coordinating nitrogens are situated nearly symmetrically with respect to the Cu-S bond.

As is shown in Figure 5a,b, when the S-C bond in CH_3S^- is perpendicular to the trigonal plane, the copper orbital containing the unpaired electron becomes nearly symmetrical to the Cu-S bond direction, but when the S-C bond is removed from the perpendicular plane, the copper orbital containing the unpaired electron becomes extensively unsymmetrical about the two nitrogens, causing a large difference between overlaps of the orbitals of the two nitrogens.

A marked difference between the overlaps of the copper orbital containing the unpaired electron with the two different nitrogens can be seen also for azurin, in which two nitrogens are situated unsymmetrically with respect to the Cu-S bond (Figure 5c). These unsymmetrical spin distributions about the two nitrogens are consistent with the observed results showing the very different two ^{14}N hfc's, although quantitative agreement with the experimental hfc values is not satisfactory.

It should be noted that the unpaired electron distribution on copper in the copper complexes with the N_2S trigonal structure is very sensitive to changes in the positions of the donor atoms as is shown in Figure 6. Such changes strongly affect the spin distribution onto the donor atoms. Interestingly, the copper orbital energies are not as sensitive to movement of the donor atoms in the trigonal plane, although movement of the copper ion in the direction perpendicular to the trigonal plane greatly affects the orbital energy. On the other hand, in the system having the tetragonal structure, the copper orbital energies are sensitive to deformation of the coordination structure, even when the coordinating atoms move in the tetragonal plane. The observation that the unpaired electron distribution in the trigonal system is very sensitive to changes that result from only small perturbations in energy may be related to the enzymatic function of the blue copper proteins.

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Synthesis, Structure, and Reactivity of a Novel Series of Propargylic Cationic Derivatives: $[Co_2(CO)_6(CH{\equiv}CCH_2SR_1R_2)]BF_4$, $[Co_2(CO)_6(CH{\equiv}CCH_2PR_3)]BF_4$, and $[Co_2(CO)_6(CH{\equiv}CCH_2Py)]BF_4$

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Treatment of the propargylic cation complex $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$ with sulfides SR_1R_2 [$R_1 = R_2 = Me$ (**1a**); $R_1 = R_2 = Et$ (**1b**); $R_1 = R_2 = Pr^i$ (**1c**); $R_1 = Me$, $R_2 = Et$ (**1d**)], phosphines PR_3 [R = Et (**2a**); R = Ph(**2b**)], and pyridine = Py (**3**) yields the corresponding complexes of the general formulas $[(Co_2(CO)_6(CH{\equiv}CCH_2SR_1R_2)]BF_4$, $[(Co_2(CO)_6(CH{\equiv}CCH_2PR_3)]BF_4$, and $[(Co_2(CO)_6(CH{\equiv}CCH_2Py)]BF_4$. The complexation of the carbenium ion complex by heteroatoms modifies both the structure and the reactivity of the starting material. The X-ray crystal structure of the phosphonium derivative $[(Co_2(CO)_6(CH{\equiv}CCH_2PEt_3)]BF_4$ (**2a**) has been determined. **2a** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ and the cell dimensions $a = 10.212$ (1) Å, $b = 15.007$ (3) Å, $c = 14.941$ (3) Å; and $\beta = 104.94$ (1)°. In addition, the reactivity of the sulfide derivatives with respect to different nucleophiles such as MeOPh, MeOH, Py, and PR_3 is also discussed.

Introduction

The propargylic cation of $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$ has proved to be an alkylating agent toward a wide range of nucleophiles and hence a useful species for organic synthesis.[1-6] However, this very reactive carbenium ion suffers from a lack of selectivity while its general instability has precluded X-ray structural determination. It should be pointed out however that a reasonable structural hypothesis for this cation has been deduced from NMR studies.[7,8] In order to overcome these limitations, we sought to introduce and examine the effects of a sulfide, pyridine, or phosphine group at the carbenium ion center ($-C^+H_2-$). This temporary complexation might be turned to an advantage in terms of reactivity and stability. In this paper we describe the synthesis of propargylic cationic derivatives of the type $[(Co_2(CO)_6(CH{\equiv}CCH_2SR_1R_2)]BF_4$ [$R_1 = R_2 = Me$ (**1a**); $R_1 = R_2 = Et$ (**1b**); $R_1 = R_2 = Pr^i$ (**1c**); $R_1 = Me$, $R_2 = Et$ (**1d**)] and $[(Co_2(CO)_6(CH{\equiv}CCH_2PR_3)]BF_4$ [R = Et (**2a**); R = Ph (**2b**)] where the presence of the heteroatom indeed modifies the stability and electrophilicity of these species relative to the dicobalt propargylic carbenium ion while suppressing the direct interaction of the adjacent ($-C^+$) atom with one of the cobalt metals in the cluster.

Experimental Section

Manipulations were carried out by using a vacuum line under argon and employing standard Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques under argon. IR spectra were recorded on a FT Bomem Michelson 100 spectrometer from samples prepared on KBr disks. NMR (^1H, ^{13}C, ^{31}P) spectra were recorded on a Bruker AM 250 instrument, and chemical shifts are relative to TMS (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). Data (^{31}P, ^{13}C) are proton decoupled, reported downfield positive with respect to the reference standard. Elemental analyses were performed by the microanalyses service of CNRS, Vernaison, France.

