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Cobalt-Complexed Conjugated Diyne Salts: A Family of Rigid Masked Dielectrophiles. Syntheses, Structures, and Double Nucleophilic Substitutions

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A family of dicationic diyne salts of the general formula $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Nu\text{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}Nu)]\text{-}[BF_4]_2$ {Nu = SMe_2 (**3**); Nu = NC_6H_7, 3-picoline, (**5**); Nu = NC_9H_7, quinoline (**7**)} were prepared and fully characterized. Three X-ray molecular structures of **3**, **5**, and the neutral starting material 2,4-hexadiyne-1,6-diol complex $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(HO{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}OH)]$ (**1**) are presented. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 14.722(2)$ Å, $b = 14.571(3)$ Å, $c = 14.722(2)$ Å, $\alpha = 105.17(1)°$, $\beta = 113.30(1)°$, $\gamma = 99.20(1)°$, and $Z = 4$. Complex **3** crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.\ 758(3)$ Å, $b = 13.360(3)$ Å, $c = 20.494(3)$ Å, $\beta = 91.44(1)°$, and $Z = 4$, and compound **5** also crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.\ 426(2)$ Å, $b = 21.739(5)$ Å, $c = 18.704(3)$ Å, $\beta = 94.86(1)°$, and $Z = 4$. The X-ray structures provide us with valuable information on the arrangement of the Co_2−alkyne units, which have a cis geometry and are in sharp contrast to that observed generally for diyne−tetracobalt compounds. Complex $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Me_2S{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}SMe_2)][BF_4]_2$ (**3**) reacts with N-, S-, and P-centered nucleophiles and affords the related substituted complexes in high yields. The stability and reactivity of the disulfonium diyne complex **3** toward nucleophiles are compared to those of the analogous disulfonium-yne complex $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Me_2S{-}CH_2{-}C{\equiv}C{-}CH_2{-}SMe_2)][BF_4]_2$ (**4**).

Introduction

Alkyne−dicobalt carbonyl complexes are well-known, and their syntheses have been performed for over 40 years.[1] Conjugated polyynes have received considerable attention owing to their important physical and chemical properties in material science.[2,3] Acetylenes are important precursors for the preparation of molecular carbon rods, and they also promote formation of connectors, bridges, and acetylenic arrays.[4] Gladysz[5a−c] and Lapinte[5d] have shown that mononuclear systems linked to the two termini of a polyyne system promote electronic communication, and Osella[5e] extended this phenomenon to multimetallic systems. However, it is well-known that the stability of the free polyynes decreases with an increase in the number of conjugated acetylenic subunits. Therefore, such a trend represents a major drawback to their formation. Thus, organometallic chemists often use cobalt−alkyne complexes to increase the stability of these polyynes. This methodology has been also used as a synthetic tool to prepare conjugated polyynes where several alkyne units (−C≡C−C≡C−) are linked together.[6]

Our interest in "M_2L_6 modifications" of propargyl alcohols, or more specifically, 2-butyne-1,4-diol where {M_2L_6 = $Co_2(CO)_6$}, led us recently to prepare a family of metal-stabilized masked 1,4- and 1,6-dicarbenium complexes. The chemistry of metal-stabilized carbenium ions has been well studied in the literature by us and several authors;[7] however, less is known about related dicarbenium complexes.[8] Pursuing our research program, we focused our investigations on the isolation and stabilization of dicarbenium ions possessing one

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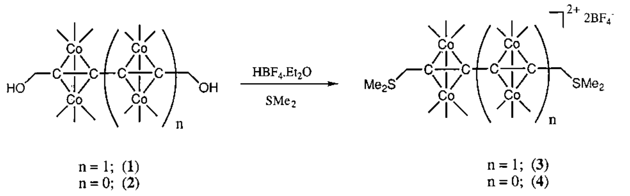
Scheme 1



or more conjugated *cobalt−alkyne units*. Thus, a comparative study of the stability and reactivity of complex **3** with two *cobalt−alkyne units* to the stability and reactivity of complex **4** with *one cobalt−alkyne* unit is reported.

In addition to the previous reasons we also find that M_2L_6−dicarbenium acetylenic complexes offer building blocks for constructing new structures {linear, cyclic, square, etc.}, and this is only possible because of the dramatic modification in the geometry of the linear acetylenic −C≡C− unit upon complexation by $-M_2L_6$ fragments. For instance, complexation of diphenylacetylene by $Co_2(CO)_6$ reduces the alkynyl angle Ph−C≡C− from 180° to around 138°.[9] Herein we report the synthesis of stable 1,4-disulfonium acetylenic−$\{Co_2(CO)_6\}_n$ and 1,6-disulfonium acetylenic−$\{Co_2(CO)_6\}_n$ complexes $n = 2$ (**3**) and $n = 1$ (**4**). Furthermore, the X-ray structure of **4** is reported. These masked dicarbenium ions undergo double nucleophilic addition with the appropriate amines, monophosphine, and the chelating diphenylphosphinobutane (dppb) to give linear and cyclic hexacarbonyldicobalt-substituted alkyne complexes.

