A General Route to Prochiral and Chiral Dicationic Molybdenum−Cobalt Acetylenic Complexes: Synthesis, Structures, and Reactivity

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Several [Co−Co]−alkyne adducts $[Co_2(CO)_6](\mu\text{-}\eta^2,\eta^2\text{-}HOCR^1R^2\text{-}C{\equiv}C{-}CR^1R^2OH)]$ were prepared ($R^1 = R^2 = H$ (**1**); $R^1 = H$, $R^2 = CH_3$ (**2**); $R^1 = R^2 = CH_3$ (**3**)) and their X-ray molecular structures determined, showing that the μ-alkyne unit adopts a specific geometry depending on the nature of the alkyne unit. The prochiral [Mo−Co]−alkyne adduct $[CpMoCo(CO)_5(\mu\text{-}\eta^2,\eta^2\text{-}HOCH_2{-}C{\equiv}C{-}CH_2OH)]$ (**4**), identified by X-ray analysis, was obtained from $[Co_2(CO)_6](\mu\text{-}\eta^2,\eta^2\text{-}HOCH_2{-}C{\equiv}C{-}CH_2OH)]$ (**1**) via replacement of a $-Co(CO)_3$ vertex by the isolobal moiety $-CpMo(CO)_2$. Complex **4** reacts with aqueous HBF_4 to produce the dicationic tetranuclear species $[\{CpMoCo(CO)_5(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{-}C{\equiv}C{-}CH_2\text{-})\}_2O][BF_4]_2$ (**5**), which reacts further with nucleophiles to give a new dicationic tetranuclear species $[\{CpMoCo(CO)_5(\mu\text{-}\eta^2,\eta^2\text{-}Nu^1{-}CH_2{-}C{\equiv}C{-}CH_2{-})\}_2O][BF_4]_2$ (Nu^1 = pyridine (**6**), 3-picoline (**7**), triphenylphosphine (**8**)), where the nucleophile has been introduced to the carbenium center ($-CH_2^+$). Subsequent treatment of these dications in acidic medium produces the carbenium ions $[CpMoCo(CO)_5(\mu\text{-}\eta^2,\eta^3\text{-}Nu^1{-}CH_2{-}C{\equiv}C{-}CH_2)][BF_4]_2$ (Nu^1 = pyridine (**9**), 3-picoline (**10**), triphenylphosphine (**11**)), which further react with nucleophile Nu^2 to produce dications $[CpMoCo(CO)_5(\mu\text{-}\eta^2,\eta^2\text{-}Nu^1{-}CH_2{-}C{\equiv}C{-}CH_2{-}Nu^2)][BF_4]_2$ {$Nu^1 = Nu^2$ = pyridine (**13**); Nu^1 = pyridine, Nu^2 = triphenylphosphine (**14**); $Nu^1 = Nu^2$ = triphenylphosphine (**15**); $Nu^1 = Nu^2$ = 3-picoline (**16**); Nu^1 = pyridine = Nu^2 = 3-picoline (**17**)). This synthetic approach is unprecedented because it allows the placement of the same or different types of nucleophiles in a stepwise fashion at the two terminal carbon atoms of the acetylenic complex, yielding, for instance, the chiral dicationic [Mo−Co] cluster $[CpMoCo(CO)_5(\mu\text{-}\eta^2,\eta^2\text{-}C_6H_5N{-}CH_2{-}C{\equiv}C{-}CH_2{-}NC_6H_4(CH_3))][BF_4]_2$ (**17**). The X-ray molecular structures of **13**, **16**, and **17** belonging to this family were determined, including the first chiral [Mo−Co] complex (**17**) possessing two different functional groups. Further, the structure shows that the coordinated functionalized alkyne can adopt a specific geometry, whereby the two positively functionalized groups are situated on the same side of the cluster unit, available to bind molecules of opposite charge.

Introduction

Propargylium ions coordinated to dinuclear $[Co_2(CO)_6]$ ([Co−Co]), $[Mo_2Cp_2(CO)_4]$ ([Mo−Mo]), and $[CoMoCp(CO)_5]$ ([Co−Mo]) have been the focus of intense investigations by us and other groups.[1] However, the chemistry of the related dicarbenium alkyne complexes remains relatively unexplored. We note, however, that Barinov et al.[2] reported the synthesis of $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^3,\eta^3\text{-}CH_2{-}C{\equiv}C{-}CH_2][BF_4]_2$, and later, Curtis et al. reported the X-ray molecular structure of this dinuclear dicarbenium molybdenum complex and examined its reactivity toward nucleophiles.[3] Recently, Amouri's group[4] reported the synthesis of the dicarbenium fulvalene complex $[FvMo_2(CO)_4(\mu\text{-}\eta^3,\eta^3\text{-}CH_2{-}C{\equiv}C{-}CH_2]\text{-}[BF_4]_2$ (Fv = fulvalene), which showed enhanced reactivity relative to the Cp system and allowed monoaddition of weak aromatic nucleophiles to one carbenium center ($-CH_2^+$), providing the related substituted cationic complexes $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{-}C{\equiv}C{-}CH_2{-}Nu]\text{-}$

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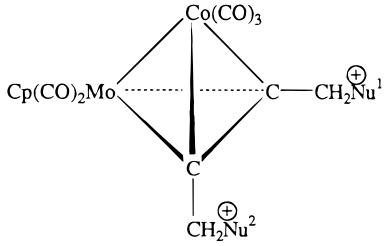

$Nu^1 = Nu^2$ = pyridine (**13**)
Nu^1 = pyridine, Nu^2 = triphenylphosphine (**14**)
$Nu^1 = Nu^2$ = triphenylphosphine (**15**)
$Nu^1 = Nu^2$ = 3-picoline (**16**)
Nu^1 = pyridine, Nu^2 = 3-picoline (**17**)

Figure 1.

$[BF_4]$. The difference in reactivity between the Cp system and that of the Fv analogue was attributed to the rigid nature of the fulvalene ligand. Finally, we note that Went et al. reported the formation of the dicarbenium cobalt complex $[Co_2(CO)_4L_2(\mu\text{-}\eta^3,\eta^3\text{-}CH_2{-}C{\equiv}C{-}CH_2][BF_4]_2$ (L = CO, $Ph_2PCH_2PPh_2$), and its reactivity was also investigated.[5] However the dicarbenium complex was not isolated.

