPh_3$ fragment in the cluster and examining its site of attachment, we reacted the cluster NEt_4·**11** with [$AuCl(PPh_3)$] in toluene. Such reactions are generally favored by the addition of $TlPF_6$, which activates the gold−chlorine bond, but, when this reagent was used, unidentified neutral products were obtained in addition to decomposition (TLC). When NEt_4·**11** was heated with

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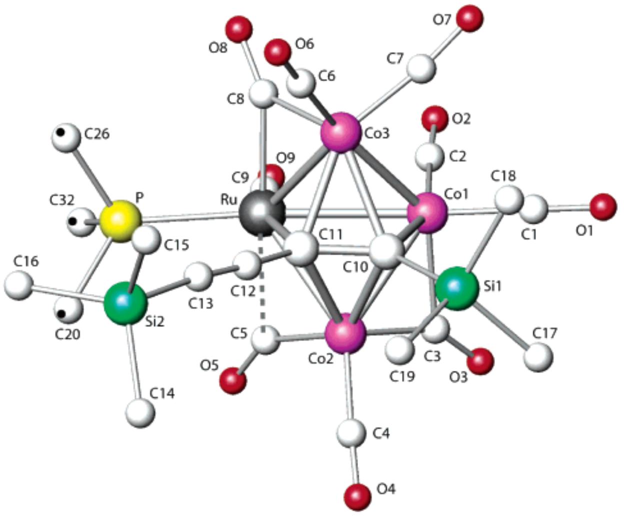
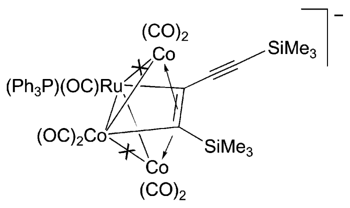


Figure 5. View of the molecular structure of the anionic cluster in **14**. Only the ipso carbons of the phenyl groups at phosphorus are shown, and the hydrogen atoms have been omitted for clarity.

[AuCl(PPh$_3$)] in toluene at reflux without addition of TlPF$_6$, the gold−phosphorus bond was broken and the phosphine liberated substituted selectively a carbonyl ligand on the ruthenium atom to afford [NEt$_4$][RuCo$_3$(CO)$_9$(PPh$_3$)(μ_4-η^2-Me$_3$SiC$_2$C≡CSiMe$_3$)] (NEt$_4$·**14**). This cluster was also obtained directly, and in higher yield, by reaction of NEt$_4$·**11** with one equivalent of PPh$_3$ in refluxing toluene. None of these reactions was observed in THF. The cluster has the same color (violet) and an IR spectrum similar to that of the related clusters [RuCo$_3$(CO)$_{10}$(μ_4-η^2-alkyne)]$^-$. As observed in **13**, the ^{1}H NMR spectrum of **14** contains only two different signals for the two −SiMe$_3$ groups, which suggests the presence of only one isomer. It was identified by X-ray diffraction, and the molecular structure of **14** is similar to those of **3**, **4**, and **11b**. A view of the molecule is shown in Figure 5, and selected bond distances and angles are given in Table 5. The nonbonding Co(2)···Co(3) distance is 3.51(1) Å, and the dihedral angle between the butterfly wings is 114°. The carbonyl C(8)O(8) is bridging between Ru and Co(3) whereas C(5)O(5) is semibridging between Ru and Co(2). The Ru−P distance of 2.345(1) is comparable to literature values.[33]



14

Table 5. Selected Bond Distances [Å] and Bond Angles [deg] for **14** with Estimated Standard Deviations in Parentheses

Ru−Co(1)	2.738(1)	Co(2)−C(3)	1.837(4)
Ru−Co(2)	2.5106(7)	Co(2)−C(4)	1.747(4)
Ru−Co(3)	2.5880(7)	Co(2)−C(5)	1.838(4)
Ru−P	2.345(1)	Co(2)−C(10)	2.081(4)
Ru−C(5)	2.191(4)	Co(2)−C(11)	2.114(4)
Ru−C(8)	2.026(4)	Co(3)−C(6)	1.765(4)
Ru−C(9)	1.872(4)	Co(3)−C(7)	1.753(5)
Ru−C(11)	2.222(4)	Co(3)−C(8)	1.951(4)
Co(1)−Co(2)	2.4407(8)	Co(3)−C(10)	2.113(4)
Co(1)−Co(3)	2.4697(8)	Co(3)−C(11)	2.031(4)
Co(1)−C(1)	1.777(5)	C(10)−C(11)	1.421(5)
Co(1)−C(2)	1.775(4)	C(11)−C(12)	1.434(5)
Co(1)−C(3)	2.055(4)	C(12)−C(13)	1.213(5)
Co(1)−C(10)	2.016(4)	Si(1)−C(10)	1.871(4)
Co(2)···Co(3)	3.51(1)	Si(2)−C(13)	1.835(4)

Co(1)−Ru−C(11)	67.7(1)	Co(1)−C(1)−O(1)	170.8(4)
Co(2)−Ru−Co(1)	55.21(2)	Co(1)−C(2)−O(2)	176.3(4)
Co(2)−Ru−Co(3)	87.05(2)	Co(1)−C(3)−O(3)	133.3(3)
Co(2)−Ru−C(11)	52.6(1)	Co(2)−C(3)−O(3)	149.3(3)
Co(3)−Ru−C(11)	49.2(1)	Co(2)−C(4)−O(4)	177.6(4)
Co(3)−Ru−Co(1)	55.17(2)	Ru−C(5)−O(5)	136.4(3)
Co(2)−Co(1)−C(10)	54.7(1)	Co(2)−C(5)−O(5)	147.0(3)
Co(2)−Co(1)−Co(3)	105.5(2)	Co(3)−C(6)−O(6)	177.3(4)
Co(2)−Co(1)−Ru	57.65(2)	Co(3)−C(7)−O(7)	172.1(5)
Co(3)−Co(1)−Ru	59.32(2)	Ru−C(8)−O(8)	145.1(3)
Co(3)−Co(1)−C(10)	55.1(1)	Co(3)−C(8)−O(8)	133.6(3)
Ru −Co(1)−C(10)	76.2(1)	Ru−C(9)−O(9)	175.0(3)
Co(1)−Co(2)−C(10)	52.2(1)	Co(1)−C(10)−Co(2)	73.1(1)
Co(1)−Co(2)−C(11)	75.4(1)	Co(1)−C(10)−Co(3)	73.4(1)
Ru−Co(2)−C(10)	80.6(1)	Co(1)−C(10)−C(11)	107.6(3)
Ru−Co(2)−C(11)	56.6(1)	Co(2)−C(10)−Co(3)	113.7(2)
Ru−Co(2)−Co(1)	67.14(2)	Co(2)−C(10)−C(11)	71.4(2)
C(10)−Co(2)−C(11)	39.6(2)	Co(3)−C(10)−C(11)	66.9(2)
Ru−Co(3)−Co(1)	65.52(2)	Ru−C(11)−Co(2)	70.7(1)
Ru−Co(3)−C(10)	78.2(1)	Ru−C(11)−Co(3)	74.8(1)
Ru−Co(3)−C(11)	55.9(1)	Ru−C(11)−C(10)	108.2(3)
Co(1)−Co(3)−C(10)	51.8(1)	Co(2)−C(11)−Co(3)	115.8(2)
Co(1)−Co(3)−C(11)	76.1(1)	Co(2)−C(11)−C(10)	69.0(2)
C(10)−Co(3)−C(11)	40.0(2)	Co(3)−C(11)−C(10)	73.1(2)

Proto-desilylation of 11. Under standard desilylation conditions,[34] NEt$_4$·**11** was treated with a catalytic amount of [n-Bu$_4$N]F (TBAF) in wet THF. In addition to the deprotection at the alkynyl group, the NEt$_4^+$ cation was partially exchanged for N(n-Bu)$_4^+$. We thus obtained a mixture of the clusters [NEt$_4$][RuCo$_3$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡CH)] (NEt$_4$·**15**) and [N(n-Bu)$_4$][RuCo$_3$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡CH)] [N(n-Bu)$_4$·**15**] (Scheme 3). We have succeeded in separating N(n-Bu)$_4$·**15** from the mixture by recrystallization, and crystals suitable for X-ray diffraction were obtained. The remaining portion of the product was a paste which contained a mixture of the two clusters. The ^{1}H NMR spectrum of the isolated N(n-Bu)$_4$·**15** contains, besides the Bu signals, two resonances at δ 0.12 and 0.25 for the nondeprotected −SiMe$_3$ group corresponding to the two isomers, and obviously two resonances at δ 3.41 and 3.51 for the HC≡ proton. The disappearance of the signals at δ 0.035 and 0.094 in **11** confirms their assignment to the C≡CSiMe$_3$ protons. Full deprotection leading to a butadiyne complex was not observed. Whereas proto-desilylation occurred here at the anticipated site, it took place at the cluster core-bound alkyne carbon in the case of the neutral, isoelectronic Co$_4$ system.[4]

The molecular structure of N(n-Bu)$_4$·**15a** was established by X-ray diffraction (Figure 6), and selected bond distances

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(33) Bouherour, S.; Braunstein, P.; Rosé, J.; Toupet, L. *Organometallics* **1999,** *18*, 4908−4915.