Results and Discussion

Syntheses and Structures of the Neutral 1,6-Diol−Diyne and the Masked Dicationic Sulfonium Complexes 1 and 3. Treatment of 2,4-hexadiyne-1,6-diol HO−CH_2−C≡C−C≡C−CH_2OH with 2 equiv of $Co_2(CO)_8$ in ether afforded the expected compound $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(HO{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}OH)]$ (**1**) as a deep-red microcrystalline material in 93% yield after purification on a silica gel column. The spectroscopic and analytical data are consistent with the proposed formula, and the X-ray structure of **1** was determined (vide infra). The compound $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(HO{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}OH)]$ (**1**) was treated by $HBF_4{\cdot}Et_2O$ in the presence of dimethyl sulfide in CH_2Cl_2 for 30 min, providing quantitatively a red microcrystalline complex identified by spectroscopic and analytical methods as the disulfonium complex $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Me_2S{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}SMe_2)][BF_4]_2$ (**3**) (Scheme 1). In addition its structure was confirmed by a single-crystal X-ray study (vide infra). The ^1H NMR data of **3** are consistent with the proposed formula where a plane of symmetry bisects the molecule into two equivalent portions and renders the two methylene groups of the diyne unit equivalent as well as methyl groups of the two coordinated sulfide units. For instance, the $-SMe_2$ groups in **3** give rise to one signal at δ_H 3.20 and δ_C 25.60, while the $-CH_2-$ groups appear at δ_H 3.91 and δ_C 50.20. The remaining carbon nuclei of the diyne chain are observed as singlets at δ_C 85.7 and δ_C 91.9. The carbonyl−dicobalt ligands gave one singlet at 197.3 ppm at room temperature persumably because of rapid trigonal rotation of the $Co(CO)_3$ units. For comparison purposes the analogous and known complex $[(Co_2(CO)_6)\text{-}\mu,\eta^2,\eta^2\text{-}(Me_2S{-}CH_2C{\equiv}CCH_2{-}SMe_2)][BF_4]_2$ (**4**) was prepared.[10]

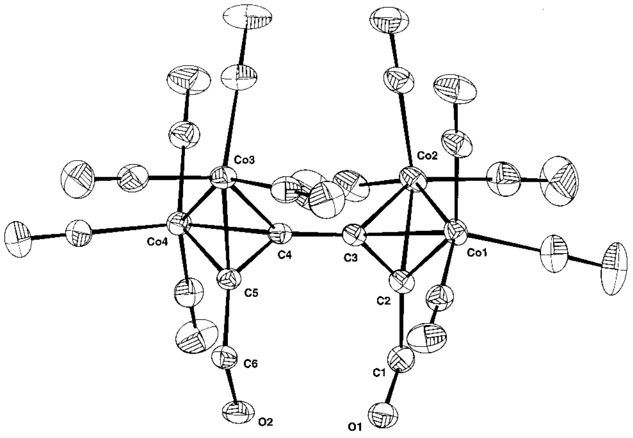


Figure 1. X-ray molecular structure of $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(HO{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}OH)]$ (**1**).

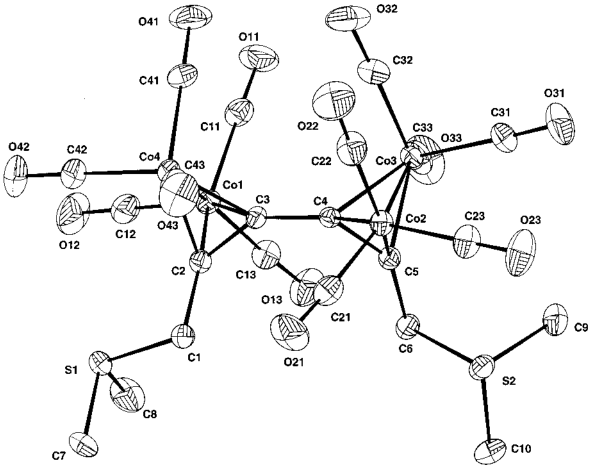


Figure 2. X-ray molecular structure of $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Me_2S{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}SMe_2)]^{2+}$ with atom numbering system.

X-ray Structures of 1 and 3. Suitable deep-red crystals of **1** were obtained by evaporation of a saturated ether solution, while orange-red crystals of complex **3** were grown from CH_3CN/Et_2O solution. CAMERON views of complex $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(HO{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}OH)]$ (**1**) and the cationic part $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Me_2S{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}SMe_2)]^{2+}$ of compound **3** are shown in Figures 1 and 2. Crystallographic data for **1** and **3** are shown in Table 1. Selected bond distances and angles for **1** and **3** are shown in Tables 2 and 3.

The X-ray structures of both molecules exhibit a general trend where (a) the two (μ-alkyne) dicobalt cores are approximately tetrahedral such that the alkyne unit is almost perpendicular to the metal−metal vector typical of perpendicular dicobalt−alkyne complexes. The metal−metal bond distances (d_{Co-Co}) are 2.4741(7) and 2.4664(7) Å for complex **1** and 2.458(1) and 2.462(1) Å for complex **3**. (b) The C_2Co_2 cores in compounds **1** and **3** are arranged in cis geometry, and this contrasts sharply with that observed generally for diyne−tetracobalt compounds.[11] The outer C atoms C1 and C6 carry hydroxyl groups in complex **1**, and SMe_2 substituents in complex **3** are also oriented cis to

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Table 1. Crystallographic Data for Compounds **1**, **3**, and **5**

parameters	1	3	5
formula	$C_{18}H_6O_{14}Co_4$	$C_{22}H_{16}O_{12}S_2Co_4$-$B_2F_8$	$C_{30}H_{18}O_{12}N_2Co_4$-$B_2F_8$
fw	682	945.8	1007.8
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	14.559(3)	12.758(3)	9.426(2)
b (Å)	14.571(3)	13.360(3)	21.739(5)
c (Å)	14.722(2)	20.494(3)	18.704(3)
α (deg)	105.17(1)		
β (deg)	113.30(1)	91.44(1)	94.86(1)
γ (deg)	109.61(2)		
V (Å^3)	2405(1)	3492(1)	3819(1)
Z	4	4	4
ρ_{calc} (g cm^{-3})	1.88	1.80	1.75
temp (°C)	22	22	22
λ (Mo Kα) (Å)	0.710 72	0.710 72	0.710 72
μ (cm^{-1})	27.7	20.7	18.01
$R(F_o)^a$	0.0342	0.0602	0.0474
$R_w(F_o)^b$	0.0394	0.0714	0.0564