None of the above dicarbenium complexes possess a chiral or heterobimetallic cluster. In this paper, we report the synthesis of the first class of heterobimetallic dicationic complexes possessing a chiral cluster [Mo−Co] via a general and elegant route. In these dicationic organometallic clusters, the positive charges are located on the two phosphonium or ammonium termini (see Figure 1). The synthesis of such complexes and their X-ray structures and reactivity are presented.

Results and Discussion

I. Syntheses, Characterization, and X-ray Structures of Dinuclear Alkyne Adducts Possessing a Rigid Tetrahedron Geometry Core. Treatment of $Co_2(CO)_8$ with the alkyne-1,4-diol $\{HOCR^1R^2{-}C{\equiv}C{-}CR^1R^2OH\}$ leads to the neutral alkyne adducts $[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^2{-}HOCR^1R^2\text{-}C{\equiv}C{-}CR^1R^2OH)]$ ($R^1 = R^2 =$ H (**1**); R^1 = H, $R^2 = CH_3$ (**2**); $R^1 = R^2 = CH_3$ (**3**)) obtained as deep red solids in 70−80% yields. The prochiral heterobimetallic [Mo−Co]−alkyne adduct $[CpMoCo(CO)_5(\mu\text{-}\eta^2,\eta^2\text{-}HOCH_2{-}C{\equiv}C{-}CH_2OH)]$ (**4**) was obtained in 72% yield from $[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^2\text{-}HOCH_2{-}C{\equiv}C{-}CH_2OH)]$ (**1**) via replacement of a $-Co(CO)_3$ vertex by the isolobal moiety $-CpMo(CO)_2$.[6] These compounds (**1**−**4**) were characterized completely, and their X-ray molecular structures were obtained. Crystals of complexes **1**−**4** were obtained from slow evaporation of saturated ether solutions. Cameron views of **1** and **4** are shown in Figures 2 and 3, and crystallographic data for **1** and **4** are given in Table 1.

As a general trend, the cluster cores "$-M_2(-C{\equiv}C-)$" of complexes **1**−**4** show the common tetrahedron geometry where the alkyne unit is almost perpendicular to the metal−metal bond with d(M−M) = 2.472 Å (**1**), 2.474 Å (**2**), 2.461 Å (**3**), and 2.663 Å (**4**). The structures also show that the difunctional acetylenic ligands fold-

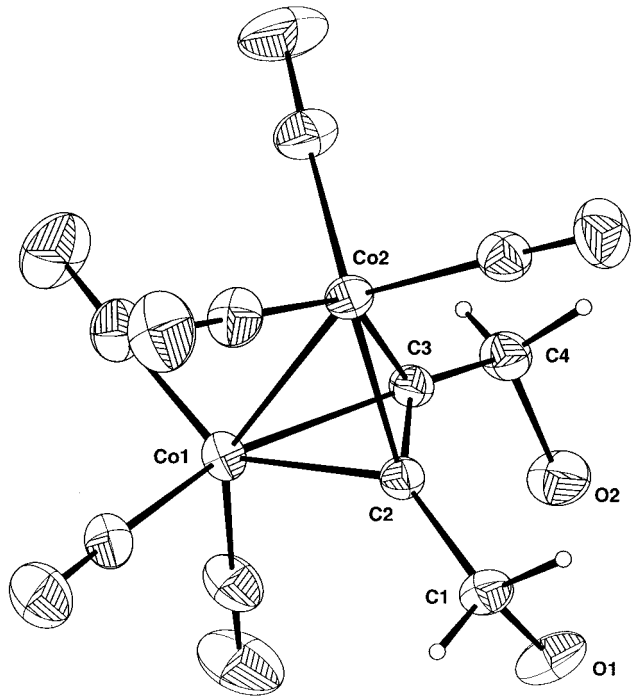

Figure 2. X-ray molecular structure of $[Co_2(CO)_6(\mu,\eta^2,\eta^2\text{-}HOCH_2C{\equiv}CCH_2OH)]$ (**1**). Selected bond distances (Å) and angles (deg): Co(1)−Co(2) 2.4722(6), Co(1)−C(2) 1.953(3), Co(2)−C(2) 1.956(3), O(1)−C(1) 1.417(4), C(1)−C(2) 1.489(4), C(3)−C(4) 1.485(4), O(1)−O(2) 2.754(4), Co(1)−C(3) 1.963(3), Co(2)−C(3) 1.943(3), O(2)−C(4) 1.423(4), C(2)−C(3) 1.344(4); O(1)−C(1)−C(2) 110.3(3), C(1)−C(2)−C(3) 136.1(3), C(2)−C(3)−C(4) 137.1(3), O(2)−C(4)−C(3) 111.1(2).

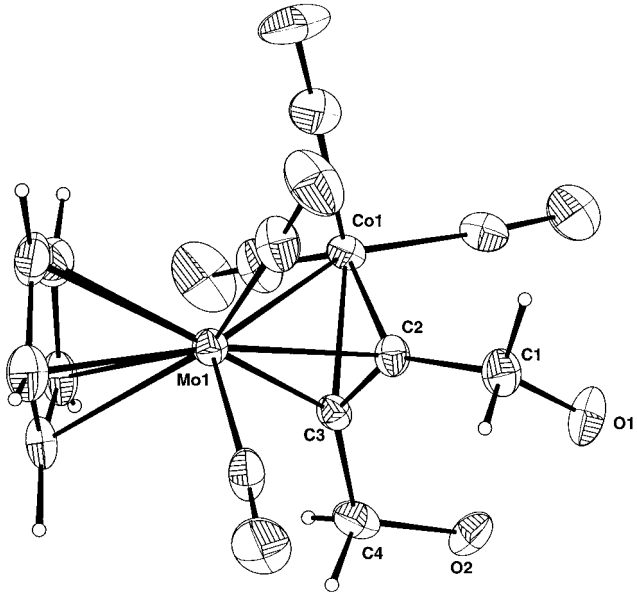

Figure 3. X-ray molecular structure of $[CpMoCo(CO)_5(\mu,\eta^2,\eta^2\text{-}HOCH_2C{\equiv}CCH_2OH)]$ (**4**). Selected bond distances (Å) and angles (deg): Mo(1)−Co(1) 2.663(1), Mo(1)−C(2) 2.167(8), Co(1)−C(2) 1.96(1), O(1)−C(1) 1.39(1), C(1)−C(2) 1.51(1), C(3)−C(4) 1.49(1), O(1)−O(2) 2.814(12), Mo(1)−C(3) 2.122(9), Co(1)−C(3) 1.962(9), O(2)−C(4) 1.40(1), C(2)−C(3) 1.34(1); O(1)−C(1)−C(2) 111.3(8), C(1)−C(2)−C(3) 136.2(11), C(2)−C(3)−C(4) 133.6(9), O(2)−C(4)−C(3) 114.1(8).