$[Co_2(CO)_6(CH{\equiv}CCH_2SMe_2)]BF_4$ (1a). A solution of an excess of SMe_2 (2 mL) was added to a suspension of $[(Co_2(CO)_6(CH{\equiv}CCH_2)]$-$BF_4$ (424 mg, 1.03 mmol) in 10 mL of CH_2Cl_2. The mixture was stirred under argon for 1 h; later 10 mL of diethyl ether was added, providing an orange-red bright microcrystalline compound. Complex **1a** was washed several times with ether and recrystallized from CH_2Cl_2/diethyl ether. Yield: 88% (429 mg). Anal. Calcd for $C_{11}H_9O_6SBF_4Co_2$: C, 27.84; H, 1.89; S, 6.75. Found: C, 27.95; H, 1.66; S, 6.66. ^1H NMR (CD_3CN): δ 6.51 (CH-, s, 1 H), 4.81 ($-CH_2-S$, s, 2 H), 2.94 (CH_3-S, s, 6 H).

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$[Co_2(CO)_6(CH{\equiv}CCH_2SR_1R_2)]BF_4$ [$R_1 = R_2 =$ Et (1b); $R_1 = R_2 =$ Pr^i (1c); $R_1 =$ Me, $R_2 =$ Et (1d)]. These complexes were obtained by the procedure described already for **1a**. Yield: **1b**, 85% (439 mg); **1c**, 75% (409 mg); **1d**, 80% (402 mg).

The spectroscopic data for **1b** are as follows. ^{1}H NMR (CD_2Cl_2): δ 6.27 (CH-, s, 1 H), 4.98 (-CH_2-S, s, 2 H), 3.63 (S-CH_2-C, q, 4 H), 1.60 (S-C-CH_3, t, 6 H). ^{13}C NMR (CD_2Cl_2): δ 198 (CO, m), 78.62 (-C, s), 74.88 (CH, s), 45.1 (-CH_2-S, s), 35.2 (S-C-CH_3, s), 9.61 (S-CH_2-C, s).

Analytical and spectroscopic data for **1c** are as follows. Anal. Calcd for $C_{15}H_{17}O_6SBF_4Co_2$: C, 33.96; H, 3.2; S, 6.03. Found: C, 33.64; H, 3.08; S, 6.05. ^{1}H NMR (CD_2Cl_2): δ 6.3 (-CH, s, 1 H), 4.82 (-CH_2-S, s, 2 H), 4 (CH(CH_3)$_2$, 2 H, sep, J_{H-H} = 7 Hz), 1.69 ((CH_3)$_2$CH, d, 6 H_a, methyl group diastereotopic protons), 1.66 ((CH_3)$_2$CH, d, 6 H_b, methyl group diastereotopic protons).

The spectroscopic data **1d** are as follows. ^{1}H NMR (CD_2Cl_2): δ 6.13 (-CH, s, 1 H), 4.89 (-CH_2-S, s, 2 H), 3.52 (S-CH_2-C, q, 2 H, J_{H-H} = 7 Hz), 1.57 (S-C-CH_3, t, 3 H), 2.96 (S-CH_3, s, 3 H). ^{13}C NMR (CD_2Cl_2): δ 197 (CO, m), 78 (-C, s), 74.7 (-CH, s), 47.58 (-CH_2-S, s), 37.40 (S-C-CH_3, s), 9.33 (S-CH_2-C, s), 22.77 (S-CH_3, s).

$[Co_2(CO)_6(CH{\equiv}CCH_2PEt_3)]BF_4$ (2a). PEt_3 (80 μL, 0.51 mmol) was injected via a microsyringe into a Schlenk tube containing a suspension of $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$ (200 mg, 0.5 mmol) in 10 mL of dichloromethane. The mixture was stirred under argon for 1 h. Later 10 mL of diethyl ether was added, providing an orange microcrystalline precipitate. The complex was separated and washed several times with diethyl ether. Yield: 70% (186 mg). ^{1}H NMR ($CDCl_3$): δ 6.24 (CH, d, 1 H, J_{P-H} = 2 Hz), 4 (-CH_2-P, d, J_{P-H} = 13 Hz), 2.32 (P-CH_2-CH_3, m, 6 H), 1.33 (P-CH_2-CH_3, dt, 9 H). ^{13}C NMR (CD_2Cl_2): δ 197 (CO, m), 77.31 (-C, s), 73.11 (-CH, s), 24 (-CH_2-P, d, J_{P-C} = 37 Hz), 12.1 (P-C-CH_3, d, J_{P-C} = 37 Hz), 5.78 (P-CH_2-C, d, J_{P-C} = 5 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 39.2 (s).

$[Co_2(CO)_6(CH{\equiv}CCH_2PPh_3)]BF_4$ (2b). This compound was prepared following the procedure described already, using 412 mg (1 mmol) of $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$ in 6 mL of CH_2Cl_2 and 262 mg (1 mmol) of PPh_3 in 9 mL of CH_2Cl_2. Addition of diethyl ether provided an orange-red compound. This complex was isolated, washed several times with diethyl ether, and recrystallized from dichloromethane/diethyl ether. Yield: 60% (400 mg). ^{1}H NMR ($(CD_3)_2CO$): δ 7.7-8.2 (-CH, aromatic, m, 15 H), 6.3 (CH, d, 1 H, J_{P-H} = 2 Hz), 5.78 (CH_2-P, d, 2 H, J_{P-H} = 15 Hz). ^{13}C NMR (CD_2Cl_2): δ 198 (CO, m), 135.90 (d, 133.82 (d), 130.86 (C, aromatic, d), 77.25 (-C, s), 74.15 (CH, s), 29.50 (CH_2-P, d, J_{P-C} = 42 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 20.55 (s).