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

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for **1**

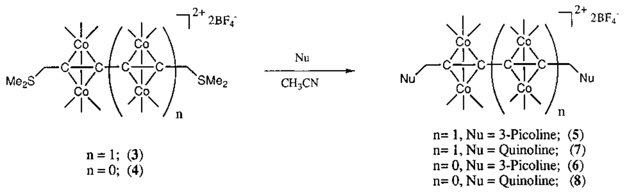
Molecule a			
Co(1)−Co(2)	2.4741(7)	Co(3)−Co(4)	2.4664(7)
Co(1)−C(2)	1.957(3)	Co(1)−C(3)	1.967(3)
Co(2)−C(2)	1.945(4)	Co(2)−C(3)	1.966(3)
Co(3)−C(4)	1.969(3)	Co(3)−C(5)	1.945(3)
Co(4)−C(4)	1.966(3)	Co(4)−C(5)	1.955(3)
O(1)−C(1)	1.416(6)	O(2)−C(6)	1.424(5)
C(1)−C(2)	1.476(5)	C(2)−C(3)	1.347(5)
C(3)−C(4)	1.420(5)	C(4)−C(5)	1.355(5)
C(5)−C(6)	1.476(5)		
O(1)−C(1)−C(2)	112.4(3)	C(1)−C(2)−C(3)	138.7(3)
C(2)−C(3)−C(4)	140.5(3)	C(3)−C(4)−C(5)	141.1(3)
C(4)−C(5)−C(6)	138.9(3)	O(2)−C(6)−C(5)	111.2(3)
Molecule b			
Co(101)−Co(102)	2.4735(7)	Co(103)−Co(104)	2.4665(7)
Co(101)−C(102)	1.951(4)	Co(101)−C(103)	1.964(3)
Co(102)−C(102)	1.954(4)	Co(102)−C(103)	1.964(3)
Co(103)−C(104)	1.969(3)	Co(103)−C(105)	1.944(3)
Co(104)−C(104)	1.964(3)	Co(104)−C(105)	1.957(3)
O(101)−C(101)	1.424(5)	O(102)−C(106)	1.413(5)
C(101)−C(102)	1.484(5)	C(102)−C(103)	1.346(5)
C(103)−C(104)	1.420(5)	C(104)−C(105)	1.348(5)
C(105)−C(106)	1.490(5)		
O(101)−C(101)−C(102)	111.6(3)	C(101)−C(102)−C(103)	138.9(3)
C(102)−C(103)−C(104)	140.3(3)	C(103)−C(104)−C(105)	140.8(3)
C(104)−C(105)−C(106)	139.2(3)	O(102)−C(106)−C(105)	111.7(3)

each other. Further, the two $C_2Co_2(CO)_6$ units are linked via a short C3−C4 single bond between the two carbyne C atoms, 1.420(5) Å for complex **1** and 1.438(8) for complex **3**. The alkyne C−C bonds are much shorter; for instance, C2−C3 = 1.347 (5) Å and C4−C5 = 1.355(5) Å for complex **1**, and C2−C3 = 1.343 (9) Å and C4−C5 = 1.370(8) Å for complex **3**. These bond lengths are in good agreement with those reported for analogous diyne−tetracobalt complexes.[11] After elucidation of the structure of complex **3**, we investigated its reactivity toward aromatic amines and phosphine nucleophiles and compared these reactions with the analogous alkyne−dicobalt complex $[(Co_2(CO)_6)$-μ,η^2,η^2-$(Me_2S{-}CH_2C{\equiv}CCH_2{-}SMe_2)]$-$[BF_4]_2$ (**4**).

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) for **3**

Co(1)−Co(2)	2.458(1)	Co(3)−Co(4)	2.462(1)
Co(1)−C(2)	1.938(6)	Co(1)−C(3)	1.946(6)
Co(2)−C(2)	1.936(6)	Co(2)−C(3)	1.959(6)
Co(3)−C(4)	1.947(6)	Co(3)−C(5)	1.954(6)
Co(4)−C(4)	1.957(6)	Co(4)−C(5)	1.951(6)
S(1)−C(1)	1.816(7)	S(1)−C(7)	1.792(8)
S(1)−C(8)	1.800(9)	S(2)−C(6)	1.808(7)
S(2)−C(9)	1.782(8)	S(2)−C(10)	1.803(9)
C(1)−C(2)	1.498(9)	C(2)−C(3)	1.343(9)
C(3)−C(4)	1.438(8)	C(4)−C(5)	1.370(8)
C(5)−C(6)	1.482(9)		
C(1)−S(1)−C(7)	101.0(4)	C(1)−S(1)−C(8)	103.0(4)
C(7)−S(1)−C(8)	101.7(5)	C(6)−S(2)−C(9)	103.0(4)
C(6)−S(2)−C(10)	102.7(4)	C(9)−S(2)−C(10)	101.5(5)
S(1)−C(1)−C(2)	110.7(4)	C(1)−C(2)−C(3)	137.1(6)
C(2)−C(3)−C(4)	141.6(6)	C(3)−C(4)−C(5)	140.8(5)
C(4)−C(5)−C(6)	136.4(6)	S(2)−C(6)−C(5)	111.0(5)