(34) (a) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810−822. (b) Mohr, W.; Peters, T. B.; Bohling, J. C.; Hampel, F.; Arif, A. M.; Gladysz, J. A. *C. R. Chim.* **2002**, *5*, 111−118. (c) Dembinski, R.; Lis, T.; Szafert, S.; Mayne, C. L.; Bartik, T.; Gladysz, J. A. *J. Organomet. Chem.* **1999**, *578*, 229−246.

Scheme 3

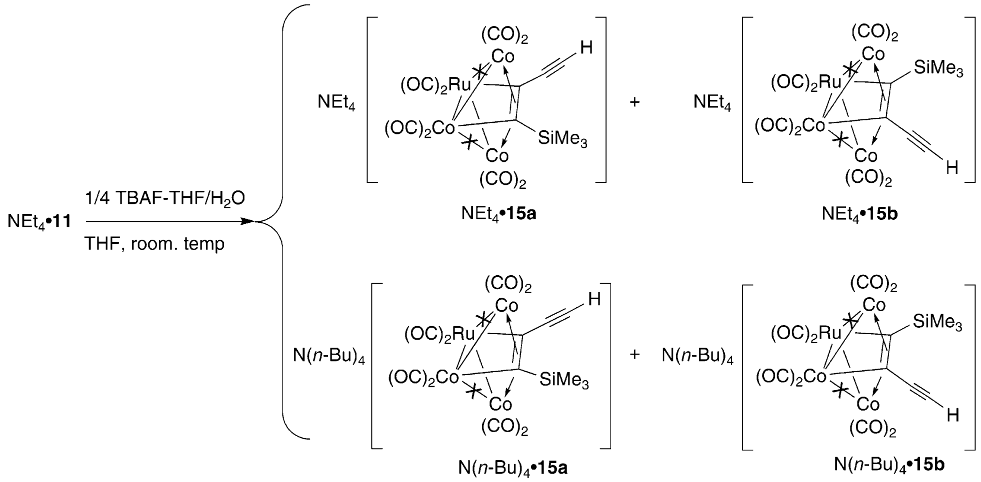


Table 6. Selected Bond Distances [Å] and Bond Angles [deg] for the Anion **15a** with Estimated Standard Deviations in Parentheses

Molecule A							
Ru(1)−Co(1)	2.738(1)	Ru(1)−C(12)	2.137(7)	Co(1)−C(11)	2.051(6)	Co(3)−C(7)	1.791(8)
Ru(1)−Co(2)	2.519(1)	Co(1)−Co(2)	2.445(1)	Co(2)−C(4)	1.835(8)	Co(3)−C(8)	1.886(8)
Ru(1)−Co(3)	2.552(1)	Co(1)−Co(3)	2.474(1)	Co(2)−C(5)	1.759(8)	Co(3)−C(11)	2.116(7)
Ru(1)−C(6)	2.199(8)	Co(1)−C(1)	1.808(8)	Co(2)−C(6)	1.818(8)	Co(3)−C(12)	2.059(7)
Ru(1)−C(8)	2.093(8)	Co(1)−C(2)	1.77(1)	Co(2)−C(11)	2.105(8)	C(11)−C12)	1.43(1)
Ru(1)−C(9)	1.884(8)	Co(1)−C(3)	2.549(9)	Co(2)−C(12)	2.104(7)	C(12)−C(13)	1.44(1)
Ru(1)−C(10)	1.89(1)	Co(1)−C(4)	2.069(7)	Co(3)−C(3)	1.781(8)	C(13)−C(14)	1.17(1)
C(12)−Ru(1)−Co(2)	52.96(2)	C(11)−Co(2)−Co(1)	52.9(2)	O(3)−C(3)−Co(1)	125.9(7)	C(12)−C(11)−Co(2)	70.0(4)
C(12)−Ru(1)−Co(3)	51.2(2)	C(12)−Co(2)−Co(1)	75.6(2)	O(3)−C(3)−Co(3)	167.1(8)	Co(1)−C(11)−Co(2)	72.1(2)
Co(2)−Ru(1)−Co(3)	88.26(3)	C(11)−Co(2)−Ru(1)	79.2(2)	O(4)−C(4)−Co(1)	134.0(6)	C(12)−C(11)−Co(3)	67.8(4)
C(12)−Ru(1)−Co(1)	66.87(2)	C(12)−Co(2)−Ru(1)	54.2(2)	O(4)−C(4)−Co(2)	148.6(7)	Co(1)−C(11)−Co(3)	72.8(2)
Co(2)−Ru(1)−Co(1)	55.24(3)	Co(1)−Co(2)−Ru(1)	66.92(3)	O(5)−C(5)−Co(2)	178.3(7)	Co(2)−C(11)−Co(3)	113.6(3)
Co(3)−Ru(1)−Co(1)	55.65(3)	C(11)−Co(3)−C(12)	39.9(3)	O(6)−C(6)−Co(2)	148.2(6)	C(11)−C(12)−Co(3)	72.0(4)
C(11)−Co(1)−Co(2)	55.0(2)	C(11)−Co(3)−Co(1)	52.4(2)	O(6)−C(6)−Ru(1)	134.6(6)	C(11)−C(12)−Co(2)	70.1(4)
C(11)−Co(1)−Co(3)	54.78(2)	C(12)−Co(3)−Co(1)	75.7(2)	O(7)−C(7)−Co(3)	176.6(7)	Co(3)−C(12)−Co(2)	116.0(3)
Co(2)−Co(1)−Co(3)	91.74(4)	C(11)−Co(3)−Ru(1)	78.2(2)	O(8)−C(8)−Co(3)	141.3(7)	C(11)−C(12)−Ru(1)	110.6(4)
C(11)−Co(1)−Ru(1)	75.0(2)	C(12)−Co(3)−Ru(1)	54.0(2)	O(8)−C(8)−Ru(1)	138.8(7)	Co(3)−C(12)−Ru(1)	74.9(2)
Co(2)−Co(1)−Ru(1)	57.803(3)	Co(1)−Co(3)−Ru(1)	65.99(3)	O(9)−C(9)−Ru(1)	176.3(8)	Co(2)−C(12)−Ru(1)	72.9(2)
Co(3)−Co(1)−Ru(1)	58.37(3)	O(1)−C(1)−Co(1)	174.7(9)	O(10)−C(10)−Ru(1)	178.9(7)	C(12)−C(13)−C(14)	175.0(9)
C(11)−Co(2)−C(12)	39.9(3)	O(2)−C(2)−Co(1)	178.7(8)	C(12)−C(11)−Co(1)	105.6(5)		
Molecule B							
Ru(2)−Co(4)	2.765(1)	Ru(2)−C(29)	2.149(7)	Co(4)−C(28)	2.064(7)	Co(6)−C(23)	1.759(9)
Ru(2)−Co(5)	2.54(1)	Co(4)−Co(5)	2.47(1)	Co(5)−C(20)	1.796(8)	Co(6)−C(24)	1.837(8)
Ru(2)−Co(6)	2.528(1)	Co(4)−Co(6)	2.459(2)	Co(5)−C(21)	1.757(9)	Co(6)−C(28)	2.117(8)
Ru(2)−C(24)	2.146(7)	Co(4)−C(18)	1.79(1)	Co(5)−C(27)	1.858(8)	Co(6)−C(29)	2.080(7)
Ru(2)−C(25)	1.874(9)	Co(4)−C(19)	1.79(1)	Co(5)−C(28)	2.121(7)	C(28)−C(29)	1.41(1)
Ru(2)−C(26)	1.889(8)	Co(4)−C(20)	2.279(9)	Co(5)−C(29)	2.084(7)	C(29)−C(30)	1.45(1)
Ru(2)−C(27)	2.124(9)	Co(4)−C(22)	2.235(9)	Co(6)−C(22)	1.808(8)	C(30)−C(31)	1.20(1)
C(29)−Ru(2)−Co(6)	52.0(2)	C(28)−Co(4)−Co(6)	55.0(2)	O(11)−C(18)−Co(4)	174.6(9)	C(29)−C(28)−Co(4)	105.8(5)
C(29)−Ru(2)−Co(5)	52.0(2)	C(29)−Co(5)−C(28)	39.2(3)	O(12)−C(19)−Co(4)	179.1(8)	Co(4)−C(28)−Co(6)	112.8(3)
Co(6)−Ru(2)−Co(5)	88.33(4)	C(29)−Co(5)−Co(4)	75.4(2)	O(13)−C(20)−Co(4)	129.9(7)	C(29)−C(28)−Co(5)	69.0(4)
C(29)−Ru(2)−Co(4)	68.2(2)	C(28)−Co(5)−Co(4)	52.8(2)	O(15)−C(22)−Co(6)	155.7(7)	Co(4)−C(28)−Co(5)	72.2(2)
Co(6)−Ru(2)−Co(4)	55.13(3)	C(29)−Co(5)−Ru(2)	54.3(2)	O(16)−C(23)−Co(6)	179.7(7)	Co(6)−C(28)−Co(5)	112.8(3)
Co(5)−Ru(2)−Co(4)	55.23(3)	C(28)−Co(5)−Ru(2)	78.8(2)	O(17)−C(24)−Co(6)	145.2(6)	C(28)−C(29)−Co(5)	71.8(4)
C(28)−Co(6)−C(29)	39.3(3)	Co(4)−Co(5)−Ru(2)	67.05(4)	O(13)−C(20)−Co(5)	156.7(8)	C(28)−C(29)−Co(6)	71.8(4)
C(28)−Co(4)−Co(5)	54.9(2)	C(28)−Co(6)−Co(4)	53.0(2)	O(14)−C(21)−Co(5)	173.7(8)	Co(5)−C(29)−Co(6)	116.0(3)
Co(6)−Co(4)−Co(5)	91.58(4)	C(29)−Co(6)−Co(4)	75.7(2)	O(17)−C(24)−Ru(2)	136.2(6)	C(28)−C(29)−Ru(2)	111.6(5)
C(28)−Co(4)−Ru(2)	74.4(2)	C(28)−Co(6)−Ru(2)	79.1(2)	O(18)−C(25)−Ru(2)	177.8(7)	Co(5)−C(29)−Ru(2)	73.7(2)
Co(6)−Co(4)−Ru(2)	57.53(3)	C(29)−Co(6)−Ru(2)	54.56(2)	O(19)−C(26)−Ru(2)	177.7(6)	Co(6)−C(29)−Ru(2)	116.0(3)
Co(5)−Co(4)−Ru(2)	57.72(3)	Co(4)−Co(6)−Ru(2)	67.34(4)	O(20)−C(27)−Ru(2)	136.8(6)	C(29)−C(30)−C(31)	174.4(8)