$[Co_2(CO)_6(CH{\equiv}CCH_2Py)]BF_4$ (3). This compound was prepared by two methods using either (I) the carbenium ion as starting material, in a similar way as described above or (II) the sulfide derivatives. For method II, an excess of pyridine (2 mL) was added dropwise to a solution of complex **1b** (100 mg, 0.2 mmol) in 10 mL of dichloromethane and the reaction mixture was stirred for 30 min under argon. Addition of diethyl ether (10 mL) provided a bright red microcrystalline species. The compound **3** was separated and washed several times with diethyl ether. Recrystallization was from dichloromethane/diethyl ether. Yield: 60% (59 mg). ^{1}H NMR ($(CD_3)_2CO$): δ 8.8, 8.6, 8.13 (-CH, pyridine, t, 1 H t, 2 H, d, 2 H, J_{H-H} = 6 Hz), 6.9 (CH, s, 1 H), 6.3 (CH_2-Py, s, 2 H). ^{13}C NMR (CD_2Cl_2): δ 198 (CO, m), 147.11 (s), 145.03 (s), 129.12 (C_5H_5N, s), 88 (-C, s), 76 (-CH, s), 63.94 (CH_2-N, s).

$[Co_2(CO)_6(CH{\equiv}CCH_2OMe)]$[7] (4). **1a** (100 mg, 0.21 mmol) was dissolved in 10 mL of methanol, and the reaction was followed by thin-layer chromatography over silica plates, using a 50:50 ether/pentane solution as eluant. After 30 min, complex **1a** was transformed completely to $[(Co_2(CO)_6(CH{\equiv}CCH_2OMe)]$. ^{1}H NMR ($CDCl_3$): δ 6.06 (CH, s, 1 H), 4.61 (CH_2, s, 2 H), 3.50 (-O-CH_3, s, 3 H).

$[Co_2(CO)_6(CH{\equiv}CCH_2PhOMe)]$ (Para, 5a; Ortho, 5b). This reaction was carried out by following the method reported by Nicholas et al. and in the presence of an excess of anisole: (I) in CH_2Cl_2 or (II) in neat anisole. For method II, **1b** (350 mg, 0.7 mmol) was added to a Schlenk tube containing 5 mL of pure anisole. The orange-red suspension was stirred under argon for 24 h. At this stage the reaction was stopped and the filtrate was separated. The solvent was evaporated to give an oily residue. Extraction with diethyl ether, followed by chromatography on thin-layer silica plates using a 1:10 ether/pentane solution as eluant, provided compounds **5a** and **5b**. Yield: 40%.

The spectroscopic data for **5a** are as follows. ^{1}H NMR ($CDCl_3$): δ 7 (CH, aromatic, dd, 4 H, J_{H-H} = 7 Hz), 6.06 (CH, s, 1 H), 4.02 (-CH_2-PhOMe, s, 2 H), 3.7 (PhO-CH_3, s, 3 H).

The spectroscopic data for **5b** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.15 (CH, aromatic, m, 4 H), 6 (CH, s, 1 H), 4.11 (-CH_2-PhOMe, s, 2 H), 3.83 (PhO-CH_3, s, 3 H).

X-ray Crystallography. Complex **2a** was crystallized from acetone solution with ether as a cosolvent, by following the method of slow diffusion. The selected crystal was set up on an automatic four-circle diffractometer. Accurate unit cell dimensions and a crystal orientation matrix were obtained from least-squares refinements of the setting angle of 25 reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other pertinent information are summarized in Table I. Corrections were made for Lorentz and polarization effects. Computations were performed by using CRYSTALS[9] adapted for a MICROVAX II computer. Atomic form factors for neutral Co, C, P, B, F, and H atoms were taken from ref 10. The structure was solved by using SHELXS.[11] High thermal motion was initially observed for the ethyl groups. Further investigations revealed two orientations of 50% occupancy each for the three ethyl groups. The two disordered models are related to each other by a 17° rotation around the C(1)-P(1) bond. Disordered positions were also found for BF_4^- with eight F atoms around a B atom. Refinement was by block-approximation least-squares calculations with constraints[12,13] applied to the disordered models: for ethyl groups, (a) C-C = 1.50 ± 0.02 Å, (b) C-C-C = 109 ± 1°, and (c) difference in root-mean-square (rms) amplitude of vibration in the direction of the C-C bond of two bonded C atoms 0.000 ± 001 Å^2; for BF_4^-, (a) B-F = 1.4 ± 0.02 Å, (b) F-B-F = 109 ± 1°, and (c) difference in rms amplitude of vibration in the direction of the B-F bond 0.000 ± 0.01 Å^2. Hydrogen atoms were introduced in calculated positions. Their coordinates were calculated after each cycle. They were allocated an isotropic thermal parameter 20% higher than that of the carbon on which they are attached. Anisotropic temperature factors were introduced for all non-hydrogen atoms. The criteria for a satisfactory complete analysis were the ratio of the rms shift to standard deviation being less than 0.5 and no significant features in the final difference map. Atomic coordinates are given in Table II.