Scheme 2



Reactions with 3-Picoline and Quinoline. Treatment of the masked carbenium ion complexes, either $[(Co_2(CO)_6)_2$-μ,η^2,η^2-$(Me_2S{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}SMe_2)][BF_4]_2$ (**3**) or $[[(Co_2(CO)_6)$-μ,η^2,η^2-$(Me_2S{-}CH_2C{\equiv}CCH_2{-}SMe_2)][BF_4]_2$ (**4**), with an excess of the appropriate amine afforded the dicationic complexes of general formula $[(Co_2(CO)_6)_2$-μ,η^2,η^2-$(Nu{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}Nu)][BF_4]_2$ {Nu = NC_6H_7, 3-picoline (**5**); Nu = NC_9H_7 quinoline (**7**)} or $[(Co_2(CO)_6)$-μ,η^2,η^2-$(Nu{-}CH_2C{\equiv}CCH_2{-}Nu)][BF_4]_2$ {Nu = NC_6H_7, 3-picoline (**6**); Nu = NC_9H_7, quinoline (**8**)} (Scheme 2). All of these compounds were characterized by spectroscopic analysis (^1H, ^{13}C NMR spectra and infrared). The microanalytical data obtained for **5**−**8** were in accord with the proposed formulas. Furthermore, an X-ray structural determination of complex **5** belonging to the above family was carried out (vide infra). The ^1H NMR of these compounds **5**−**8** recorded in CD_3CN displayed a common feature due to the presence of a plane of symmetry rendering the methylene protons of the coordinated alkyne equivalent and appearing as a singlet at δ_H 6.30 (**5**), 6.94 (**7**) and at δ_H 6.31 (**6**), 6.95 (**8**), respectively. The phenyl protons of the amine nucleophiles appeared as multiplets in the aromatic region and in the range 8.30−9.30 ppm. The methyl group of the 3-picoline resonated as a singlet at δ_H 2.72 (**5**) and 2.71 (**7**). We have found that complexes containing quinoline as substituents were less stable and dissociation in solution occurred after several hours at room temperature, affording the diol complex starting material and the free quinoline ligand. No doubt this is related to the weak electron-donating property of the quinoline ligand.

X-ray Molecular Structure of 5. Suitable red crystals of $[(Co_2(CO)_6)_2$-μ,η^2,η^2-$(C_6H_7N{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}NC_6H_7)]$-$[BF_4]_2$ (**5**) for an X-ray structure study were obtained using the slow evaporation method from a CH_3CN/Et_2O solution. Complex **5** crystallizes in the $P2_1/n$ unit cell. Figure 3 shows the CAMERON view of the cationic part of molecule **5** with the atom numbering system. Crystallographic data for **5** are shown in Table 1. Selected bond distances and angles are given in Table 4. The structure is very similar to that of **3**, where the two C_2Co_2 cores are arranged in a cis geometry, and in each case the alkyne unit is perpendicular to the metal−metal bond with distances d_{Co-Co} = 2.467(2) and 2.471(2) Å. These metal−metal bond distances are analogous to those found in the parent complex **1** but slightly longer than those reported for compound

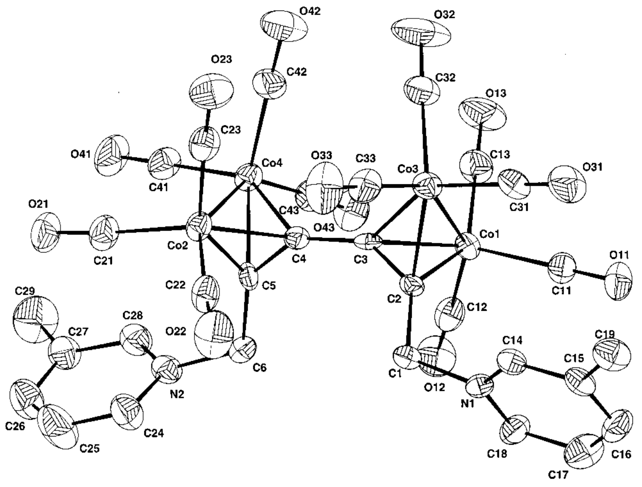


Figure 3. X-ray molecular structure of $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(C_6H_7N-CH_2C{\equiv}C-C{\equiv}CCH_2-NC_6H_7)]^{2+}$ with atom numbering system.

Table 4. Selected Interatomic Distances (Å) and Bond Angles (deg) for **5**

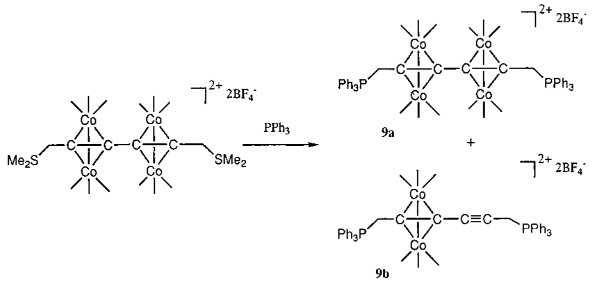
Co(1)−Co(2)	2.467(2)	Co(3)−Co(4)	2.471(2)
Co(1)−C(2)	1.938(7)	Co(1)−C(3)	1.969(8)
Co(2)−C(2)	1.949(8)	Co(2)−C(3)	1.976(8)
Co(3)−C(4)	1.960(8)	Co(3)−C(5)	1.923(9)
Co(4)−C(4)	1.972(8)	Co(4)−C(5)	1.930(9)
N(1)−C(1)	1.47(1)	N(2)−C(6)	1.48(1)
C(1)−C(2)	1.47(1)	C(2)−C(3)	1.34(1)
C(3)−C(4)	1.43(1)	C(4)−C(5)	1.31(1)
C(5)−C(6)	1.50(1)		
N(1)−C(1)−C(2)	112.3(7)	C(1)−C(2)−C(3)	137.9(8)
C(2)−C(3)−C(4)	141.3(8)	C(3)−C(4)−C(5)	143.9(8)
C(4)−C(5)−C(6)	137.8(8)	N(2)−C(6)−C(5)	112.6(7)

3 (vide supra). The outer C atoms C1 and C6 carrying 3-picoline substituents are also oriented cis to each other. These observations contrast sharply with other well-known tetracobalt diyne complexes where generally the cluster units or/and the substituent groups are in a trans geometry. The two $C_2Co_2(CO)_6$ units are linked via a short 1.45(1) Å C3−C4 single bond between two carbyne C atoms; this C3−C4 bond distance is slightly longer than that observed for **3**.