and angles are given in Table 6. The structure is similar to that of **11b**, and two different, almost identical molecules, **A** and **B**, are present in the asymmetric unit. The C(4)O(4) and C(8)O(8) carbonyl ligands in **15aA** are bridging between Co(1), Co(2) and Ru(1), Co(3), respectively. The Co(1)−C(3) and Ru(1)−C(6) distances of 2.549(9) and 2.199(8) Å, respectively, are considerably longer than the Co(3)−C(3) and Co(2)−C(6) distances of 1.781(8) and 1.818(8) Å, respectively, which suggests that C(3)O(3) and C(6)O(6) occupy a bent semibridging position.[22] The remaining carbonyls are terminal. The nonbonding Co(2)⋯Co(3) and Co(5)⋯Co(6) distances in the molecules **A** and **B** are both 3.53(1) Å, and the dihedral angles between the butterfly wings are 113.4 and 116.4°, respectively.

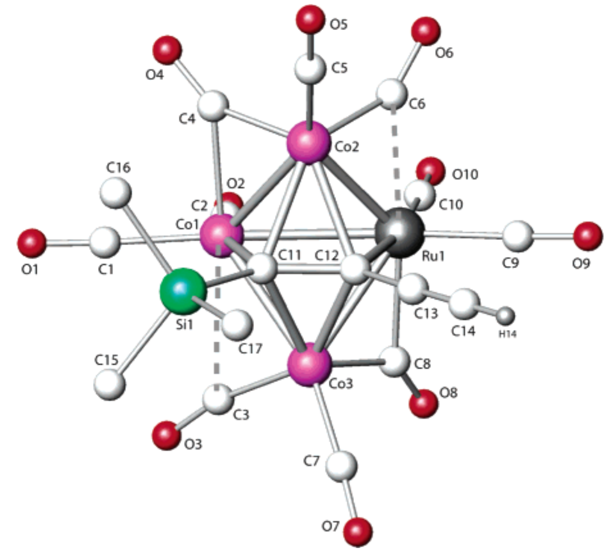


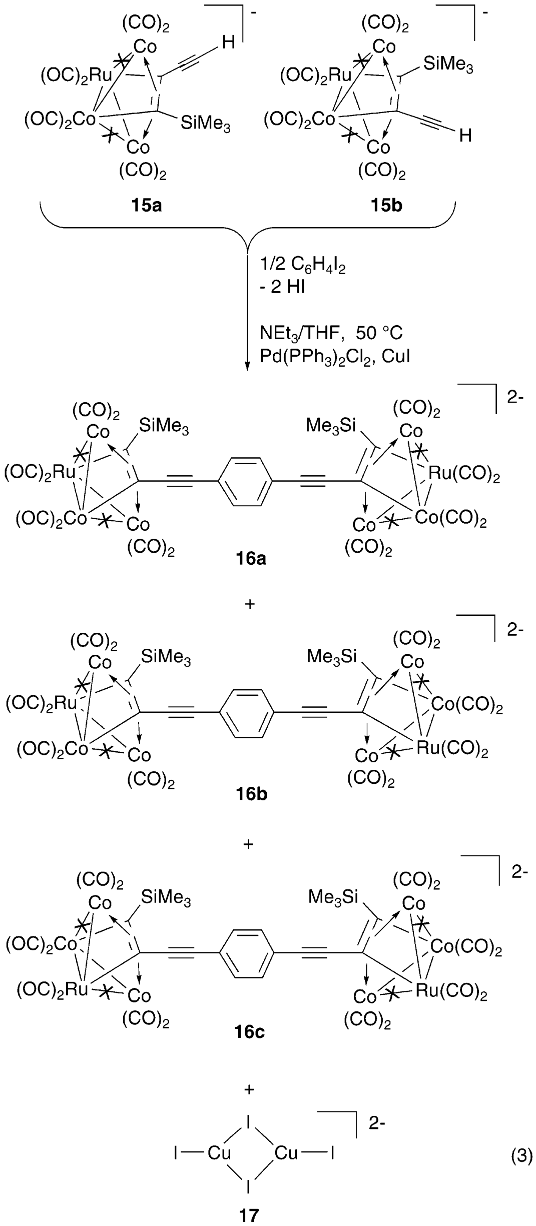
Figure 6. View of the molecular structure of the anionic cluster in **15a**. Hydrogen atoms have been omitted for clarity.

To avoid the cation exchange in NEt_4·**11** for $N(n\text{-}Bu)_4^+$, we first prepared the cluster [PPN][$RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$] (PPN·**11**) by cation metathesis since subsequent replacement of PPN^+ with $N(n\text{-}Bu)_4^+$ should not occur during the desilylation step. As expected, PPN·**11** was obtained in two isomeric forms and treatment with TBAF afforded [PPN][$RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)$] (PPN·**15**) in high yield and also in two isomeric forms (eq 2). This cluster was readily characterized by its spectroscopic properties, which included resonances in the ^{1}H NMR spectrum for the HC≡ proton at δ 3.23 and 3.44.

$$NEt_4\cdot\mathbf{11} \xrightarrow[\text{THF,}\ 60\ °C,\ 2\ h]{[PPN]Cl} PPN\cdot\mathbf{11} \xrightarrow[\text{THF, room. temp}]{1/4\ \text{TBAF-THF/}H_2O} PPN\cdot\mathbf{15} \quad (2)$$

Coupling of the Diyne Cluster To Form a Linked "Dicluster" Compound through π-Delocalized Organic Frameworks. As shown in eq 3, the synthesis of the dianion **16** could be achieved through the Pd(II)/Cu(I) catalytic Sonogashira coupling reaction of cluster [$RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)$]$^-$ (**15**) with 1,4-diiodobenzene.[35] The benzene ring represents a suitable spacer for a π-conjugated system linking cluster molecules. Since it was difficult to separate NEt_4·**15** from $N(n\text{-}Bu)_4$·**15**, we have used the mixture for the coupling reaction. The reaction was performed in THF/NEt_3 at 50 °C for 18 h, and the color of the solution changed from violet to brown. Extraction with hexane removed a yellow, copper iodide complex (see below), and purification of the remaining product with toluene/pentane afforded **16**. The solution IR spectrum of this latter exhibits the characteristic ν(CO) pattern seen for e.g. **15**. In the ^{1}H NMR spectrum we observe the disappearance of the HC≡ signals present in **15**, and negative ion electrospray mass spectrometry (CH_2Cl_2 solution) showed the highest mass molecular weight ions at m/z 717.5 ($Z = 2$) corresponding to the doubly charged, coupled clusters, with fragments resulting from loss of CO groups. When PPN·**15** was used, the yellow product could be characterized by X-ray diffraction to be the centrosymmetric dimer $[PPN]_2$-[$Cu_2(\mu\text{-}I)_2I_2$] ($[PPN]_2$·**17**). These data are not reported here since complexes containing $[Cu_2I_4]^{2-}$ associated with large cations $[NR_4]^+$, $[PR_4]^+$, or $[AsR_4]^+$ (R = alkyl or phenyl) have already been described in the literature.[36]

Unfortunately, the oxidative coupling of **15**, using standard Eglinton−Glaser conditions[37] ($Cu(OAc)_2$, pyridine, 25 °C), failed.