Table I. Crystal Data for **2a**

mol formula	$C_{15}H_{18}O_6PCo_2BF_4$	M_r	530
a, Å	10.212 (1)	cryst system	monoclinic
b, Å	15.007 (3)	space group	$P2_1/n$
c, Å	14.941 (3)	T, °C	20
β	104.94 (1)	λ	0.710 69
V, Å^3	2212 (8)	ρ(calcd), g·cm^{-3}	1.591
Z	4	μ(Mo Kα), cm^{-1}	16
transm coeff (max/min)	1.27/1.0	$R(F_o)$	0.0673
		$R_w(F_o)$	0.0658
max residual	0.24 e/Å^3		

Results

The sulfide complexes (**1a-d**) were prepared in good yield by treatment of the propargylic cationic complex $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$ with an excess of the corresponding sulfide ligands (SR_1R_2: $R_1 = R_2 =$ Me, **1a**; $R_1 = R_2 =$ Et, **1b**; $R_1 = R_2 =$ Pr^i, **1c**; $R_1 =$ Me, $R_2 =$ Et, **1d**) in dichloromethane. However for reasons of bulkiness or electronic delocalization, no sulfonium ion complex has been isolated with diphenyl sulfide. The phosphine derivatives (**2a,b**) however were obtained by using stoichiometric quantities of the starting materials. It is noteworthy that without the protecting $Co_2(CO)_6$ unit the propargylic sulfonium salts and the phosphonium salts isomerize in solution to give the corresponding allenes.[15,16]

The stable products were isolated as orange-red microcrystalline powders, by addition of diethyl ether solution, and characterized by infrared and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopies and microanalyses. As a general trend, the infrared spectra for the sulfide series (**1a-d**) and the phosphine derivatives (**2a,b**) show the presence of a strong band at ν_{B-F} 1070 cm^{-1}, corresponding to the free anion BF_4^-, and strong absorptions between 2035 and 2103 cm^{-1}, attributed to the terminal carbonyl stretching bands (see Table IV).

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Table II. Fractional Atomic Coordinates with Esd's in Parentheses and Equivalent Isotropic Thermal Parameters[a]

atom	x/a	y/b	z/c	U(eq), Å²
Co(1)	0.1905 (2)	0.8031 (1)	0.0101 (1)	0.0675
C(11)	0.042 (1)	0.8553 (9)	0.0288 (9)	0.0870
O(11)	-0.050 (1)	0.8899 (8)	0.0406 (8)	0.1260
C(12)	0.274 (1)	0.904 (1)	-0.0106 (9)	0.0895
O(12)	0.329 (1)	0.9672 (7)	-0.0194 (8)	0.1233
C(13)	0.121 (1)	0.751 (1)	-0.1023 (9)	0.0857
O(13)	0.078 (1)	0.7184 (8)	-0.1714 (7)	0.1187
Co(2)	0.3899 (2)	0.7057 (1)	0.0631 (1)	0.0690
C(21)	0.519 (1)	0.785 (1)	0.050 (1)	0.0904
O(21)	0.598 (1)	0.8345 (8)	0.044 (1)	0.1228
C(22)	0.370 (1)	0.629 (1)	-0.035 (1)	0.0887
O(22)	0.350 (1)	0.5813 (8)	-0.0929 (8)	0.1184
C(23)	0.494 (1)	0.635 (1)	0.148 (1)	0.0983
O(23)	0.560 (1)	0.5928 (8)	0.2048 (9)	0.1314
C(1)	0.125 (1)	0.6224 (7)	0.0997 (7)	0.0603
C(2)	0.214 (1)	0.6982 (8)	0.0919 (7)	0.0556
C(3)	0.283 (1)	0.7658 (7)	0.1366 (8)	0.0634
P(1)	0.0647 (3)	0.6204 (2)	0.2024 (2)	0.0692
C(4)	0.207 (2)	0.623 (1)	0.306 (1)	0.0825
C(5)	0.295 (2)	0.543 (1)	0.312 (2)	0.0860
C(6)	-0.031 (2)	0.517 (1)	0.196 (1)	0.0797
C(7)	-0.100 (2)	0.509 (1)	0.276 (1)	0.0916
C(8)	-0.042 (2)	0.719 (1)	0.194 (1)	0.0857
C(9)	-0.110 (2)	0.727 (1)	0.271 (1)	0.0969
C(41)	0.210 (3)	0.598 (2)	0.302 (2)	0.0783
C(51)	0.282 (4)	0.514 (2)	0.293 (3)	0.0831
C(61)	-0.066 (3)	0.534 (2)	0.187 (2)	0.0728
C(71)	-0.053 (4)	0.479 (2)	0.275 (2)	0.0749
C(81)	-0.002 (3)	0.727 (1)	0.230 (2)	0.0806
C(91)	-0.151 (3)	0.733 (2)	0.184 (3)	0.0915
B(1)	0.247 (1)	0.3642 (9)	0.083 (1)	0.1945
F(1)	0.167 (2)	0.434 (1)	0.050 (2)	0.1826
F(2)	0.168 (2)	0.291 (1)	0.046 (2)	0.1877
F(3)	0.363 (2)	0.352 (2)	0.062 (2)	0.2106
F(4)	0.272 (3)	0.356 (1)	0.175 (1)	0.1927
F(11)	0.146 (2)	0.369 (2)	0.125 (2)	0.1954
F(12)	0.292 (3)	0.286 (1)	0.063 (2)	0.1951
F(13)	0.352 (2)	0.421 (2)	0.125 (2)	0.1907
F(14)	0.214 (3)	0.407 (2)	0.002 (2)	0.2098

[a] $U(eq) = [U(11)\ U(22)\ U(33)]^{1/3}$.