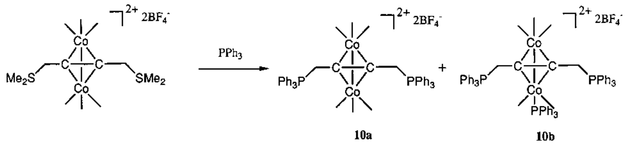
The alkyne C−C bonds C2−C3 (1.34(1) Å) and C4−C5 (1.31(1) Å) are slightly shorter than those found for complexes **1** and **3**.

Reactions with PPh$_3$ and dppb and Comparative Stability of the Mono- and Diyne Complexes. To increase the stability of our diyne salts, efforts were directed to the use of stronger coordinated ligands such as phosphines. Thus, treatment of complexes **3** and **4** with 2 equiv of PPh_3 in CH_3CN for 30 min gave different compounds depending on the alkyne starting material (Scheme 3). For instance, the diyne complex $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Me_2S-CH_2C{\equiv}C-C{\equiv}CCH_2-SMe_2)][BF_4]_2$ (**3**), reacted with PPh_3 to give the derivatives $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Ph_3P-CH_2C{\equiv}C-C{\equiv}CCH_2-PPh_3)][BF_4]_2$ (**9a**) and $[(Co_2(CO)_6)\text{-}\mu,\eta^2,\eta^2\text{-}(Ph_3P-CH_2C{\equiv}C-C{\equiv}CCH_2-PPh_3)][BF_4]_2$ (**9b**) in 9/1 ratio. As one might expect in this reaction, a double displacement of the SMe_2 occurred, yielding **9a**, and also a loss of one $Co_2(CO)_6$ unit was observed, affording complex **9b**. Addition of $Co_2(CO)_8$ to a CD_3CN sample of **9a** and **9b** restored the second alkyne coordination and yielded exclusively **9a**. Extrusion of one $Co_2(CO)_6$ unit is no doubt the result of steric interactions where coordination of the phosphine ligand to the cobalt center occurs as the first step and provokes the cleavage of one $Co_2(CO)_6$ unit; similar results were reported previously.[11d]

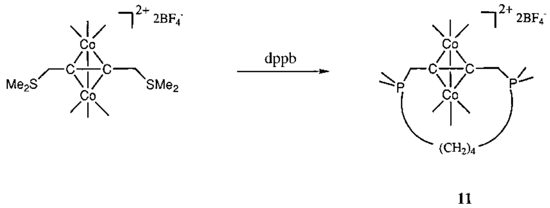
Scheme 3



Scheme 4



Scheme 5



We also confirmed the previous results by examining the reaction of complex $[(Co_2(CO)_6)\text{-}\mu,\eta^2,\eta^2\text{-}(Me_2S-CH_2C{\equiv}CCH_2-SMe_2)][BF_4]_2$ (**4**) with PPh_3 under the same experimental conditions (Scheme 4). In addition to the expected complex $[(Co_2(CO)_6\text{-}\mu,\eta^2,\eta^2\text{-}(PPh_3\text{-}CH_2C{\equiv}CCH_2-PPh_3)][BF_4]_2$ (**10a**) a new compound identified as $[(Co_2(CO)_5PPh_3)\text{-}\mu,\eta^2,\eta^2\text{-}(PPh_3\text{-}CH_2C{\equiv}CCH_2-PPh_3)][BF_4]_2$ (**10b**) was isolated in a 10/1 ratio. In this compound a third phosphine ligand is coordinated to the cobalt center (Scheme 3). The ^{31}P NMR spectrum of **10b** exhibited two singlets at δ_P 20.42 attributed to $(-CH_2-PPh_3)$ and at δ_P 39.66, which is in agreement with chemical shifts of a phosphine ligand coordinated to a cobalt center.

We feel from the above results that tetracobalt−diyne complexes are sterically congested compared to the monoalkyne cobalt complexes and that addition of a relatively bulky ligand provokes the dissociation of one $Co_2(CO)_6$ unit. Similar observations were reported previously.[11d] We feel that lack of stability in these cobalt−alkyne complexes should increase along with higher cobalt nuclearity.

When complexes **3** and **4** were treated with chelating phosphine such as dppb, different results were obtained depending on the alkyne starting material. For instance compound **4** reacted with dppb to give the cobalt derivative $[(Co_2(CO)_6\text{-}\mu,\eta^2,\eta^2\text{-}(-CH_2C{\equiv}CCH_2-)-(PPh_2-(CH_2)_4-PPh_2][BF_4]_2$ (**11**) (Scheme 5). In this cyclic Co_2−alkyne complex the bidentate phosphine ligand is coordinated to the two alkyne termini. This new compound was completely characterized by spectroscopic methods and microanalytical data. The ^{31}P NMR spectrum of **11** exhibited one singlet at δ_P 26.22 attributed to the two equivalent phosphine ligands, while the ^1H NMR spectrum of **11** recorded in $(CD_3)_2CO$ is in accord with the proposed formula suggesting the presence of a plane of symmetry that bisects the molecule into two equal halves. For instance the two methylene groups of the alkyne unit $(-CH_2-P)$ are equivalent and appeared as a doublet at δ_H 5.56, $J_{P-H} = 15.1$ Hz, while the methylene groups of the chelating phosphine dppb appeared as multiplets at δ_H 3.49 and δ_H 2.44. Further, the phenyl protons appeared as multiplets in the aromatic region and in the range 7.6−8.40 ppm.