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Table 1. Crystal Data for 1 and 4

	1	4
formula	$C_{10}H_6O_8Co_2$	$C_{14}H_{11}O_7CoMo$
fw	372	446.1
a (Å)	27.391(4)	9.019(2)
b (Å)	7.810(1)	12.006(3)
c (Å)	12.987(2)	14.629(2)
α (deg)	90	90
β (deg)	102.16(2)	90
γ (deg)	90	90
V (Å^3)	2715.8(8)	1584.0(6)
Z	8	4
cryst syst	monoclinic	orthorhombic
space group	*C*2/*c*	*Pn*2$_1$*a* (no. 33)
linear abs coeff, *μ* (cm^{-1})	24.7	18.5
density, *ρ* (g cm^{-3})	1.82	1.87
diffractometer	CAD4 Enraf-Nonius	CAD4 Enraf-Nonius
radiation	Mo Kα (*λ* = 0.710 69 Å)	Mo Kα (*λ* = 0.710 69 Å)
scan type	*ω*/2*θ*	*ω*/2*θ*
scan range (deg)	0.8 + 0.345 tan *θ*	0.8 + 0.345 tan *θ*
θ limits	1−30	1−28
temperature	room temperature	room temperature
octants collected	−38,37; 0,10; 0,18	0,11; 0,15; 0,19
no. of data collected	4376	2201
no. of unique data collected	3939	1996
no. of unique data used	2994 $(F_o)^2 > 3\sigma(F_o)^2$	1479 $(F_o)^2 > 3\sigma(F_o)^2$
R^a	0.0311	0.0326
$R_w{}^b$	0.0328	0.0379
ext param	191	217
no. of variables	195	210
$\Delta\rho_{min}$ (e Å^{-3})	−0.32	−0.48
$\Delta\rho_{max}$ (e Å^{-3})	0.45	0.45

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

in upon coordination to the cluster core; for instance, the angle *θ* of C1C2C3 changes from 180° in free acetylene to 136.1° in **1** and 136.2° in **4**. Therefore, the distance between the two methylene groups decreases and allows the two hydroxyl functions at C1 and C4 to form hydrogen bonding, with *d*(O1−O2) = 2.754 Å (**1**), *d*(O1−O2) = 2.75 Å (**2**), *d*(O1−O2) = 3.629 Å (**3**), and *d*(O1−O4) = 2.814 Å (**4**).

In the tertiary alkyne complex **3**, the larger *d*(O1−O2) was attributed to the steric effect caused by the two methyl groups and, therefore, this complex was not chosen for the following steps. Further, this complex undergoes an elimination reaction in acidic medium and produces the related olefinic compounds.

Overall, we notice in these alkyne dinuclear clusters that the two hydroxyl groups of the coordinated alkyne come closer in a well-defined rigid geometry. This phenomenon is rather interesting because it suggests that any charged functional groups at these positions will be disposed in a clamplike fashion and are potentially available to bind ions of opposite charge.[7]

II. Reaction with Aqueous HBF_4 and Stepwise Nucleophilic Additions Affording Achiral and Chiral Dicationic [Mo−Co]−Alkyne Adducts. We present a general synthetic approach to chiral dicationic [Mo−Co] complexes possessing two different nucleophiles at both carbenium centers (Scheme 1). Our method involves the preparation of the tetranuclear cluster [{CpMoCo(CO)$_5$(*μ*-*η*^{2},*η*^{3}-CH$_2$−C≡C−CH$_2$-)}$_2$O][BF$_4$]$_2$ (**5**; Figure 4), which is the key molecule for the preparation of the new class of chiral dicationic complexes.

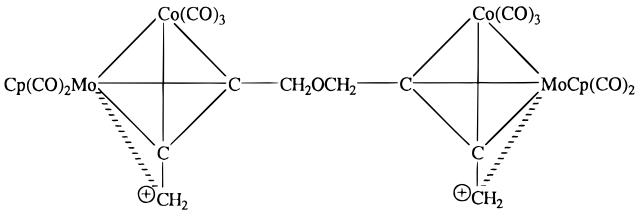

Figure 4. Schematic drawing of the tetranuclear cluster [{CpMoCo(CO)$_5$(CH$_2$C≡C−CH$_2$−)}$_2$O][BF$_4$]$_2$ (**5**).

The tetranuclear cluster **5** can be simply considered as a monocarbenium dimer, where both carbenium units are linked by an ether group. Complex **5** was obtained in good yield by treatment of the prochiral [Mo−Co]−alkyne adduct [CpMoCo(CO)$_5$(*μ*-*η*^{2},*η*^{2}-HOCH$_2$−C≡C−CH$_2$OH)] (**4**) with aqueous HBF_4 in ether solution. The ^{1}H NMR, IR, and analytical data are consistent with the proposed formula. Further, we note that the carbenium centers in complex **5** are stabilized by the molybdenum centers (Mo−CH$_2^+$) and not the cobalt atoms; this is not a surprising result; previously, we have reported several X-ray structures of heterobimetallic chiral [Mo−Co] propargylium complexes, which show that the carbenium center (−CH$_2^+$) is bent toward the molybdenum rather than the cobalt; this deformation is a clear indication that the molybdenum atom is alleviating the electron deficiency at the α-carbon center.[8] We also note that Went et al. suggested the formation of a bridged thioether tetranuclear alkyne complex of cobalt.[5]

The identity of complex **5** was also confirmed by addition of pyridine to a solution of **5** in acetonitrile, to give two diastereomers of the related dicationic tetranuclear pyridinium complex [{CpMoCo(CO)$_5$(*μ*-*η*^{2},*η*^{2}−Py−CH$_2$−C≡C−CH$_2$−)}$_2$O][BF$_4$]$_2$ (**6**), where the chiral cluster is either racemic (*R*,*R*; *S*,*S*) or meso (*R*,*S*) (Scheme 2).