Table III. Selected Interatomic Distances (Å) and Bond Angles (deg)[a]

Co(1)-C(11)	1.79 (1)	Co(2)-C(22)	1.83 (1)
Co(1)-C(12)	1.80 (1)	Co(2)-C(23)	1.78 (2)
Co(1)-C(13)	1.82 (1)	Co(2)-C(2)	1.96 (1)
Co(1)-Co(2)	2.465 (2)	Co(2)-C(3)	1.95 (1)
Co(1)-C(2)	1.97 (1)	C(21)-O(21)	1.11 (1)
Co(1)-C(3)	1.96 (1)	C(22)-O(22)	1.10 (1)
C(11)-O(11)	1.13 (1)	C(23)-O(23)	1.13 (2)
C(12)-O(12)	1.13 (1)	C(1)-C(2)	1.48 (1)
C(13)-O(13)	1.13 (1)	C(1)-P(1)	1.80 (1)
Co(2)-C(21)	1.82 (1)	C(2)-C(3)	1.32 (1)
C(12)-Co(12)-C(11)	96.6 (6)	C(23)-Co(2)-C(21)	98.7 (7)
C(13)-Co(1)-C(11)	100.8 (6)	C(23)-Co(2)-C(22)	96.5 (7)
C(13)-Co(1)-C(12)	106.8 (6)	C(2)-Co(2)-C(21)	142.3 (6)
Co(2)-Co(1)-C(11)	150.6 (4)	C(2)-Co(2)-C(22)	102.6 (5)
Co(2)-Co(1)-C(12)	99.6 (5)	C(2)-Co(2)-C(23)	102.8 (6)
Co(2)-Co(1)-C(13)	97.8 (5)	C(3)-Co(2)-C(21)	106.3 (5)
C(2)-Co(1)-C(11)	103.0 (5)	C(3)-Co(2)-C(22)	140.8 (5)
C(2)-Co(1)-C(12)	142.3 (5)	C(3)-Co(2)—C(23)	101.1 (6)
C(2)-Co(1)-C(13)	100.8 (5)	O(21)-C(21)-Co(2)	178.5 (14)
C(3)-Co(1)-C(11)	101.1 (5)	O(22)-C(22)-Co(2)	175.8 (13)
C(3)-Co(1)-C(12)	105.8 (5)	O(2)3-C(23)-Co(2)	176.7 (15)
C(3)-Co(1)-C(13)	137.9 (5)	P(1)-C(1)-C(2)	115.7 (8)
O(11)-C(11)-Co(1)	178.5 (13)	C(1)-C(2)-Co(1)	133.3 (7)
O(12)-C(12)-Co(1)	176.8 (14)	C(1)-C(2)-Co(2)	132.7 (8)
O(13)-C(13)-Co(1)	179.2 (13)	C(3)-C(2)-C(1)	144.5 (10)

[a] Esd's in parentheses refer to the last significant digit.

Discussion

Complexes **1b**, **2a**, and **3** display IR absorption bands for the terminal carbonyls, which are shifted to lower wavenumbers, when compared to the values of ν_{CO} reported for the carbenium ion compound. This may be explained by a decrease in the electrophilic character at the cobalt centers, and a consequent increase of the $d\pi_{Co} \rightarrow p\pi^*_{CO}$ donation. Moreover, the IR values seem to indicate that the complexation of the carbonium center ($-C-^+$) by a heteroatom generates a new complex where the charge density on the cluster moiety is between those of the dicobalt propargylic alcohol complex and the $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$ complex. The ^1H NMR spectra of this series show, by integration, the presence of 1 equiv of sulfide SR_1R_2, phosphine PR_3, or pyridine per 1 equiv of the coordinated propargylic moiety. However, the ^{13}C NMR spectra recorded for these complexes were the most informative (see Table V). By reference to chemical shifts reported by Nicholas et al. for the methylene group (C(1)) of the propargylic cationic complex, a significant upfield shift is observed for the series $[(Co_2(CO)_6(CH{\equiv}CCH_2Py)]BF_4$, $[(Co_2(CO)_6(CH{\equiv}CCH_2SR_1R_2)]BF_4$, and $[(Co_2(CO)_6(CH{\equiv}CCH_2PR_3)]BF_4$. This phenomenon is probably due to the electron-donating character of the pyridine, sulfide, and phosphine groups toward the α-methylene moiety ($-CH_2-$). In the case of phosphine derivative **2a**, the large difference in chemical shift ($\Delta\delta(C(1)) = 107-24 = 83$ ppm) is attributed to the high basicity and nucleophilicity of the PEt_3 ligand;[17] consequently the nature of the bonding between the heteroatom and the methylene group is most likely a "donor–acceptor" interaction.

Table IV. IR Values of the Carbonyl Bands for Dichloromethane Solutions of $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$, $[(Co_2(CO)_6(CH{\equiv}CCH_2OH)]$, and the Novel Series **1b**, **2a**, and **3**

compd	ν_{CO},[a] cm⁻¹	ref
$[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$	2130 (m), 2105 (s), 2085 (s)	21
$[(Co_2(CO)_6(CH{\equiv}CCH_2OH)]$	2090 (m), 2050 (s), 2025 (s)	21
$[(Co_2(CO)_6(CH{\equiv}CCH_2SEt_2)]BF_4$ (**1b**)	2103 (m), 2066 (s), 2035 (s)	this work
$[(Co_2(CO)_6(CH{\equiv}CCH_2PEt_3)]BF_4$ (**2a**)	2101 (m), 2062 (s), 2037 (s)	this work
$[(Co_2(CO)_6(CH{\equiv}CCH_2Py)]BF_4$ (**3**)	2103 (m), 2067 (s), 2025 (s)	this work

[a] m = medium, s = strong.

Table V. ^{13}C NMR Data for $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$, $[(Co_2(CO)_6(CH{\equiv}CCH_2OH)]$, and the Novel Series **1b**, **2a**, and **3**

compd	δ(C(1))[a]	δ(C(2))[a]	δ(C(3))[a]	ref
$[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$	107[b]	117	79.5	7
$[(Co_2(CO)_6(CH{\equiv}CCH_2OH)]$	63.5[b,c]	100	73	7
$[(Co_2(CO)_6(CH{\equiv}CCH_2SEt_2)]BF_4$ (**1b**)	45.1[c]	78.6	74.8	this work
$[(Co_2(CO)_6(CH{\equiv}CCH_2PEt_3)]BF_4$ (**2a**)	24[c]	77.3	73.1	this work
$[(Co_2(CO)_6(CH{\equiv}CCH_2Py)]BF_4$ (**3**)	63.94[d]	88	76	this work

[a] The carbon atoms were numbered following the same order as that indicated on the X-ray structure of complex **2a** (Figure 1). [b] Obtained at 20 MHz in SO_2 solution. [c] Obtained at 62.87 MHz in CD_2Cl_2 solution. [d] Obtained at 62.87 MHz in CD_3CN solution.