Formation of Bimetallic Particles by the Sol−Gel Method. As indicated in the Introduction, we considered the use of alkynes containing a $-Si(OR)_3$ group as a way to

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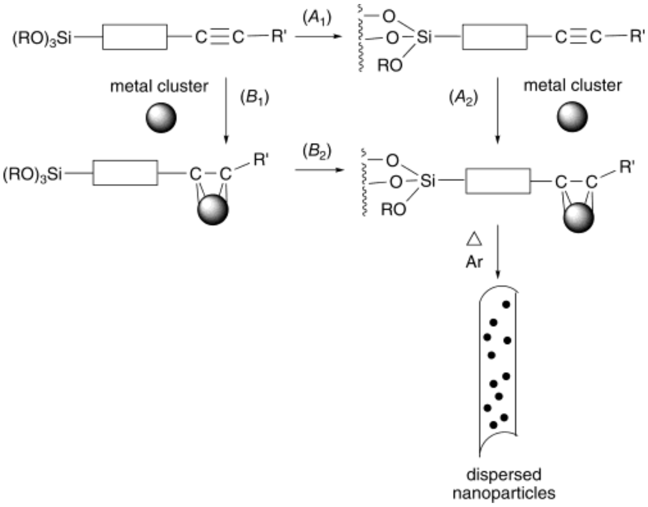
Scheme 4. Complementary Strategies Based on Functional Alkyne Ligands for the Covalent Grafting of Metal Clusters, Followed by Thermal Treatment to Generate Nanoparticles



covalently anchor metal carbonyl clusters onto surfaces and form new cluster-derived nanomaterials. Two complementary approaches are conceivable: first attach the $-Si(OR)_3$ end of the ligand to the inorganic matrix (Scheme 4, A_1) and then react its alkyne function with the molecular cluster (Scheme 4, A_2), or first prepare the alkyne cluster (Scheme 4, B_1) and react its $-Si(OR)_3$ group with the host matrix to generate the covalent linkage (Scheme 4, B_2).[2]

In a preliminary study, we have used the newly reported[5] trialkoxysilyl alkyne $HC{\equiv}C(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3$ to prepare a xerogel according to Scheme 4, A_1. It was characterized by ^{29}Si CP-MAS NMR spectroscopy and shown to remain highly porous, 657 m^2/g (determined by nitrogen adsorption isotherms), despite the grafting of the functional alkyne, with a mean pore diameter of 11 nm. Anchoring of $[RuCo_3(CO)_{12}]^-$ was done by reaction of the cluster in THF with the functionalized xerogel. Thermal decomposition was followed in situ in a magnetic thermobalance[1a] and led to spherical particles of 2.2−5.5 nm in diameter (TEM). X-ray diffraction showed the presence of a hexagonal phase of a $RuCo_3$ alloy. Magnetic measurements show that these particles display ferromagnetic behavior.[38] Further studies are in progress to explore the scope of this sol−gel method applied to mixed-metal clusters for the preparation of bimetallic nanoparticles.

Conclusion

In this work we have described the synthesis and characterization of a series of new alkyne clusters of the type $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}RC_2R')]^-$ (**1**−**5**) obtained in excellent yields by reaction of the tetrahedral cluster $[RuCo_3(CO)_{12}]^-$ with $MeOC(O)C{\equiv}CC(O)OMe$, $PhC{\equiv}CH$, $HC{\equiv}C(Me)\text{-}C{=}CH_2$, $HC{\equiv}CCH_2OCH_2C{\equiv}CH$, and the new alkyne $HC{\equiv}CCH_2NHC(O)C{\equiv}CPh$, respectively. All the alkynes were linked to the cluster in a $\mu_4\text{-}\eta^2$ fashion. Reactions of the anionic clusters **1**−**3** with $[Cu(NCMe)_4]BF_4$ led to their selective fragmentation to the trinuclear neutral clusters **6**−**8**. The coordinated alkynes in clusters **1**, **3**−**5**, and **8** offer the potential of further derivatization. The functionalization of clusters $[RuCo_3(CO)_{12}]^-$ and $[FeCo_3(CO)_{12}]^-$ was also performed directly by reaction with $PhC{\equiv}CC(O)NH(CH_2)_3\text{-}Si(OMe)_3$ (**L**^{2}), which is of interest for future condensation with a silica matrix via the sol−gel method. Indeed, preliminary results indicate the potential of porous gels, obtained from $HC{\equiv}C(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3$, for tethering alkyne mixed-metal clusters which can be used as precursors to bimetallic particles. Reaction of 1,4-bis(trimethylsilyl)-butadiyne with $[RuCo_3(CO)_{12}]^-$ afforded the air-stable cluster **11** whose reaction with $[Cu(NCMe)_4]BF_4$ led, in addition to fragmentation, to the unexpected proto-desilylation of the core-bound $SiMe_3$ group due to the presence of fluoride ions. The thermal reaction of **11** with $[AuCl(PPh_3)]$ or PPh_3 led to selective substitution of a carbonyl ligand on the ruthenium atom by triphenylphosphine. Although CO ligands on cobalt are more labile than on ruthenium, the latter center is more electron-deficient and will form stronger bonds with the phosphine. Proto-desilylation of **11** using TBAF/THF−H_2O occurred at the expected site to yield $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)]^-$. A Sonogashira coupling reaction between cluster $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)]^-$ (**15**) and 1,4-diiodobenzene afforded an isomeric mixture of the diclusters $[\{RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}C)\}_2C_6H_4]^{2-}$ (**16**), the properties of which will be the subject of future work.

Experimental Section

All the 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 ligand $PhC{\equiv}CC(O)NH(CH_2)_3Si(OMe)_3$[4] and the clusters $[NEt_4][RuCo_3(CO)_{12}]$[24c] and $[NEt_4][FeCo_3(CO)_{12}]$[39] were prepared according to literature methods. Elemental C, H, and N analyses 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 spectrometer. The ^1H NMR spectra were recorded at 200.13, 300.13, 400.13, or 500.13 MHz on a Bruker AC200, AC300, AVANCE 300, AVANCE 400, or AVANCE 500 instrument.

Synthesis of the ligand $PhC{\equiv}CC(O)NHCH_2C{\equiv}CH$ (L^1). A solution of propargylamine (0.783 mL, 11.42 mmol) in 20 mL of toluene was added dropwise to a toluene solution of 3-phenylpropynoyl chloride, obtained by reaction of phenylpropynoic acid (0.459 g, 3.425 mmol) with thionyl chloride (0.300 mL, 4.110 mmol). After the addition was complete, the mixture was stirred at room temperature for 1 h and then poored into 60 mL of cold water. The mixture was filtered, and the solid was discarded. The layers were separated, and the organic fraction was dried over $MgSO_4$ and then evaporated to afford **L^1** (0.496 g, 2.710 mmol, 79% (based on 3-phenylpropiolic acid)) as a yellow solid. IR ($CHCl_3$): 3439 (m, ν_{NH}), 3307 (s, $\nu_{\equiv CH}$), 2223 (vs, $\nu_{C\equiv C}$), 1654 (vs, $\nu_{C=O}$), 1506 (vs, δ_{NH}). ^1H NMR (300.13 MHz, $CDCl_3$): δ 2.28 (t, $^4J(HH)$ =

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2.6 Hz, 1H, HC≡), 4.15 (dd, ^{3}J(HH) = 5.4 Hz, ^{4}J(HH) = 2.6 Hz, 2 H, CH_2N), 6.22 (br, NH), 7.25−7.53 (m, 5H, Ph). $^{13}C\{^{1}H\}$ NMR (100.62 MHz, $CDCl_3$) δ: 29.62 (s, NCH_2), 72.27 (s, H*C*≡C), 78.61 (s, HC≡*C*), 82.42 (s, PhC≡*C*), 85.74 (s, Ph*C*≡C), 120.0, 127.1, 128.3, 128.6, 130.3 (5 s, C_6H_5), 132.6 (s, C_{ipso} of C_6H_5), 153.0 (s, C=O). Anal. Calcd for $C_{12}H_9NO$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.82; H, 5.12; N, 7.78.