Unexpectedly, treatment of complex **3** with dppb did not afford any isolable complexes; instead complete decomposition was observed along with the formation of perhaps paramagnetic compounds, which exhibited broad and massive signals in ^1H NMR spectroscopy. We presume that substitution at the cobalt center is taking place and provoking the decoordination of the cluster $Co_2(CO)_6$ units.

Concluding Remarks

In this paper we reported high-yield syntheses of several tetracobalt−diyne complexes. Three X-ray structures belonging to this family were ascertained by X-ray analysis. The solid-state molecular structures of **1**, **3**, and **5** showed that the $Co_2(CO)_6$−alkyne units, as well as the substituents at the alkyne termini, are arranged in cis geometry and are in sharp contrast to other well-known tetracobalt−diyne complexes reported in the literature. Further, we found that nucleophilic substitution reactions by weak nucleophiles such as 3-picoline and quinoline on the masked dielectrophiles $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Me_2S{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}SMe_2)][BF_4]_2$ (**3**) and $[(Co_2(CO)_6)\text{-}\mu,\eta^2,\eta^2\text{-}(Me_2S{-}CH_2C{\equiv}CCH_2{-}SMe_2)][BF_4]_2$ (**4**) afforded the expected disubstituted salts $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Nu{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}Nu)][BF_4]_2$ {Nu = 3-picoline (**5**); Nu = quinoline (**7**)} and $[(Co_2(CO)_6)\text{-}\mu,\eta^2,\eta^2\text{-}(Nu{-}CH_2C{\equiv}CCH_2{-}Nu)][BF_4]_2$ {Nu = 3-picoline (**6**); Nu = quinoline (**8**)}, respectively. However, by use of strong nucleophiles such as phosphines, different compounds were obtained depending on the alkyne−cobalt starting material. For instance, the tetracobalt−diyne complex **3** reacted with PPh_3 by loss of one $Co_2(CO)_6$ unit, unlike the dicobalt−alkyne complex **4**, which showed no sign of decomposition, suggesting that the tetracobalt−diyne complexes are sterically congested and relatively unstable.

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, and methylene chloride and acetonitrile were distilled from sodium hydride. Pentane was treated by sulfuric acid and distilled on sodium. Triphenylphosphine (PPh_3), diphenylphosphinobutane (dppb), $Co_2(CO)_8$, HBF_4/Et_2O, CD_2Cl_2, $CDCl_3$, and acetone-d_6 were used as purchased. The amines were freshly distilled on Na prior to use. IR spectra were collected on a Bio-rad FTS 165 spectrometer from KBr disks. All absorptions are expressed in wavenumbers (cm^{-1}). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AM instrument, using standard programs for proton (299 MHz), carbon (75 MHz), and phosphorus (124 MHz) spectra. NMR chemical shifts are reported in (ppm) relative to TMS (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). Data for (^{13}C, ^{31}P) are proton-decoupled. Elemental analyses were performed by "Centre régional de microanalyse, Université Pierre et Marie Curie". Compounds **2** and **4** were prepared according to literature methods.[9]

Synthesis of $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(HO{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}OH)]$ (1). To an ethereal solution (50 mL) of 2.25 g of $Co_2(CO)_8$ (6.5 mmol) was added 0.36 g (3.3 mmol) of 2,4-hexadiyn-1,6-diol. The mixture was stirred at room temperature for 1 h, then filtered and flash-chromatographed on silica gel using ether as the eluant. Further crystallization from ether led to the expected complex. Yield: 2.06 g, 93%.^1H NMR ($(CD_3)_2CO$): δ 5.10 (t, J = 5.8 Hz 2H, −OH), 4.91 (d, J = 5.8 Hz, 4H, H-2−6). ^{13}C NMR ($(CD_3)_2CO$): δ 200.4 (CO), 105.9 (C_{3-4}), 86.1 (C_{2-5}), 63.5 (C_{1-6}). IR, ν(CO), cm^{-1}: 2104, 2084, 2064, 2035, 2025, 2016, 2001. Anal. Calcd for $C_{18}H_6O_{14}Co_4$: C, 32.85; H, 0.88. Found: C, 32.37; H, 0.84.

Synthesis of $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Me_2S{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}SMe_2)][BF_4]_2$ (3). To a CH_2Cl_2 solution (40 mL) of compound $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(HO{-}CH_2C{\equiv}CC{\equiv}CCH_2{-}OH)]$ (**1**) (274 mg, 0.4 mmol) and dimethyl sulfide SMe_2 (1 mL, excess) was added dropwise $HBF_4{\cdot}Et_2O$ (0.12 mL, 0.8 mmol). The solution turned from brown to deep-red, and a red microcrystalline precipitate appeared. The reaction was left to proceed for 0.5 h. The solvent was removed and the precipitate was washed several times with ether under argon and then dried under vacuum. Yield: 295 mg, 78%. ^1H NMR (CD_3CN): δ 4.91 (s, 4H, H1,6), 3.20 (s, 12H, $-CH_3$). ^{13}C NMR (CD_3CN): δ 197.3 (CO), 91.9 (C_{3-4}), 85.7 (C_{2-5}), 50.2 (C_{1-6}), 25.6 ($-CH_3$). IR, ν(CO), cm^{-1}: 2115, 2095, 2064, 2073, 2041, 2029, 2016. Anal. Calcd for $C_{22}H_{16}O_{12}S_2Co_4B_2F_8$: C, 27.93; H, 1.70. Found: C, 27.77; H, 1.53.