The ^{1}H NMR of **6** recorded in acetone-d_6 exhibits three signals at 5.62, 5.63, and 5.69 ppm attributed to the Cp ligands in a 2:2:1 ratio. This result is consistent with previous ^{1}H NMR data reported for a mixture of diastereomeric monocationic [Mo−Co] propargylium complexes.[9] Subsequent treatment of **6**, **7**, or **8** in acidic medium (HBF_4/Et_2O) followed by addition of a nucleophile[10] gave a series of dicationic complexes of general formula [CpMoCo(CO)$_5$(*μ*-*η*^{2},*η*^{2}-Nu$_1$−CH$_2$−C≡C−CH$_2$−Nu$_2$)][BF$_4$]$_2$ (Nu^1 = Nu^2 = pyridine (**13**); Nu^1 = pyridine, Nu^2 = triphenylphosphine (**14**); Nu^1 = Nu^2 = triphenylphosphine (**15**); Nu^1 = Nu^2 = 3-picoline (**16**); Nu^1 = pyridine, Nu^2 = 3-picoline (**17**); Scheme 1).

These compounds are obtained by formation of the monocarbenium complexes [CpMoCo(CO)$_5$(*μ*-*η*^{2},*η*^{3}-Nu^1-CH$_2$−C≡C−CH$_2$)][BF$_4$]$_2$ (Nu^1 = pyridine (**9**); Nu^1 = 3-picoline (**10**); Nu^1 = triphenylphosphine (**11**)), which are quenched by the added nucleophiles to give the dicationic compounds **13**−**17**. These novel complexes were completely characterized by spectroscopic methods

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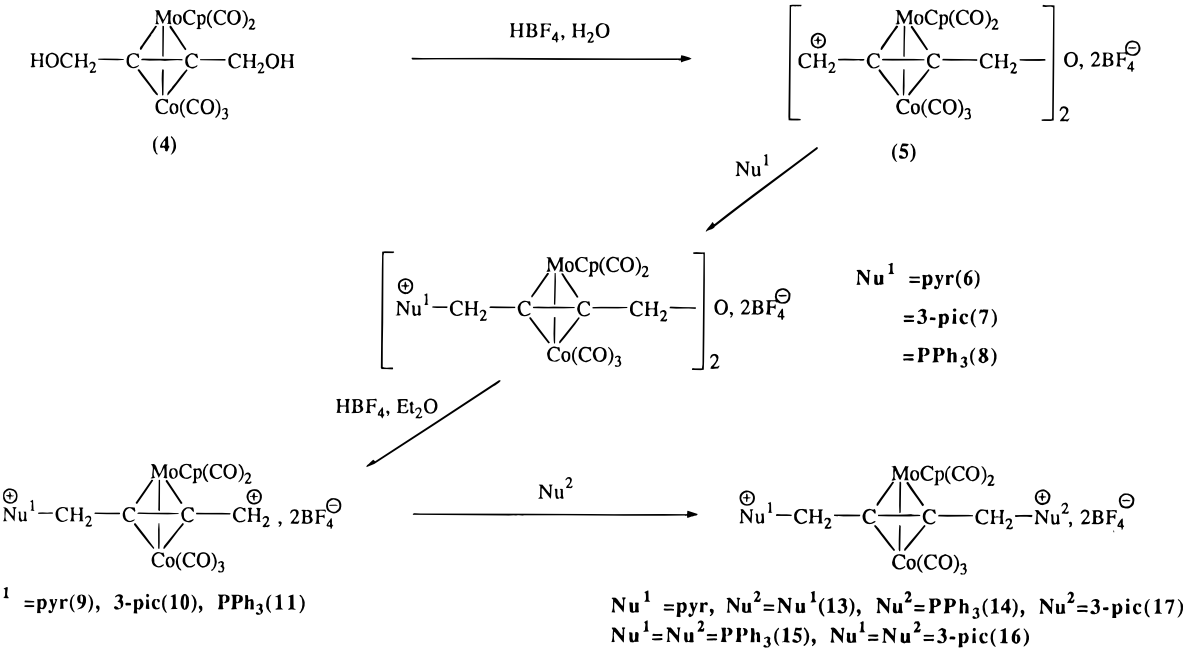
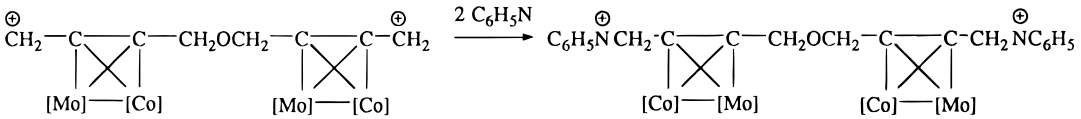
Scheme 1. General Route to the Synthesis of Prochiral and Chiral Dicationic Complexes[a]



[a] pyr = pyridine, pic = picoline.

Scheme 2. Formation of the Dicationic Tetranuclear Pyridinium Complex (6) from the Dicarbenium Tetranuclear Ion (5)



(R)(R), (S)(S)
or meso (R)(S)

and elemental analyses. Further, three X-ray molecular structures of three compounds belonging to this family were unambiguously identified **13**, **16**, and **17**; **17** is the first functionalized dication [Mo−Co] chiral cluster possessing two different substituents at the carbenium centers ($-CH_2^+$).