Synthesis of $[NEt_4][RuCo_3(CO)_{10}\{\mu_4\text{-}\eta^2\text{-}MeOC(O)C_2C(O)OMe\}]$ (NEt_4·1). To a solution of $[NEt_4][RuCo_3(CO)_{12}]$ (0.550 g, 0.739 mmol) in 50 mL of THF was added dimethylacetylene dicarboxylate (dmad) (0.460 mL, 3.736 mmol). The mixture was heated to reflux, and the progress of the reaction was monitored by IR spectroscopy. After ca. 7 h the reaction was complete. Recrystallization of the residue from CH_2Cl_2/hexane yielded violet crystals of NEt_4·**1** (0.450 g, 0.542 mmol, 73%). IR (CH_2Cl_2): 2059 (m), 2015 (vs), 1988 (s, sh), 1833 (m), $\nu_{C\equiv O}$, 1712 (m, $\nu_{C=O}$). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.28 (m, 12 H, $CH_2C\mathit{H}_3$), 3.20 (m, 8 H, CH_2), 3.50 (s, 3 H, OCH_3), 3.57 (s, 3 H, OCH_3). Anal. Calcd for $C_{24}H_{26}Co_3NO_{14}Ru$: C, 34.72; H, 3.16; N, 1.69. Found: C, 34.84; H, 3.23; N, 1.76.

Synthesis of $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2Ph)]$ (NEt_4·2). Similary to the synthesis of NEt_4·**1**, the reaction of $[NEt_4][RuCo_3(CO)_{12}]$ (0.740 g, 0.994 mmol) in 50 mL of THF with phenylacetylene (0.556 mL, 5.064 mmol) was monitored by IR, which indicated the completion of the reaction after ca. 7 h. After filtration, the solvent was removed under vacuum. The residue was washed with hexane and recrystallized from CH_2Cl_2/hexane to yield violet crystals of NEt_4·**2** (0.576 g, 0.729 mmol, 73%). IR (CH_2Cl_2, ν_{CO}): 2049 (m), 2005 (vs), 1975 (sh), 1820 (m). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.27 (m, 12 H, CH_3), 3.11 (m, 8 H, CH_2), 6.80−7.26 (m, 5 H, Ph), 8.36 (br s, 0.25 H, HC_2 of one isomer), 8.84 (br s, 0.75 H, HC_2 of the other isomer). Anal. Calcd for $C_{26}H_{26}Co_3NO_{10}Ru$: C, 39.51; H, 3.32; N, 1.77. Found: C, 39.67; H, 3.25; N, 1.61.

Synthesis of $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2(Me)C{=}CH_2]$ (NEt_4·3). By a procedure similar to that detailed for NEt_4·**1**, the reaction of $[NEt_4][RuCo_3(CO)_{12}]$ (0.670 g, 0.900 mmol) in 50 mL of THF with 2-methyl-1-buten-3-yne (0.407 mL, 4.277 mmol) at reflux for 5 h afforded, after workup, cluster NEt_4·**3** (0.539 g, 0.715 mmol, 80%) as violet crystals, which were further washed with hexane. IR (CH_2Cl_2, ν_{CO}): 2048 (m), 2003 (vs), 1973 (s), 1817 (m). The two isomers were separated manually under the microscope and their NMR spectra recorded. Isomer NEt_4·**3a** gives rise to large, parallelepipedic crystals whereas NEt_4·**3b** crystallized as thin plates. ^{1}H NMR for NEt_4·**3a** (300.13 MHz, $CDCl_3$): δ 1.37 (m, 12H, $CH_2C\mathit{H}_3$), 1.75 (m, 3H, $CH^AH^B{=}C(C\mathit{H}_3)$, X_3 part of an ABX_3 spin system), 3.24 (m, 8H, $C\mathit{H}_2CH_3$), 4.40 (m, 1H, $C\mathit{H}^AH^B{=}C(CH_3)$, A part of an ABX_3 spin system), 4.54 (m, 1H, $CH^A\mathit{H}^B{=}C(CH_3)$, B part of an ABX_3 spin system), 8.72 (br s, 1H, HC_2). ^{1}H NMR for NEt_4·**3b** (300.13 MHz, $CDCl_3$): δ 1.37 (m, 12H, $CH_2C\mathit{H}_3$), 1.82 (m, 3H, $CH^AH^B{=}C(C\mathit{H}_3)$, X_3 part of an ABX_3 spin system), 3.25 (m, 8H, $C\mathit{H}_2CH_3$), 4.55 (m, 1H, $C\mathit{H}^AH^B{=}C(CH_3)$, A part of an ABX_3 spin system), 4.92 (m, 1H, $CH^A\mathit{H}^B{=}C(CH_3)$, B part of an ABX_3 spin system), 8.17 (br s, 1 H, HC_2). Anal. Calcd for $C_{23}H_{26}Co_3NO_{10}Ru$: C, 36.62; H, 3.47; N, 1.86. Found: C, 36.45; H, 3.29; N, 1.75.

Synthesis of $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2CH_2OCH_2\text{-}C{\equiv}CH)]$ (NEt_4·4a). A solution of $[NEt_4][RuCo_3(CO)_{12}]$ (0.275 g, 0.369 mmol) and propargyl ether (0.042 mL, 0.408 mmol) was refluxed in 50 mL of THF for 5 h. The solution was filtered and evaporated under vacuum. Violet crystals of NEt_4·**4a** (0.266 g, 0.340 mmol, 92%) were obtained by recrystallization of the product from CH_2Cl_2/hexane. IR (CH_2Cl_2, ν_{CO}): 2049 (m), 2003 (vs), 1970 (s), 1819 (m). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.38 (m, 12 H, $CH_2C\mathit{H}_3$), 2.30 (br s, 1 H, ≡CH), 3.60 (m, 8 H, $C\mathit{H}_2CH_3$), 3.93 (s, 2 H, OCH_2), 4.09 (s, 2 H, OCH_2), 8.76 (br s, 1 H, HC_2). Anal. Calcd for $C_{24}H_{26}Co_3NO_{11}Ru$: C, 36.85; H, 3.35; N, 1.79. Found: C, 36.98; H, 3.41; N, 1.83.

Synthesis of $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HC_2C(O)NHCH_2\text{-}C{\equiv}CPh]$ (NEt_4·5). By a procedure similar to that described for NEt_4·**1**, the cluster NEt_4·**5** (0.278 g, 0.320 mmol, 95%) was obtained by reaction of $[NEt_4][RuCo_3(CO)_{12}]$ (0.250 g, 0.336 mmol) with $PhC{\equiv}CC(O)NHCH_2C{\equiv}CH$ ($\mathbf{L^1}$) (0.062 g, 0.339 mmol) in 50 mL refluxing THF for 5 h, and recrystallization from CH_2Cl_2/hexane. IR (CH_2Cl_2): 2051 (m), 2007 (vs), 1972 (s), 1820 (m) $\nu_{C\equiv O}$, 1646 (w, $\nu_{C=O}$). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.36 (m, 12H, $CH_2C\mathit{H}_3$), 3.25 (m, 8H, $C\mathit{H}_2CH_3$), 3.95 (m, 2H, $HNC\mathit{H}_2$), 5.65 (br, NH), 7.26−7.53 (m, 5H, Ph), 8.70 (br s, 1H, HC_2). Anal. Calcd. for $C_{30}H_{29}Co_3N_2O_{11}Ru$: C, 41.35; H, 3.35; N, 3.21. Found: C, 41.48; H, 3.17; N, 3.08.