(i) Molecular Structure of 2a. The X-ray structure of **2a** consists of four discrete molecules of $[(Co_2(CO)_6(CH{\equiv}CCH_2PEt_3)]^+$ with BF_4^- as a counteranion. The ORTEP view of the cation with the labeling scheme is shown in Figure 1; selected intramolecular bond lengths and angles are presented in Table III. The cationic part of molecule **2a** consists of a quasi-tetrahedral Co_2C_2 core with the $-C{\equiv}C-$ bond of the acetylene in a perpendicular orientation at an angle of 81.57° relative to the Co–Co bond. The metal–metal bond length 2.479 Å conforms with previous literature values for a single Co–Co bond[18] and is in good agreement with the metal–metal distance reported for $PPh_3Co_2(CO)_5(CH{\equiv}CCH_2OH)$.[19] This suggests that the positive

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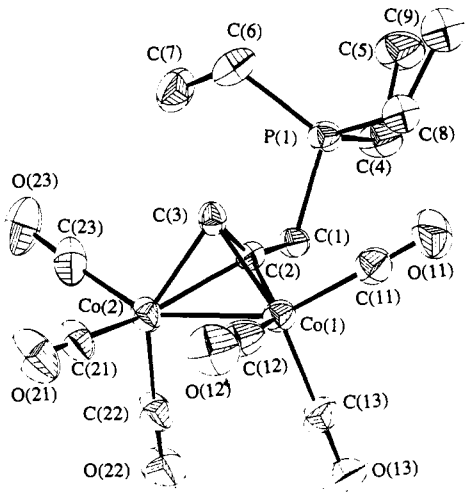


Figure 1. X-ray crystal structure of $[(Co_2(CO)_6(CH{\equiv}CCH_2PEt_3)]^+$ (**2a**).

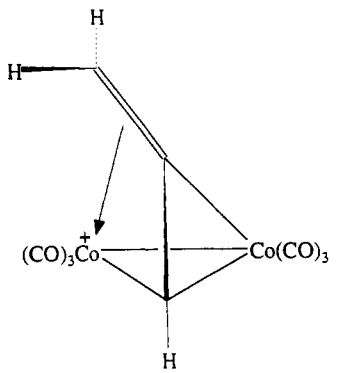
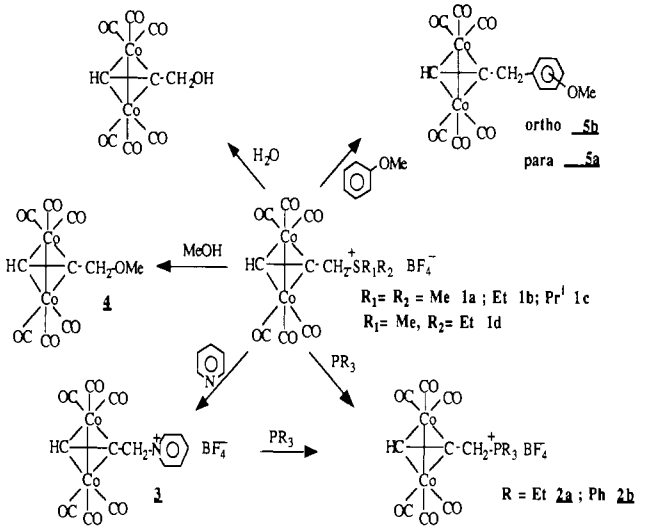


Figure 2. Proposed structure of the propargylic cationic complex.

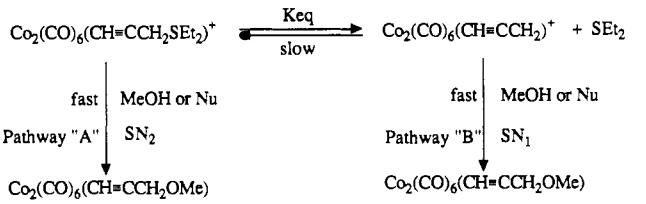
charge most likely resides on the phosphorus atom rather than the cobalt center. Indeed, the data obtained from the X-ray structure of complex **2a** exclude any direct stabilizing interaction between the cobalt centers and the α-methylene group, in contrast to the case of the carbenium ion complex $[(Co_2(CO)_6(CH{\equiv}CCH_2)]^+$, where the metal center stabilizes the carbenium atom (C^+) (see Figure 2). This type of stabilization can also be expected although to a lesser extent with the other heteroatoms S and N. This interaction is expected to induce new reactivity for these species. Finally, the coordination geometry around either Co(1) or Co(2) is a distorted octahedron described by the acetylene carbon atoms C(2) and C(3) and the three carbonyls C(11)O(11), C(12)O(12), and C(13)O(13) or C(21)O(21), C(22)O(22), and C(23)O(23) with the metal–metal bond occupying one apex of this octahedron.