III. X-ray Molecular Structures of the Dicationic [Mo−Co] Complexes 13, 16, and 17. X-ray molecular structures of three dicationic clusters of general formula $[CpMoCo(CO)_5(\mu\text{-}\eta^2,\eta^2\text{-}Nu_1{-}CH_2{-}C{\equiv}C{-}CH_2{-}Nu_2)][BF_4]_2$ ($Nu^1 = Nu^2$ = pyridine (**13**); $Nu^1 = Nu^2$ = 3-picoline (**16**); Nu^1 = pyridine, Nu^2 = 3-picoline (**17**)) were determined. Crystals of the above complexes were grown from CH_3CN/Et_2O solution. Complexes **13**, **16**, and **17** crystallize in the $P\bar{1}$ space groups. Figure 5 shows the Cameron view of the dicationic compound **17**. Crystallographic data for **17** are given in Table 2. The tetrahedron cluster cores in these charged complexes (**13**, **16**, and **17** look comparable to that of the neutral precursor **4**, with d(Mo−Co) = 2.697 Å (**17**) slightly longer than d(Mo−Co) = 2.663 Å observed for complex **4**, while the distance of the coordinated alkyne d(C2−C3) = 1.47 Å (**17**) is slightly shorter than that in complex **4** with d(C2−C3) = 1.491 Å. However, the major difference between the neutral complex **4** and the dications **13**, **16**, and **17** is the relative positions of the two charged nitrogen atoms which are located far away, as one would expect, due to repulsion of the positive charges on the two nitrogen atoms. Nevertheless, the two positively charged nucleophiles are situated on the same side relative to the cluster core "−MoCo(−C≡C−)". This result is important since it shows that the two ammonium functions are situated facially and are potentially available to bind molecules of opposite charge.

Concluding Remarks

In this paper, we reported a general procedure for the synthesis of dicationic acetylenic complexes of general formula $[CpMoCo(CO)_5(\mu\text{-}\eta^2,\eta^2\text{-}Nu_1{-}CH_2{-}C{\equiv}C{-}CH_2{-}Nu_2)][BF_4]_2$. Our synthetic approach is practical and unprecedented, as it involves the preparation of the tetranuclear complex $[\{CpMoCo(CO)_5(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{-}C{\equiv}C{-}CH_2\text{-})\}_2O][BF_4]_2$ (**5**), which represents the key molecule for the above syntheses. Subsequent treatment of **5** with the same or different nucleophiles allows the placement of the two nucleophiles on the carbenium centers ($-CH_2^+$) in a stepwise fashion. The X-ray molecular structures of several dicationic species were presented, including the first chiral complex $[CpMoCo(CO)_5(\mu\text{-}\eta^2,\eta^2\text{-}Nu^1{-}CH_2{-}C{\equiv}C{-}CH_2{-}Nu^2)][BF_4]_2$ (Nu^1 = pyridine, Nu^2 = 3-picoline (**17**)) possessing two different nucleophiles. The structure of complex **17** shows that the two nitrogen atoms are located on the same side of the cluster core and are 6.12 Å apart; this represents the maximal possible distance between the two nitrogen

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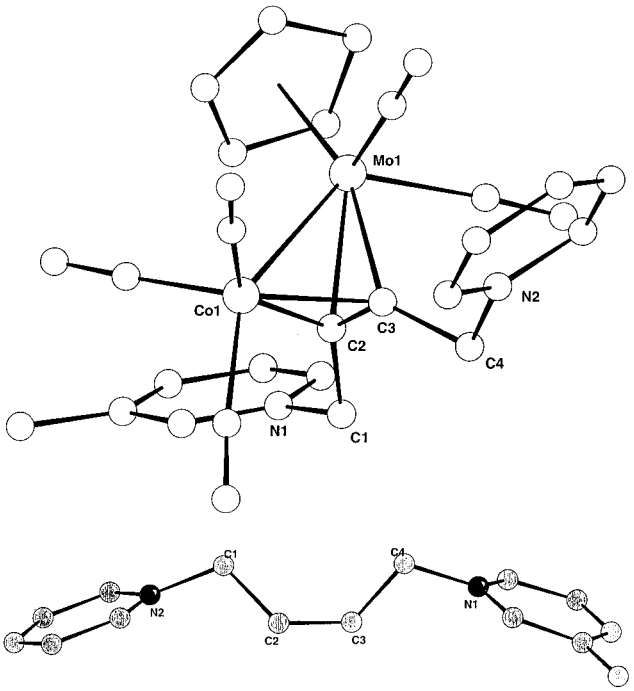

Figure 5. (top) X-ray molecular structure of [CpMoCo(CO)$_5$(μ,η^2,η^2-Nu^{1}CH$_2$C≡CCH$_2$Nu^2)][BF$_4$]$_2$ (Nu^1 = Pyridine, Nu^2 = 3-picoline) (**17**). Selected bond distances (Å) and angles (deg): Mo(1)−Co(1) 2.696(3), Mo(1)−C(2) 2.18(2), Co(1)−C(2) 1.95(2), N(2)−C(1) 1.49(2), C(1)−C(2) 1.51(3), C(3)−C(4) 1.47(2), N(1)−N(2) 6.12, Mo(1)−C(3) 2.15(2), Co(1)−C(3) 1.99(2), N(1)−C(4) 1.47(2), C(2)−C(3) 1.36(2); N(2)−C(1)−C(2) 110.4(14), C(1)−C(2)−C(3) 132.5(16), C(2)−C(3)−C(4) 131.4(16), N(1)−C(4)−C(3) 112.3(15). (bottom) Representation of the dicationic compound (**17**) in the C(1)−C(2)−C(3) plane (the metallic vertexes are omitted).

Table 2. Crystal Data for 17

formula	$C_{25}H_{21}N_2O_5CoMoB_2F_8$
fw	757.9
a (Å)	10.091(5)
b (Å)	12.712(8)
c (Å)	12.854(5)
α (deg)	64.83(5)
β (deg)	82.37(5)
γ (deg)	77.42(5)
V (Å^3)	1455(2)
Z	2
cryst syst	triclinic
space group	$P\bar{1}$
linear abs coeff, μ (cm^{-1})	10.8
density, ρ (g cm^{-3})	1.73
diffractometer	CAD4 Enraf-Nonius
radiation	Mo Kα (λ = 0.710 69 Å)
scan type	$\omega/2\theta$
scan range (deg)	0.8 + 0.345 tan θ
θ limits (deg)	1−25
temperature	room temperature
octants collected	0,11; −14,15; −15,15
no. of data collected	5420
no. of unique data collected	5101
no. of unique data used	2496 (F_o)^2 > 3σ(F_o)^2
R^a	0.095
$R_w{}^b$	0.105
ext param	no
no. of variables	348
$\Delta\rho_{min}$ (e Å^{-3})	−0.99
$\Delta\rho_{max}$ (e Å^{-3})	1.30

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

atoms. This N^+N^+ orientation could be the result of optimal crystal packing, although free rotation around C−(alkyne)-CH$_2$X is expected to occur. However, we have found that the methylene protons CH$_2$−N$^+$ in **13**, **16**, and **17** appear with an AB spin system even in achiral compounds **13** and **16**. This suggests that the rotation around C−(alkyne)−CH$_2$N$^+$ is either hampered or slow on the NMR time scale.