Synthesis of $[RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}MeOC(O)C_2C(O)OMe]$ (6). Solid $[Cu(NCMe)_4]BF_4$ (0.227 g, 0.724 mmol) was added to a solution of NEt_4·**1** (0.300 g, 0.361 mmol) in 50 mL THF. After the mixture was stirred for 2.5 h at room temperature, a second equivalent of $[Cu(NCMe)_4]BF_4$ was added. The reaction occurs with a change of color from violet to red, and it was stopped after ca. 5 h. The reaction mixture was then filtered and the solvent was evaporated under vacuum. Extraction of the residue with hexane afforded the neutral cluster **6** (0.119 g, 0.195 mmol, 54%). IR (hexane): 2108 (m), 2075 (vs), 2058 (sh), 2042 (vs), 2016 (sh), 1911 (w), $\nu_{C\equiv O}$, 1721 (m, $\nu_{C=O}$). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 3.78 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3). Anal. Calcd for $C_{15}H_6Co_2O_{13}Ru$: C, 29.38; H, 0.99. Found: C, 29.59; H, 1.15.

Synthesis of $[RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)]$ (7). Cluster **7** (0.047 g, 0.082 mmol, 34%) was obtained as red crystals by a procedure and workup similar to those for **6** by addition of $[Cu(NCMe)_4]BF_4$ (0.074 g, 0.237 mmol) to a solution of NEt_4·**2** (0.187 g, 0.237 mmol) in 30 mL THF. IR (hexane, ν_{CO}): 2098 (s), 2062 (vs), 2047 (vs), 2036 (vs), 2012 (s), 1900 (m, br). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.10−7.45 (m, 5H, Ph), 7.97 (br s, 0.5 H, CH of one isomer), 9.59 (br s, 0.5 H, CH of the other isomer). Anal. Calcd for $C_{17}H_6Co_2O_9Ru$: C, 35.62; H, 1.06. Found: C, 35.84; H, 1.19.

Synthesis of $[RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2(Me)C{=}CH_2)]$ (8). By a procedure similar to that leading to **6** or **7**, cluster **8** (0.099 g, 0.186 mmol, 38%) was obtained by reaction of NEt_4·**3** (0.364 g, 0.483 mmol) in 35 mL of THF with $[Cu(NCMe)_4]BF_4$ (0.304 g, 0.966 mmol). IR (hexane, ν_{CO}): 2098 (m), 2061 (vs), 2046 (vs), 2034 (vs), 2022 (s), 2010 (s), 1902 (br,w). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.98 (m, 1.5H, $CH^AH^B{=}C(C\mathit{H}_3)$, X_3 part of an ABX_3 spin system of the first isomer), 2.19 (m, 1.5H, $CH^AH^B{=}C(C\mathit{H}_3)$, X_3 part of an ABX_3 spin system of the second isomer), 4.78 (m, 0.5H, $C\mathit{H}^AH^B{=}C(CH_3)$, A part of an ABX_3 spin system of the first isomer), 4.81 (m, 0.5H, $CH^A\mathit{H}^B{=}C(CH_3)$, B part of an ABX_3 spin system of the first isomer), 4.84 (m, 0.5H, $C\mathit{H}^AH^B{=}C(CH_3)$, A part of an ABX_3 spin system of the second isomer), 4.98 (m, 0.5H, $CH^A\mathit{H}^B{=}C(CH_3)$, B part of an ABX_3 spin system of the second isomer), 7.83 (br s, 0.5H, HC_2 of the second isomer), 9.36 (br s, 0.5H, HC_2 of the first isomer). Anal. Calcd for $C_{14}H_6Co_2O_9Ru$: C, 31.31; H, 1.13. Found: C, 31.46; H, 1.25.

Synthesis of $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC_2C(O)NH(CH_2)_3Si(OMe)_3]$ (NEt_4·9). A slight excess of $PhC{\equiv}CC(O)NH(CH_2)_3Si(OMe)_3$ ($\mathbf{L^2}$) (0.122 g, 0.397 mmol) was reacted with $[NEt_4][RuCo_3(CO)_{12}]$ (0.212 g, 0.284 mmol) in 50 mL refluxing THF for 6 h. Treatment of the solution by the procedures detailed above for related clusters and purification by repeated reprecipitations of the product from CH_2Cl_2/pentane and then CH_2Cl_2/hexane afforded

NEt$_4$·**9** (0.240 g, 0.241 mmol, 85%) as a violet powder. IR (CH$_2$Cl$_2$): 2052 (m), 2011 (vs), 1976 (s), 1826 (m), $\nu_{C\equiv O}$, 1650 (m, $\nu_{C=O}$). ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$): δ 0.34 (m, 1H, SiCH$_2$ of one isomer), 0.49 (m, 1H, SiCH$_2$ of the other isomer), 1.19 (m, 13H, $\mathrm{CH_2C}\mathit{H_2}\mathrm{CH_2}$ of one isomer and $\mathrm{NCH_2C}\mathit{H_3}$), 1.45 (m, 1H, $\mathrm{CH_2C}\mathit{H_2}\mathrm{CH_2}$ of the other isomer), 2.86 (m, 1H, NCH$_2$, of one isomer), 3.10 (m, 9H, NCH$_2$ of the other isomer and $\mathrm{NC}\mathit{H_2}\mathrm{CH_3}$), 3.47 (s, 4.5H, Si(OMe)$_3$ of one isomer), 3.50 (s, 4.5H, Si(OMe)$_3$ of the other isomer), 5.30 (br, NH of one isomer), 5.85 (br, NH of the other isomer), 7.03−7.11 (m, 5H, Ph). Anal. Calcd for $C_{33}H_{41}Co_3N_2O_{14}RuSi\cdot{}^1/_3C_6H_{14}$: C, 41.05; H, 4.49; N, 2.73. Found: C, 40.83; H, 3.91; N, 2.91.

Synthesis of [NEt$_4$][FeCo$_3$(CO)$_{10}$(μ_4-η^2-PhC$_2$C(O)NH(CH$_2$)$_3$Si(OMe)$_3$] (NEt$_4$·10). A 4-fold excess of PhC≡CC(O)NH(CH$_2$)$_3$Si(OMe)$_3$ (**L^2**) (0.443 g, 1.44 mmol) was reacted with [NEt$_4$][FeCo$_3$(CO)$_{12}$] (0.250 g, 0.357 mmol) in 50 mL refluxing THF for 4 h. The intense violet-black product was isolated by a procedure similar to that for NEt$_4$·**2**. Purification by repeated reprecipitation from CH$_2$Cl$_2$/pentane and then CH$_2$Cl$_2$/hexane at −20 °C afforded NEt$_4$·**10** (0.280 g, 0.295 mmol, 83%). IR (CH$_2$Cl$_2$): 2051 (m), 2003 (vs), 1996 (sh), 1932 (m,sh), 1813 (m,br), $\nu_{C\equiv O}$, 1650 (m, $\nu_{C=O}$). ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 0.40 (m, 1H, SiCH$_2$ of one isomer), 0.50 (m, 1H, SiCH$_2$ of the other isomer), 1.13 (t, ^3J(HH) = 7.1 Hz, 12H, $\mathrm{CH_2C}\mathit{H_3}$), 1.30 (m, 2H, $\mathrm{CH_2C}\mathit{H_2}\mathrm{CH_2}$), 2.97 (m, 1H, NCH$_2$ of one isomer), 3.11 (m, 1H, NCH$_2$ of the other isomer), 3.44 (q, ^3J(HH) = 7.1 Hz, 8H, $\mathrm{C}\mathit{H_2}\mathrm{CH_3}$), 3.48 (s, 4.5H, Si(OMe)$_3$ of one isomer), 3.50 (s, 4.5H, Si(OMe)$_3$) of the other isomer), 5.64 (br, NH of one isomer), 6.20 (br, NH of the other isomer), 6.74−7.85 (m, 5H, Ph). Anal. Calcd for $C_{33}H_{41}Co_3FeN_2O_{14}Si\cdot{}^1/_2C_6H_{14}$: C, 43.52; H, 4.87; N, 2.82. Found: C, 43.27; H, 4.39; N, 3.36.

Synthesis of [NEt$_4$][RuCo$_3$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡CSiMe$_3$)] (NEt$_4$·11). To a solution of [NEt$_4$][RuCo$_3$(CO)$_{12}$] (0.206 g, 0.276 mmol) in 30 mL THF was added 1,4-bis(trimethylsilyl)butadiyne (0.059 g, 0.303 mmol). After refluxing for 7 h, the solution was evaporated under reduced pressure, and the resulting solid was washed with hexane to remove excess alkyne. The resulting solid was extracted with CH$_2$Cl$_2$, the solution was filtered and concentrated, and addition of hexane afforded violet, air-stable crystals of NEt$_4$·**11** (0.166 g, 0.188 mmol, 68%). IR (CH$_2$Cl$_2$, ν_{CO}): 2047 (m), 2004 (vs), 1973 (s), 1820 (m). ^{1}H NMR (500.13 MHz, CDCl$_3$): δ 0.035 (s, 5.4H, ≡CSiMe$_3$ of the first isomer), 0.094 (s, 3.6H, ≡CSiMe$_3$ of the second isomer), 0.108 (s, 3.6H, C$_2$SiMe$_3$ of second isomer), 0.24 (s, 5.4H, C$_2$SiMe$_3$ of the first isomer), 1.39 (m, 12H, $\mathrm{CH_2C}\mathit{H_3}$), 3.27 (m, 8H, $\mathrm{C}\mathit{H_2}\mathrm{CH_3}$). Anal. Calcd for $C_{28}H_{38}Co_3NO_{10}RuSi_2$: C, 38.10; H, 4.34; N, 1.59. Found: C, 37.81; H, 4.39; N, 1.57.