(ii) Reactivity of the Sulfonium Derivatives. In order to study a possible modification of reactivity with respect to that of the metal-stabilized α-carbenium ion species, we have started investigating the behavior of the organometallic sulfonium derivatives (see Scheme I). Several reviews have reported the alkylating properties of the organic sulfonium salts.[20] In the presence of moisture these complexes gave the parent alcohol compound $[(Co_2(CO)_6(CH{\equiv}CCH_2OH)]$; however they show less tendency toward hydrolysis compared to the propargylic cation.[21] Furthermore, the novel series **1a–d** reacts rapidly with phosphines (PR_3; R = Ph, Et) to give the phosphonium derivatives **2a,b** in good yield, analogous to the direct reaction observed with the

Scheme I. Reactivity of the Sulfonium Derivatives with Various Nucleophiles



Scheme II. Proposed Mechanism for the Substitution Reactions



compound $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$. In particular, sulfide complex **1b**, when treated with an excess of pyridine in dichloromethane, gave a burgundy-colored species identified as the pyridinium salt $[(Co_2(CO)_6(CH{\equiv}CCH_2Py)]BF_4$ (**3**). The ^1H NMR (CD_3CN) spectrum of complex **3**, recorded at room temperature, exhibits a set of multiplets at 8.13 ppm (t, 2 H), 8.6 ppm (t, 1 H), and 8.8 ppm (d, 2 H), for the coordinated pyridine, in 1:1 ratio to the propargylic moiety. This stable compound reacted slowly with phosphines to give the corresponding derivatives **2a,b**; however it showed no reactivity toward methanol. On the contrary, the sulfide derivatives reacted rapidly and quantitatively with methanol at room temperature to give the methoxy derivative $[(Co_2(CO_6)(CH{\equiv}CCH_2OMe)]$ (**4**). Interestingly the complex $[(Co_2(CO)_6(CH{\equiv}CCH_2SPr^i_2)]BF_4$ (**1c**) was the most reactive among the sulfide derivatives toward methanol. This may be due to the bulkiness of the isopropyl group, which renders the diisopropyl sulfide a good leaving group, thus allowing a facile nucleophilic attack by MeOH on the α-methylene group adjacent to the cluster moiety. In addition, sulfide complex **1b** reacts with anisole, initially forming a suspension. After 1 day, a small amount of the starting material **1b** was recovered as an orange-red precipitate, while the filtrate upon work-up gave the two isomers **5a** and **5b**, respectively, the para and ortho derivatives in the ratio 2:1. This result is not without precedent; Nicholas et al. have reported the reaction of the propargylic carbenium ion complex $[(Co_2(CO)_6(CH{\equiv}CCH_2)_2]BF_4$ with anisole. The authors indicated that the reaction was over after 1 h and the two isomers **5a,b** were isolated in a comparable ratio.[2]

A crucial point in the above substitution reactions (Scheme I) is whether the reactive species is the sulfonium derivative **1b** or the propargylic cation complex $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$. In order to answer this question, we followed the reaction with MeOH by ^1H NMR spectroscopy as a function of methanol concentration. Three solutions of 5×10^{-2} mmol of complex **1b** in 0.5 mL of CD_2Cl_2 were prepared and 1, 2, and 3 equiv of MeOH were added, respectively; the reaction was monitored by ^1H NMR spectroscopy for 15 min. During this period, 15%, 20%, and 32% of methoxy derivative **4** were obtained relative to the starting material; hence the rate of formation of complex **4** is

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proportional to the concentration of MeOH supporting an S_N2 mechanism (see Scheme II, pathway "A"). Pathway "B" invokes an S_N1 mechanism where the rate of formation of $[(Co_2(CO)_6(CH{\equiv}CCH_2OMe)]$ (**4**) is dependent on the equilibrium constant K_{eq} and not on the methanol concentration. These results suggest that the route in which preliminary decomplexation of the sulfide ligand occurs to give the propargylic cation complex, which then reacts with methanol, is less favored.

Further reactivity studies with these organometallic species are currently under investigation, including reactions with other types of bases and nucleophiles.

Conclusion

The presence of heteroatoms, such as S, N, or P, has increased the stability of the propargylic cationic complex, while its reactivity toward nucleophiles may be selectively modified, as shown with the pyridinium complex compared to the sulfonium complexes. Moreover the reactivity of these latter complexes is attributed to the sulfide derivatives and not to the propargylic cation complex $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$. These substituted propargylic cationic compounds therefore have the potential for selective tuning toward nucleophilic attack, and further investigations of this reactivity are in progress.

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Supplementary Material Available: For **2a**, tables listing crystal data, bond distances and angles, and anisotropic thermal parameters (4 pages); a listing of observed and calculated structure factors for **2a** (8 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Synthesis and Structural Characterization of New Boron-Substituted Monocarbon Carborane Adducts: *nido*-8-L-7-$CB_{10}H_{12}$ (L = SMe_2, PPh_3)

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Introduction

Synthetic pathways have previously been reported for the formation of the carbon-substituted members of the *nido*-7-L-$CB_{10}H_{12}$ family of monocarbon carboranes.[1-5] Although two B-substituted analogues, *nido*-9-L-7-$[(CH_3)_3Si)_2CH]CB_{10}H_{11}$[6,7] (L = $(CH_3)_2S$ or $(C_6H_5)_3P$) and *nido*-2-$(CH_3)_2S$-9-C_6H_{11}-7-$[NH(t\text{-}C_4H_9)]CB_{10}H_{10}$[8] have been reported, no general procedures have been developed for the production of the parent B-substituted compounds. We report herein a simple synthesis of *nido*-8-$(CH_3)_2S$-7-$CB_{10}H_{12}$ (I), the structural characterization of its triphenylphosphine analogue *nido*-8-$(C_6H_5)_3P$-7-$CB_{10}H_{12}$ (II), and some initial chemical studies of I which indicate that it may serve as a useful starting material for the construction of a variety of monocarbon carborane clusters.