We are currently exploring the binding capacity of these new dicationic acetylenic complexes, and the results of these investigations will be the subject of future reports.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry argon. Solvents were dried and distilled using standard techniques. Diethyl ether and THF were distilled from sodium benzophenone ketyl; methylene chloride and acetonitrile from sodium hydride; pentane was treated with sulfuric acid and distilled on sodium. Pyridine and 3-picoline were distilled under reduced pressure on potassium hydroxide. 2-Butyne-1,4-diol, triphenylphosphine, Mo$_2$Cp$_2$(CO)$_6$, Co$_2$(CO)$_8$, HBF$_4$/Et$_2$O, aqueous 40% HBF$_4$, CD$_3$CN, CD$_3$Cl, and acetone-d_6 were used as purchased. IR spectra were collected on a Bio-rad FTS 165 spectrometer from KBr disks. All absorptions are expressed in wavenumbers (cm^{-1}). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Brucker AM instrument, using standard programs for proton (299.MHz), carbon (75 MHz), and phosphorus (124 MHz) spectra. NMR chemical shifts are reported in δ (ppm) relative to TMS (^{1}H, ^{13}C) or 85% H$_3$PO$_4$ (^{31}P); data (^{13}C, ^{31}P) are proton decoupled. Elemental analyses were performed by Centre régional de microanalyse-Université Pierre et Marie Curie.

General Procedure for the Synthesis of [(Co$_2$(CO)$_6$-(HO(R^1)(R^2)CC≡CC(R^1)(R^2)OH)] (R^1=R^2=H (1); R^1=H, R^2=CH$_3$ (2); R^1=R^2=CH$_3$ (3). To an ethereal solution (30 mL) of 1 g of Co$_2$(CO)$_6$ (3 mmol) was added 2.7 mmol of the acetylenic diol. The mixture was stirred at room temperature for 0.5 h, then filtered and flash chromatographed on silica gel using ether as the eluent. Further crystallization from ether leads to the expected complexes **1**−**3** in 80−90% yield. IR: **1** 2097, 2059, 2049, 2031, 2013 cm^{-1}; **2** 2095, 2056, 2024 cm^{-1}; **3** 2090, 2051, 2028 cm^{-1}. ^{1}H NMR: **1** (acetone-d_6) δ 4.84 (d, J = 6.0 Hz, 8H), 4.70 (t, J = 6.0 Hz, 2H); **2** (CDCl$_3$, isomeric mixture, 2:1) δ 5.07(m, 6H), 3.19 (d, J = 3.3 Hz, 2H major), 3.00 (d, J = 2.6 Hz, 2H minor), 1.58 (d, J = 6.0 Hz, 6H major), 1.56 (d, J = 6.0 Hz, 6H minor); **3** (CDCl$_3$) δ 2.89 (s, 2H), 1.63 (s, 12H). ^{13}C NMR: **1** (CDCl$_3$) δ 199.21, 95.35, 64.03; **2** (two isomers CDCl$_3$) δ 199.59, 101.82 (minor)−101.36 (major), 69.13 (major)−68.72 (minor), 25.38 (major)−24.95(minor); **3** (CDCl$_3$) δ 199.47, 106.06, 73.64, 33.46. Anal. Calcd for **1**, $C_{10}H_6O_8Co_2$: C, 32.27; H, 1.61. Found: C, 32.35; H, 1.47. Anal. Calcd for **2**, $C_{12}H_{10}O_8Co_2$: C, 36.02; H, 2.51. Found: C, 36.06; H, 2.63. Anal. Calcd for **3**, $C_{14}H_{14}O_8Co_2$: C, 39.27; H, 3.29. Found: C, 39.33; H, 3.32. Mp: **1** 64 °C; **2** 159 °C (dec); **3** 142 °C (dec).

Synthesis of [(MoCp(CO)$_2$Co(CO)$_3$(HOCH$_2$C≡CCH$_2$OH)] (4). To a solution of 0.37 g (1 mmol) of **1** in 20 mL of THF was added a solution of NaMoCp(CO)$_3$ prepared as follows: 0.27 g (0.55 mmol) of Cp$_2$Mo$_2$(CO)$_6$ in 10 mL of THF was added to an amalgam (0.05 g of Na) with 2.5 g of Hg. The reaction is complete after 0.5 h at reflux. After removing the solvent, the red-brown residue was chromatographed on silica gel using ether as the eluent. Further crystallization in toluene affords the pure **4** complex in 72% yield. IR: 2046, 2001, 1977, 1953 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.42 (s, 5H), 4.85 (s, 4H), 2.75 (s, 2H). ^{13}C NMR (CDCl$_3$): δ 224.55, 93.91, 90.47, 66.66. Anal. Calcd for $C_{14}H_{11}O_7CoMo$: C, 37.67; H, 2.47. Found: C, 37.83; H, 2.52. Mp; 65 °C (dec).

Synthesis of [{CpMoCo(CO)$_5$(μ-η^2,η^3-CH$_2$−C≡C−CH$_2$−)}$_2$O][BF$_4$]$_2$ (5). To a solution of 0.45 g of **4** in 10 mL of

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CH_2Cl_2 was added dropwise, at room temperature, a solution of 0.2 mL of 40% aqueous HBF_4 in 20 mL of ether. The color of the solution changed from red to orange and a red-orange precipitate appeared. After addition of the acidic solution, the mixture was stirred for 0.5 h. The precipitate was washed 5 times with ether and dried under vacuum. The resulting yellow-orange powder was identified as complex **5** and obtained in 90% yield. IR: 2100, 2065, 2047, 2010 cm^{-1}. ^1H NMR (acetone-d_6): δ 6.32−6.30−6.29 (s, 5H), 6.19−6.16−6.14 (s, 1H), 5.40−5.03 (m, 3H). Anal. Calcd for $C_{28}H_{18}O_{11}Co_2Mo_2B_2F_8$: C, 33.18; H, 1.79. Found: C, 31.65; H, 1.99.