Synthesis of [RuCo$_2$(CO)$_9$(μ_3-η^2-HC$_2$C≡CSiMe$_3$)] (12). The red cluster **12** (0.017 g, 0.029 mmol, 22%) was obtained similarly to **6**−**8** by reaction of NEt$_4$·**11** (0.118 g, 0.134 mmol) with [Cu(NCMe)$_4$]BF$_4$ (0.084 g, 0.268 mmol) in 25 mL of THF at room temperature. Surprisingly, partial desilylation of the ligand occurred (see text). IR (hexane, ν_{CO}): 2100 (m), 2066 (vs), 2055 (vs), 2037 (vs), 2011 (m,w), 1903 (w). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 0.15 (s, 4.5H, SiMe$_3$ of one isomer), 0.19 (s, 4.5H, SiMe$_3$ of the other isomer), 8.02 (br s, 0.5H, HC$_2$ of one isomer), 9.48 (br s, 0.5H, HC$_2$ of the other isomer). FAB$^+$/MS: *m/z* 594 (M$^+$), 566 (M − CO)$^+$, 538 (M$^+$ − 2CO)$^+$, 510 (M − 3CO)$^+$, 482 (M − 4CO)$^+$, 454 (M − 5CO)$^+$, 426 (M − 6CO)$^+$, 398 (M − 7CO)$^+$. Satisfactory elemental analyses could not be obtained.

Synthesis of [RuCo$_3$(CO)$_9$(NO)(μ_4-η^2-Me$_3$SiC$_2$C≡CSiMe$_3$)] (13). Solid [NO]BF$_4$ (0.057 g, 0.490 mmol) was added to a suspension of NEt$_4$·**11** (0.226 g, 0.256 mmol) in 25 mL CH$_2$Cl$_2$. After the mixture was stirred for 40 min at room temperature, the reaction was stopped and the solution was filtered and concentrated under reduced pressure. Separation by preparative TLC (SiO$_2$) using hexane as eluent afforded two bands. The first red band contains **12** (0.016 g, 0.028 mmol, 11%) described above, and the brown band contains **13** (0.040 g, 0.053 mmol, 21%) with the following data. IR (hexane): 2084 (m), 2055 (vs), 2045 (s), 2037 (s), 2022 (m), 2005 (m), 1915 (s), 1888 (m), 1874 (m), $\nu_{C\equiv O}$, 1805 (m, ν_{NO}). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 0.09 (s, 9H, SiMe$_3$), 0.35 (s, 9H, SiMe$_3$). FAB$^+$/MS: *m/z* 755 (M$^+$), 727 (M − CO)$^+$, 699 (M − 2CO)$^+$, 671 (M − 3CO)$^+$, 643 (M − 4CO)$^+$, 615 (M − 5CO)$^+$, 587 (M − 6CO)$^+$, 531 (M − 8CO)$^+$, 503 (M − 9CO)$^+$. Satisfactory elemental analyses could not be obtained.

Synthesis of [NEt$_4$][RuCo$_3$(CO)$_9$(PPh$_3$)(μ_4-η^2-Me$_3$SiC$_2$C≡CSiMe$_3$)] (NEt$_4$·14). Cluster NEt$_4$·**11** (0.161 g, 0.182 mmol) and [AuCl(PPh$_3$)] (0.090 g, 0.182 mmol) were refluxed in 40 mL of toluene for 3 h. The dark-brown solution was filtered and evaporated, and the solid was recrystallized from CH$_2$Cl$_2$/pentane to yield violet crystals of NEt$_4$·**14** (0.081 g, 0.073 mmol, 41%). This product was also obtained, in a better yield (55%), by reaction of NEt$_4$·**11** with one equivalent of PPh$_3$ in refluxing toluene. IR (CH$_2$Cl$_2$, ν_{CO}): 2060 (w), 2021 (s), 1969 (vs), 1948 (sh), 1798 (m). ^{1}H NMR (300.13 MHz, acetone-d_6): δ −0.47 (s, 9H, ≡CSiMe$_3$), 0.35 (s, 9H, −C$_2$SiMe$_3$), 1.33 (m, 12H, $\mathrm{CH_2C}\mathit{H_3}$), 3.43 (m, 8H, $\mathrm{C}\mathit{H_2}\mathrm{CH_3}$), 7.57−7.95 (m, 15H, Ph). ^{31}P{^{1}H} NMR (acetone-d_6) δ: 44.0 (s, $w_{1/2}$ = 50 Hz). Anal. Calcd for $C_{45}H_{53}Co_3NO_9PRuSi_2$: C, 48.39; H, 4.78; N, 1.25. Found: C, 48.58; H, 4.96; N, 1.39.

Proto-desilylation of [NEt$_4$][RuCo$_3$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡CSiMe$_3$)] (NEt$_4$·11). To a solution of NEt$_4$·**11** (0.274 g, 0.311 mmol) in 10 mL of THF was added dropwise N(*n*-Bu)$_4$F (1.0 M in THF/5 wt % H$_2$O; 0.077 mL, 0.077 mmol) with stirring. After 45 min, the solvent was evaporated to dryness, the product was extracted from CH$_2$Cl$_2$, and the solution was filtered and concentrated; addition of hexane afforded after 10 days violet crystals of [N(*n*-Bu)$_4$)][RuCo$_3$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡CH)] ([N(*n*-Bu)$_4$]·**15**) (0.051 g, 0.055 mmol, 18%) and a paste containing a mixture of [NEt$_4$][RuCo$_3$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡CH)] (NEt$_4$·**15**) and N(*n*-Bu)$_4$·**15** (0.179 g). Data for N(*n*-Bu)$_4$·**15** are as follows. IR (CDCl$_3$, ν_{CO}): 2048 (m), 2005 (vs), 1972 (s), 1818 (m). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 0.12 (s, 3H, C$_2$SiMe$_3$ of the first isomer), 0.25 (s, 6H, C$_2$SiMe$_3$ of the second isomer), 1.04 (m, 12H, $\mathrm{CH_2C}\mathit{H_3}$), 1.42 (m, 8H, $\mathrm{C}\mathit{H_2}\mathrm{CH_3}$), 1.59 (m, 8H, $\mathrm{CH_2C}\mathit{H_2}\mathrm{CH_2}$), 3.25 (m, 8H, NCH$_2$), 3.41 (s, 0.66H, C−H of the second isomer), 3.51 (s, 0.34H, C−H of the first isomer).

Synthesis and Proto-desilylation of [PPN][RuCo$_3$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡CSiMe$_3$)] (PPN·11). A solution of NEt$_4$·**11** (0.218 g, 0.247 mmol) and solid PPNCl (0.156 g, 0.272 mmol) in 20 mL of THF was heated at 60 °C for 2 h. The solution was cooled to −20 °C and then filtered, and the solvent was evaporated. Purification from toluene/pentane afforded violet PPN·**11** (0.303 g, 0.234 mmol, 95%), characterized by its ^{1}H NMR spectrum. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 0.012 (s, 5.4H, ≡CSiMe$_3$ of the first isomer), 0.097 (s, 3.6H, ≡CSiMe$_3$ of the second isomer), 0.118 (s, 3.6H, C$_2$SiMe$_3$ of the second isomer), 0.23 (s, 5.4H, C$_2$SiMe$_3$ of the first isomer), 7.17−7.82 (m, 30H, Ph).