Experimental Section

The $CB_{10}H_{13}^-$ anion was prepared according to the published procedure.[4] Dimethyl sulfide, sodium hydride, and triphenylphosphine were purchased from Aldrich Chemicals and used as received. Cyclopentadienylnickel carbonyl dimer was obtained from Alfa Products/Ventron Division. Toluene and concentrated sulfuric acid were obtained from Baker Chemical Co. All reaction solvents were reagent grade and dried according to literature methods.

Proton NMR spectra at 200 MHz were obtained on a Bruker WP-200 Fourier transform spectrometer. Boron-11 NMR spectra at 160.5 MHz were obtained on a Bruker AM-500 Fourier transform spectrometer. All boron-11 chemical shifts are referenced to $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual solvent from the lock solvents used and are referenced to tetramethylsilane (0.0 ppm) with positive values indicating downfield shifts. Two-dimensional ^{11}B-^{11}B NMR experiments were conducted as described previously.[9]

High- and low-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer and/or a VG Micromass 7070H mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer.

8-$(CH_3)_2S$-7-$CB_{10}H_{12}$ (I). In a 200-mL Erlenmeyer flask were placed 0.5 g (2.4 mmol) of $[NMe_4]^+[CB_{10}H_{13}]^-$ and 60 mL of anhydrous dimethyl sulfide. To the resulting suspension was quickly added 10 mL of concentrated sulfuric acid, and the resulting two-phase solution stirred at room temperature for 2 h. The dimethyl sulfide layer was then extracted with methylene chloride. The oily solid that was obtained upon evaporation of the methylene chloride was washed with three 15-mL portions of cold water, filtered, and dried under vacuum at 60 °C for 12 h. The resulting white solid (0.33 g, 1.7 mmol, 71% yield) was identified as 8-$(CH_3)_2S$-7-$CB_{10}H_{12}$, mp 110-112 °C. Exact mass for $^{12}C_3{}^1H_{18}{}^{11}B_{10}{}^{32}S$: calcd, 196.206; found 196.206. ^{11}B NMR (160.5 MHz, C_6D_6 (*J*, assignment)): δ 0.32 (142 Hz, B5), -4.72 (s, B8), -8.37 (155 Hz, B3), -10.29 (100 Hz, B2 or B11), -10.97 (140 Hz, B2 or B11), -17.01 (129 Hz, B9), -23.46 (143 Hz, B1), -25.74 (122 Hz, B10), -29.00 (142 Hz, B4,6). ^1H NMR (200-MHz boron spin-decoupled, C_6D_6, d (intensity, assignment)): δ 3.21 (1, BH), 2.71 (2, BH), 2.26 (3, BH), 1.83 (1, CH), 1.61 (1, BH), 1.38 (3, CH_3S), 1.32 (3, CH_3S), -2.87 (1, BHB), -3.35 (1, BHB). IR (KBr pellet, cm^{-1}): 3020 s, 2925 m, 2560 sh, 2537 s, 1980 w, 1420 s, 1340 m, 1105 m, 1080 m, 1050 m, 1040 m, 1010 m, 980 s, br, 920 m, 880 w, 810 sh, 750 m, 710 m, 670 w, 629 m.

8-PPh_3-7-$CB_{10}H_{12}$ (II). In a one-piece 100-mL reaction flask equipped with a high-vacuum stopcock adapter, were placed 0.30 g (1.5 mmol) of I, 0.40 g (1.5 mmol) of triphenylphosphine, and 30 mL of dry benzene. The resulting solution was then heated in vacuo at reflux for 18 h with periodic degassings. The volatile components of the reaction were then removed in vacuo, and the resulting yellow solid was extracted with 5 mL of dry methylene chloride. Pentane (5 mL) was added and the solution cooled to -5 °C, which resulted in the precipitation of white crystals of 8-$(C_6H_5)_3P$-7-$CB_{10}H_{12}$ (II) [0.37 g (0.94 mmol), 63% yield; mp 233-234 °C]. Exact mass measurements for $^{12}C_{19}{}^1H_{27}{}^{11}B_{10}{}^{31}P$, $(P-2)^+$: calcd, 394.2624; found, 394.2688 (the parent ion was not observed). ^{11}B NMR (160.5 MHz, C_6D_6 (*J*, intensity)): δ 0.85 (139 Hz, 1), -8.05 (150 Hz, 2), -10.37 (130 Hz, 1), -11.99 (154 Hz, 1), -18.87 (135 Hz, 1), -21.03 (s, 1), -22.50 (121 Hz, 1), -25.22 (128 Hz, 1), -28.57 (146 Hz, 1). ^1H NMR (200 MHz, C_6D_6, d (intensity, assignment)): δ 7.57 (15, Ph), 1.83 (1, CH), -3.21 (2, BHB). IR (KBr, cm^{-1}): 3020 w, 2980 w, 2960 w, 2550 s, 1420 s, 1330 w, 1260 s, 1190 w, 1110 m, 1050 sh, 1020 w, 990 sh, 910 w, 890 w, 870 w, 850 w, 800 s, 750 m, 730 s, 700 m, 680 w, 650 m, 630 m, 610 m, 530 s, 500 sh, 480 m, 440 m, 400 s.

Thermolysis of 8-$(CH_3)_2S$-7-$CB_{10}H_{12}$. In a 100-mL one-neck round-bottom flask equipped with a high-vacuum stopcock adapter were placed 0.10 g (0.52 mmol) of I and 25 mL of dry toluene. The solution was heated at reflux for 25 h in vacuo with periodic removal of noncon-

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