Syntheses of the Dications [{CpMoCo(CO)$_5$(μ-η^2,η^2-Nu-CH$_2$−C≡C−CH$_2$−)}$_2$O][BF$_4$]$_2$ (Nu = Pyridine (6), 3-Picoline (7), Triphenylphosphine (8)). To a solution of 0.81 g (0.8 mmol) of **5** in 5 mL of CH_3CN was added dropwise, at room temperature, a solution of 1.68 mmol of pyridine, 3-picoline, or triphenylphosphine in 2 mL of CH_3CN. The orange solution turns cherry red. The solvent was removed under vacuum to give a red oil residue. This substance was washed 5 times with ether and dried under vacuum, forming a yellow-brown powder of **6**, **7**, or **8** isolated in quantitative yield.

Data for **6**: IR 2053, 2007, 1989, 1830 cm^{-1}; ^1H NMR (acetone-d_6) isomeric mixture δ 9.21−9.14 ((d, J = 5.6 Hz) and (d, J = 5.87 Hz), 2H), 8.81 (t, J = 7.66, 1H), 8.36 (t, J = 6.79, 2H), 6.15, 6.07, 6.07 ((q (HaHb), (s), (q (HaHb)), 2H), 5.70, 5.63, 5.62 (s, 5H), 5.16, 5.15, 4.78 ((s), (q (HaHb)), and (q (HaHb)), 2H). Anal. Calcd for $C_{38}H_{28}O_{11}N_2Co_2Mo_2B_2F_8$: C, 38.44; H, 2.38. Found: C, 38.20; H, 2.60.

Data for **7**: IR 2056, 1998, 1940 cm^{-1}. Anal. Calcd for $C_{40}H_{32}O_{11}N_2Co_2Mo_2B_2F_8$: C, 40.04; H, 2.69. Found: C, 38.39; H, 2.71.

Data for **8**: IR 2051, 2004, 1973, 1940 cm^{-1}. Anal. Calcd for $C_{64}H_{48}O_{11}N_2Co_2Mo_2B_2F_8$: C, 49.97; H, 3.14. Found: C, 49.32; H, 3.40.

Syntheses of [CpMoCo(CO)$_5$(μ-η^2,η^3-Nu-CH$_2$−C≡C−CH$_2$)][BF$_4$]$_2$, (Nu = Pyridine (9), 3-Picoline (10), Triphenylphosphine (11)). To a solution of **6**, **7**, or **8** (0.1 g, 0.084 mmol) in 5 mL of CH_2Cl_2 was added dropwise 0.25 mL of HBF_4/Et_2O, at room temperature, under stirring. The orange solution turns brown; addition of 10 mL of ether results in the formation of a yellow brown-precipitate. This compound was washed several times with ether and dried under vacuum to give **9**, **10**, or **11** in quantitative yield.

Data for **9**: IR 2114, 2056, 2009 cm^{-1}. Anal. Calcd for $C_{19}H_{14}O_5NCoMoB_2F_8$: C, 34.33; H, 2.12. Found: C, 32.94; H, 2.53.

Data for **10**: IR 2102, 2056, 2004 cm^{-1}. Anal. Calcd for $C_{20}H_{16}O_5NCoMoB_2F_8$: C, 35.39; H, 2.38. Found: C, 30.39; H, 2.84.

Data for **11**: IR 2104, 2055, 2006 cm^{-1}. Anal. Calcd for $C_{32}H_{24}O_5NCoMoB_2F_8$: C, 45.33; H, 2.85. Found: C, 39.59; H, 2.62.

Synthesis of [CpMoCo(CO)$_5$(μ-η^2,η^2-C$_6$H$_5$N−CH$_2$−C≡C−CH$_2$−OH)][BF$_4$]$_2$ (12). Complex **12** was obtained after dissolution of **9** in acetone-d_6 in the presence of water. ^1H NMR (acetone-d_6): δ 9.25 (d, J = 5.26 Hz, 2H), 8.80 (t, J = 7.87 Hz, 1H), 8.36 (t, J = 6.83 Hz, 1H), 6.10 (q, HaHb, 2H), 5.67 (s, 5H), 4.96 (q, HaHb, 2H).

Syntheses of [CpMoCo(CO)$_5$(μ-η^2,η^2-C$_6$H$_5$N−CH$_2$−C≡C−CH$_2$−Nu)][BF$_4$]$_2$ (Nu = C$_6$H$_5$N (13); Nu = P(C$_6$H$_5$)$_3$ (14); Nu = C$_6$H$_4$(CH$_3$)N (17)). To a solution of 0.1 mmol of **9** was added 0.11 mmol of pyridine, 3-picoline, or triphenylphosphine in 2 mL of CH_3CN, and the mixture was stirred for 1 h. Addition of ether (10 mL) results in the formation of a red oil or precipitate. After washing several times with ether, the residue was dried under vacuum, forming a red-brown powder of the expected product in quantitative yield.

[(MoCp(CO)$_2$Co(CO)$_3$(C$_6$H$_5$NCH$_2$C≡CCH$_2$C$_6$H$_5$N)]$^{2+}$-2BF$_4^-$ (13). The dipyridinium salt was crystallized by diffusion technique using CH_3CN/ether as the solvent. IR: 2057, 2017, 2003, 1985, 1972, 1960 cm^{-1}). ^1H NMR (acetone-d_6): δ 9.23 (dd, J = 6.56−1.17 Hz, 4H), 8.86 (tt, J = 7.84−1.20 Hz, 2H), 8.41 (dd, J = 7.69−6.67 Hz, 4H), 4.76 (q, HaHb, 4H), 5.66 (s, 5H). ^{13}C NMR (CD_3CN): δ 222.06, 147.80, 145.63, 129.92, 92.60, 89.34, 67.47. Anal. Calcd for $C_{24}H_{19}O_5N_2CoMoB_2F_8$: C, 38.73; H, 2.57. Found: C, 37.42; H, 2.94.