To a Schlenk flask containing PPN·**11** (0.210 g, 0.162 mmol) and THF (14 mL) was added dropwise with stirring N(*n*-Bu)$_4$F (1.0 M in THF/5 wt % H$_2$O; 0.032 mL, 0.032 mmol). After 45 min, the solvent was evaporated to dryness, the product was extracted with toluene, and the solution was filtered. Recrystallization from toluene/pentane gave violet [PPN][RuCo$_3$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡CH)] (PPN·**15**) (0.169 g, 0.139 mmol, 86%). IR (CH$_2$Cl$_2$, ν_{CO}): 2047 (m), 2005 (vs), 1973 (s), 1821 (m). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 0.11 (s, 3.6H, −C$_2$SiMe$_3$ of the first

Table 7. Summary of Crystallographic Data for Complexes NEt$_4$·**3a**, NEt$_4$·**4a**, **6**, NEt$_4$·**11b**, NEt$_4$·**14**, and N(n-Bu$_4$)·**15a**

	NEt$_4$·**3a**	NEt$_4$·**4a**	**6**	NEt$_4$·**11b**	NEt$_4$·**14**	N(n-Bu$_4$)·**15a**
empirical formula	$C_{23}H_{26}Co_3NO_{10}Ru$	$C_{24}H_{26}Co_3NO_{11}Ru$	$C_{15}H_6Co_2O_{13}Ru$	$C_{28}H_{38}Co_3NO_{10}RuSi_2$	$C_{45}H_{53}Co_3NO_9PRuSi_2$	$C_{33}H_{46}Co_3NO_{10}RuSi$
MW	754.31	782.32	613.13	882.63	1116.89	922.66
color	violet	violet	red	violet	violet	violet
cryst system	monoclinic	monoclinic	triclinic	orthorhombic	orthorhombic	triclinic
space group	$P2_1$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
a (Å)	12.037(4)	9.766(5)	8.809(1)	9.886(5)	12.531(2)	10.534(1)
b (Å)	18.318(5)	11.686(5)	8.958(1)	11.468(5)	13.382(2)	14.500(1)
c (Å)	13.362(4)	25.695(5)	13.857(1)	32.221(5)	29.276(3)	26.686(1)
α (deg)	90.00	90.00	93.529(5)	90.00	90.00	87.389(5)
β (deg)	100.958(8)	95.038(5)	106.739(5)	90.00	90.00	87.001(5)
γ (deg)	90.00	90.00	101.978(5)	90.00	90.00	86.167(5)
V (Å^3)	2892.6(15)	2921(2)	1015.72(18)	3653(3)	4909.4(12)	4057.8(5)
Z	4	4	2	4	4	4
D_{calc} (g·cm^{-3})	1.732	1.779	2.005	1.605	1.511	1.510
wavelength (Å)	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
μ (mm^{-1})	2.253	2.237	2.414	1.859	1.431	1.649
temp (K)	173(2)	173(2)	173(2)	173(2)	173(2)	293(2)
hkl limiting indices	−15/15	−14/14	−12/10	0/13	0/16	−12/13
	−21/23	0/17	−12/12	0/16	0/17	−18/17
	−17/17	0/38	−18/19	−45/45	−37/37	−34/34
F(000)	1504	1560	596	1784	2280	1880
θ limits (deg)	2.71−27.46	0.99−32.02	2.97−30.12	2.4−30.0	2.33−27.47	2.29−27.46
no. of data meas	12018	10119	5580	10356	10871	17153
no. of data ($I > 2\sigma(I)$)	6888	6256	3595	6183	8984	9646
R	0.0543	0.0333	0.1232	0.0834	0.0368	0.0815
R_w	0.1279	0.0697	0.1083	0.1551	0.0770	0.1499
GOF	0.965	0.714	1.12	1.09	0.860	1.030
largest peak in final difference (e·Å^{-3})	1.066	0.46	1.32	0.71	0.453	1.016

isomer), 0.24 (s, 5.4 H, −C$_2$SiMe$_3$ of the second isomer), 3.23 (s, 0.4H, C−H of the second isomer), 3.44 (s, 0.6H, C−H of the first isomer), 7.16−7.87 (m, 30H, Ph). Anal. Calcd for $C_{53}H_{40}Co_3NO_{10}P_2RuSi$: C, 52.23; H, 3.31; N, 1.15. Found: C, 52.48; H, 3.48; N, 1.39.

Coupling Reaction of [NEt$_4$/N(n-Bu)$_4$]·15 with C$_6$H$_4$I$_2$. To the mixture of [NEt$_4$]·**15** and [N(n-Bu)$_4$]·**15** (0.065 g), obtained by desilylation of [NEt$_4$]·**11** (see above), dissolved in THF/dry triethylamine 2/10 mL, was added a mixture of catalytic amounts of [PdCl$_2$(PPh$_3$)$_2$] and CuI. After stirring for 5 min, pure 1,4-diiodobenzene (0.012 g, 0.035 mmol) was added, the mixture was heated at 50 °C for 18 h, and the color of the solution changed from violet to brown. The solution was filtered and evaporated to dryness under vacuum, and extraction of the solid with hexane afforded yellow [NEt$_4$/(n-Bu)$_4$N]$_2$[Cu$_2$(μ-I)$_2$I$_2$] (0.01 g). Purification of the remaining solid from CH$_2$Cl$_2$/hexane at −20 °C afforded the coupled product [NEt$_4$/N(n-Bu)$_4$]$_2$[{RuCo$_3$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡C−)}$_2$C$_6$H$_4$] ([NEt$_4$/N(n-Bu)$_4$]$_2$·**16**) (0.052 g). IR (CH$_2$Cl$_2$, ν_{CO}): 2047 (m), 2004 (vs), 1972 (s), 1820 (m). ES/MS m/z of the dianion **16**$^{2-}$: 717.5 (M)$^{2-}$, 703.5 (M − CO)$^{2-}$, 689.5 (M − 2CO)$^{2-}$, 675.5 (M − 3CO)$^{2-}$, 661.5 (M − 4CO)$^{2-}$, 647.5 (M − 5CO)$^{2-}$, 633.5 (M − 6CO)$^{2-}$, 619.5 (M − 7CO)$^{2-}$, 605.5 (M − 8CO)$^{2-}$, 591.5 (M − 9CO)$^{2-}$, 577.5 (M − 10CO)$^{2-}$, 563.5 (M − 11CO)$^{2-}$, 549.5 (M − 12CO)$^{2-}$, 535.5 (M − 13CO)$^{2-}$, 521.5 (M − 14CO)$^{2-}$, 507.5 (M − 15CO)$^{2-}$. The ^{1}H NMR spectrum (300 and 500 MHz) contained numerous poorly resolved signals corresponding to the expected mixture of isomers and associated with the NEt$_4^+$ and N(n-Bu)$_4^+$ cations.

X-ray Structural Analyses of [NEt$_4$][RuCo$_3$(CO)$_{10}$(μ_4-η^2-HC$_2$(Me)C=CH$_2$] (NEt$_4$·3a), [NEt$_4$][RuCo$_3$(CO)$_{10}$(μ_4-η^2-HC$_2$CH$_2$OCH$_2$C≡CH)] (NEt$_4$·4a), [RuCo$_2$(CO)$_9$(μ_3-η^2-MeOC(O)C$_2$C(O)OMe] (6), [NEt$_4$][RuCo$_3$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡CSiMe$_3$)] (NEt$_4$·11b), [NEt$_4$][RuCo$_3$(CO)$_9$(PPh$_3$)(μ_4-η^2-Me$_3$SiC$_2$C≡CSiMe$_3$)] (NEt$_4$·14), and [n-Bu$_4$N][RuCo$_3$(CO)$_{10}$(μ_4-η^2-Me$_3$SiC$_2$C≡CH)] ([N(n-Bu)$_4$]·15a). A summary of the crystal and refinement data for NEt$_4$·**3a**, NEt$_4$·**4a**, **6**, NEt$_4$·**11b**, NEt$_4$·**14**, and [N(n-Bu)$_4$]·**15a**, is given in Table 7. 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 in Table 7. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in ϕ angle), each at 20 s exposure. The structures were solved using direct methods (SIR97) and refined against F^2 using the SHELXL97 software.[40,41] The absorption was corrected empirically with Sortav.[42] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.

Acknowledgment. We thank Dr. C. Estournès (IPCMS Strasbourg) for the TEM and magnetic studies and helpful discussions. We are grateful to the CNRS, the Université Louis Pasteur Strasbourg and the Ministère de la Recherche (Paris) (ACI Nanostructures 2001) for financial support. This project was also supported by the Fonds International de Coopération Universitaire—FICU (AUPELF-UREF, Agence Universitaire de la Francophonie) and by the International Research Training Group 532 “Physical Methods for the Structural Investigation of New Materials” (DFG Bonn, CNRS, Ministère de la Recherche, Paris).

Supporting Information Available: Crystallographic data for NEt$_4$·**3a**, NEt$_4$·**4a**, **6**, NEt$_4$·**11b**, NEt$_4$·**14**, and [N(n-Bu)$_4$]·**15** in CIF format. Views of the molecular structures of cluster **6** and the anionic clusters in **3a**, **4a**, **11b**, **14**, and **15a**. This material is

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available free of charge via the Internet at http://pubs.acs.org. This material has also been deposited in CIF format with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-218645-218650. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

IC034832K