Synthesis of $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(C_6H_7N{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}NC_6H_7)][BF_4]_2$ (5). All the nucleophilic substitution reactions were performed in a similar manner, where 2 equiv of the nucleophile was added at room temperature to the cobalt−alkyne complex in the appropriate solvent. To a CH_3CN solution (5 mL) of **3** (283 mg, 0.3 mmol) was added 0.6 mmol of 3-picoline in CH_3CN (2 mL), and the reaction was stirred for 1 h. The mixture became red-brown. The solvent was removed under vacuum, and the residue was washed several times with ether and recrystallized from CH_3CN/ether to yield red microcrystalline material. Yield: 271 mg, 90%. ^1H NMR (CD_3CN): δ 9.33 (s, 2H, ArH), 9.25 (d, J = 6.1 Hz, 2H, ArH), 8.77 (d, J = 7.9 Hz, 2H, ArH), 8.38 (dd, J = 6.1 Hz, 7.9 Hz, 2H, ArH), 6.30(s, 4H, H1,6), 2.72 (s, 6H, $-CH_3$). ^{13}C NMR (CD_3CN): δ 198.5 (CO), 148.6, 145.1, 143.7, 141.7, 129.4 (C-phenyl), 97.5 (C_{3-4}), 93.0 (C_{2-5}), 65.2 (C_{1-6}), 18.6 ($-CH_3$). IR, ν(CO), cm^{-1}: 2110, 2090, 2065, 2033, 2010. Anal. Calcd for $C_{30}H_{18}O_{12}N_2Co_4B_2F_8$: C, 35.75; H, 1.70. Found: C, 35.64; H, 1.73.

Synthesis of $[(Co_2(CO)_6)\text{-}\mu,\eta^2,\eta^2\text{-}(C_6H_7N{-}CH_2C{\equiv}CCH_2{-}NC_6H_7)][BF_4]_2$ (6). This complex was prepared in a fashion similar to that of complex **5**. Yield: 95%. ^1H NMR (CD_3CN): δ 9.28 (s, 2H, ArH), 9.16 (d, J = 6.1 Hz, 2H, ArH), 8.73 (d, J = 7.9 Hz, 2H, ArH), 8.34 (dd, J = 6.1 Hz, 7.9 Hz, 2H, ArH), 3.31 (s, 4H, H1,4), 2.69 (s, 6H, $-CH_3$). ^{13}C NMR (CD_3CN): δ 198.5 (CO), 147.93, 145.10, 142.9, 141.10, 129.19, (C-phenyl), 92.8 (C_{2-3}), 65.75 (C_{1-4}), 18.05 ($-CH_3$). IR, ν(CO), cm^{-1}: 2100, 2065, 2036, 2015, 2000.

Synthesis of $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(C_9H_7N{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}NC_9H_7)][BF_4]_2$ (7). This complex was prepared in a way similar to that of **5** and **6**. Yield: 85%. ^1H NMR ($(CD_3)_2CO$): δ 9.82 (d, J = 5.75 Hz, 2H, ArH), 9.56 (d, J = 8.3 Hz, 2H, ArH), 9.01 (d, J = 9.1 Hz, 2H, ArH), 8.67 (d, J = 8.1 Hz, 2H, ArH), 8.52 (d, J = 5.1 Hz, 7.9 Hz, 2H, ArH), 8.49 (d, J = 5.9 Hz, 2H, ArH), 8.22 (d, J = 8.1 Hz, 2H, ArH), 6.94 (s, 4H, H1,6). ^{13}C NMR (CD_3CN): δ 198.5 (CO), 150.4, 150.2, 139.5, 137.3, 132.5, 131.9, 123.7, 120.1 (C-phenyl), 97.2 (C_{3-4}), 94.8 (C_{2-3}), 61.2 (C_{1-6}). IR, ν(CO), cm^{-1}: 2111, 2092, 2032, 2007.

Synthesis of $[(Co_2(CO)_6)\text{-}\mu,\eta^2,\eta^2\text{-}(C_9H_7N{-}CH_2C{\equiv}CCH_2{-}NC_9H_7)][BF_4]_2$ (8). This compound was made in a way similar to that of **6**. Compound **8** was obtained as deep-red crystals in 92% yield. ^1H NMR ($(CD_3)_2CO$): δ 9.80 (d, J = 5.75 Hz, 2H, ArH), 9.57 (d, J = 8.3 Hz, 2H, ArH), 8.94 (d, J = 9.1 Hz, 2H, ArH), 8.69 (d, J = 8.1 Hz, 2H, ArH), 8.46 (d, J = 5.1 Hz, 7.9 Hz, 4H, ArH), 8.23 (d, J = 5.9 Hz, 2H, ArH), 6.95 (s, 4H, H1,6). ^{13}C NMR (CD_3CN): δ 198.5 (CO), 151.06, 150.09, 139.46, 137.36, 132.52, 131.85, 123.86, 120.24 (C-phenyl), 94.8 (C_{2-3}), 60.36 (C_{1-4}). IR, ν(CO), cm^{-1}: 2109, 2092, 2030, 2003.

Synthesis of $[(Co_2(CO)_6)_2\text{-}\mu,\eta^2,\eta^2\text{-}(Ph_3P{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}PPh_3)][BF_4]_2$ (9a) and $[(Co_2(CO)_6)\text{-}\mu,\eta^2,\eta^2\text{-}(Ph_3P{-}CH_2C{\equiv}C{-}C{\equiv}CCH_2{-}PPh_3)][BF_4]_2$ (9b). PPh_3 (162 mg 0.62 mmol) was added to **3** (293 mg 0.31 mmol), the mixture was then dissolved in CH_3CN (5 mL), and the reaction was left for 30 min. A mixture of inseparable products **9a** and **9b** was obtained, the relative proportions depending on stirring time. Yield of **9a**/**9b** is 10:1.