[(CpMoCo(CO)$_5$(C$_6$H$_5$)$_3$PCH$_2$C≡CCH$_2$C$_6$H$_5$N)]$^{2+}$2BF$_4^-$ (14). IR: 2058, 2009, 1949 cm^{-1}). ^1H NMR (acetone)-d_6): δ 9.01 (d, J = 6.6 Hz, 2H), 8.82 (tt, J = 7.8−1.0 Hz, 1H), 8.35 (dd, J = 7.8−6.6 Hz, 2H), 8.18 (m, 6H), 7.95 (m, 3H), 7.87 (m, 6H), 5.65 (m, 4H), 5.59 (s, 5H). ^{13}C NMR (CD_3CN): δ 223.30, 164.32 (d, J_{C-P} = 12.8 Hz), 161.00 (d, J_{C-P} = 10.2 Hz), 148.30, 146.16, 136.48 (d, J_{C-P} = 2.57 Hz), 130.01, 119.79 (d, J_{C-P} = 84.5 Hz), 93.72, 91.93, 89.90, 68.15, 31.50 (d, J_{C-P} = 44.37 Hz). ^{31}P NMR (acetone-d_6): δ 20.53. Anal. Calcd for $C_{37}H_{29}O_5NPCoMoB_2F_8$: C, 47.92; H, 3.13. Found: C, 46.97; H, 3.52.

Synthesis of [(CpMoCo(CO)$_5$(C$_6$H$_5$)$_3$PCH$_2$C≡CCH$_2$-(C$_6$H$_5$)$_3$P)]$^{2+}$2BF$_4^-$ (15). This salt was prepared in the same way as complex **13**, but using triphenylphosphine as the nucleophile. IR: 2064, 2012, 1980, 1944 cm^{-1}. ^1H NMR (acetone-d_6): δ 8.02−7.83 (m, 30H), 5.29 (s, 5H), 5.15 (oct (HaHb), J_{C-P} = 16.63 Hz, 4H). ^{13}C NMR (acetone-d_6): δ 224.00, 135.98 (d, J_{C-P} = 1.5 Hz), 134.52 (d, J_{C-P} = 9.96 Hz), 131.12 (d, J_{C-P} = 12.45 Hz), 118.28 (d, J_{C-P} = 85.13 Hz), 92.78, 89.53, 32.69 (d, J_{C-P} = 57.05 Hz). ^{31}P NMR (CD_3CN): δ 21.75. Anal. Calcd for $C_{50}H_{39}O_5P_2CoMoB_2F_8$: C, 54.09; H, 3.54. Found: C, 50.94; H, 4.01.

Synthesis of [(CpMoCo(CO)$_5$C$_6$H$_4$(CH$_3$)NCH$_2$C≡CCH$_2$-C$_6$H$_4$(CH$_3$)N)]$^{2+}$2BF$_4^-$ (16). This salt was prepared in the same way **13**, using 3-picoline as the nucleophile. IR: 2068, 2018, 2002, 1958 cm^{-1}. ^1H NMR (acetone-d_6): δ 9.08 (s, 2H), 9.03 (d, J = 6 Hz, 2H), 8.68 (d, J = 8.10 Hz, 2H), 8.29 (t, J = 8.1, 2H), 6.17(q, HaHb, 2H), 5.63 (s, 5H), 2.68 (s, 6H). ^{13}C NMR (acetone-d_6): δ 222.41, 148.41, 145.25, 143.40, 141.54, 128.41, 92.86, 90.18, 67.41, 18.55. Anal. Calcd for $C_{26}H_{23}O_5N_2CoMoB_2F_8$: C, 40.45; H, 3.00. Found: C, 40.56; H, 2.96.

[(CpMoCo(CO)$_5$C$_6$H$_5$NCH$_2$C≡CCH$_2$C$_6$H$_4$(CH$_3$)N)]$^{2+}$-2BF$_4^-$ (17). The dicationic complex **17** was crystallized in the same way as complex **13**. IR: 2061, 2020, 2000,1950 cm^{-1}. ^1H NMR (acetone-d_6): δ 9.23 (dd, J = 6.46−1.25, Hz 2H), 9.10 (s, 1H), 9.04 (d, J = 5.93 Hz, 1H), 8.87 (tt, J = 7.72−1.20 Hz, 2H), 8.69 (dd, J = 8.11−1.10 Hz, 1H), 8.42 (t, J = 6.67 Hz, 2H), 8.29 (dd, J = 6.23−1.10 Hz, 1H), 6.26 (q, HaHb, 2H), 6.19 (q, HaHb, 2H), 5.64 (s, 5H), 2.68 (s, 3H). ^{13}C NMR (acetone-d_6): δ 222.37, 148.41, 148.03, 146.16, 145.26, 143.45, 141.54, 130.18, 129.48, 92.89, 92.25, 89.75, 67.52, 67.35, 18.56, 18.50. Anal. Calcd for $C_{25}H_{21}O_5N_2CoMoB_2F_8$: C, 39.62; H, 2.79. Found: C, 39.62; H, 2.72.

Crystal Structure Determinations for 1−4, 13, 16, and 17. Suitable crystals were obtained by slow evaporation of an ether solution of **1**−**3** and of a toluene solution for of **4**. Dicationic species **13**, **16**, and **17** were crystallized using diffusion techniques from an acetonitrile/ether solution.

Accurate cell dimensions and orientation matrixes were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[11] Scattering factors and corrections for anomalous absorption were taken from ref 12, and the structures were solved by direct methods (SHELXS[13]). All refinements

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were carried out by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms, except for **17**. For this compound, the two BF_4 anions showed some disorder and restraints were applied on the B−F bond lengths and FBF angles to obtain a correct model; these atoms were isotropically refined. For compounds **1**−**3**, hydrogen atoms were located on Fourier difference maps and their coordinates were refined with an overall isotropic displacement parameter. For compounds **4**, **13**, **16**, and **17**, hydrogen atoms were introduced in calculated positions and only an overall isotropic displacement parameter was refined.

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Supporting Information Available: Tables of crystal data, interatomic distances, and bond angles for **1**, **2**, **3**, **4**, **13**, **16**, and **17** and Cameron views of **2**, **3**, **13**, and **16** (19 pages). Ordering information is given on any current masthead page.

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