Spectroscopic data for **9a**. ^1H NMR ($(CD_3)_2CO$): δ 8.20−7.18 (m, 30H, ArH), 5.37 (d, J_{P-H} = 12.9 Hz, 4H, $-(CH_2)-P$). ^{31}P NMR ($(CD_3)_2CO$): δ 22.37. IR (**9ab**), ν(CO), cm^{-1}: 2107, 2089, 2065, 2029, 1945. Spectroscopic data for **9b**. ^1H NMR ($(CD_3)_2CO$): δ 8.20−7.18 (m, 30H, ArH), 5.85 (d, J_{P-H} = 15.6 Hz, 4H, $-(CH_2)-P$) 5.37 (d, J_{P-H} = 15.6 Hz, 4H, $-(CH_2)-P$). ^{31}P NMR ($(CD_3)_2CO$): δ Pf 20.52, Pb 22.37. IR (**9ab**), ν(CO), cm^{-1}: 2107, 2089, 2065, 2029, 1945.

Synthesis of $[(Co_2(CO)_6\text{-}\mu,\eta^2,\eta^2\text{-}(PPh_3{-}CH_2C{\equiv}CCH_2{-}PPh_3)][BF_4]_2$ (10a) and $[(Co_2(CO)_5PPh_3)\text{-}\mu,\eta^2,\eta^2\text{-}(PPh_3{-}CH_2C{\equiv}CCH_2{-}$

PPh$_3$)][BF$_4$]$_2$ (10b). PPh$_3$ (162 mg 0.62 mmol) was added to **4** (197 mg 0.31 mmol), the mixture was dissolved in CH$_3$CN (5 mL), and the reaction was left for 30 min. A mixture of inseparable products **10a** and **10b** was obtained, the relative proportions depending on stirring time. Yield of **10a**/**10b** is 10:1.

Spectroscopic data for **10a**. ^{1}H NMR (CD$_3$CN): δ 7.88−7.75 (m, 30H, ArH), 4.63 (d, J_{P-H} = 13.5 Hz, 4H, −(CH$_2$)−P). ^{31}P NMR (CD$_3$CN): δ 20.42. IR (**10ab**), ν(CO), cm^{-1}: 2105, 2083, 2060, 2023, 1942.

Spectroscopic data for **10b**. ^{1}H NMR (CD$_3$CN): δ 7.73−7.53 (m, 45H, ArH), 4.36 (d, J_{P-H} = 13.5 Hz, 4H, −(CH$_2$)−P). ^{31}P NMR (CD$_3$CN): δ P−CH$_2$, 20.42, P−Co, 39.66. IR (**10a**,**b**), ν(CO), cm^{-1}: 2105, 2083, 2060, 2023, 1942.

Synthesis of [(Co$_2$(CO)$_6$-μ,η^2,η^2-(−CH$_2$C≡CCH$_2$−)−(PPh$_2$−(CH$_2$)$_4$−PPh$_2$][BF$_4$]$_2$ (11). To an acetone solution (20 mL) of complex **4** (200 mg, 0.31 mmol) was added dropwise a CH$_2$Cl$_2$ solution (16 mL) of dppb (134 mg, 0.31 mmol). The reaction was left to stir for 1.5 h during which the solution becomes deep red. The solvent was reduced under vacuum (6 mL), and ether was added, affording a red precipitate. This complex was separated and washed with ether three times recrystallized from acetone/ether. Yield: 70%, 210 mg. ^{1}H NMR ((CD$_3$)$_2$CO): δ 8.20 (dd, J = 7.2 Hz, 12.6 Hz, 8H, ArH$_{ortho}$), 7.94 (dt, J = 5.1 Hz, J = 1.9 Hz, 4H, ArH$_{para}$), 7.82 (dt, J = 5.4 Hz, J = 3.5 Hz, 8H, ArH$_{meta}$), 5.56 (d, J = 15.1 Hz, 4H, H$_{alkyne}$), 3.49 (m, 4H, −(CH$_2$)−P), 2.44 (m, 4H, −(CH$_2$)−P). ^{13}C NMR (CD$_3$CN): δ 198.2 (CO), 136.33 (s, C-phenyl), 133.87 (s, C-phenyl), 131.45 (s, C-phenyl), 119.72 (d, J_{P-C} = 83.7 Hz, C-phenyl), 81.51 (C-alkyne), 27.54 (−CH$_2$-alkyne, d, J_{P-C} = 42.2 Hz), 20.80 (d, J_{P-C} = 42.2 Hz, −(CH$_2$)$_4$−P), 17.65 (d, J_{P-C} = 7.5 Hz, −(CH$_2$)$_4$−P). IR, ν(CO), cm^{-1}: 2102, 2066, 2036. ^{31}P NMR ((CD$_3$)$_2$CO): δ P−CH$_2$, 26.22. Anal. Calcd for C$_{38}$H$_{32}$O$_6$P$_2$Co$_2$B$_2$F$_8$: C, 48.65; H, 3.44. Found: C, 48.65; H, 3.73.

X-ray Structure Determination for 1, 3, and 5. Suitable crystals of **1** were obtained from evaporation of a concentrated ether solution, while those of **2** and **3** were obtained using diffusion techniques from an acetonitrile/ether solution. The selected crystal of complex **1**, **3**, or **5** was mounted on the top of a glass stick. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. No significant variations were observed in the intensities of two checked reflections during data collection. The ψ scan curve of **1**, **3**, or **5** was flat; hence, no absorption correction was applied. Complete crystallographic data and collection parameters for **1**, **3**, and **5** are listed in Table 1. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[12] Scattering factors and corrections for anomalous dispersion were taken from ref 13. The structures of these compounds were refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter. Fractional parameters, anisotropic thermal parameters, and all bond lengths and angles are given in the Supporting Information for complexes **1**, **3**, and **5**.

Acknowledgment. We thank CNRS and Université Pierre et Marie Curie for supporting this work.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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