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Triangulo Cluster Molecules of Cobalt(0) and Nickel(0) Containing Trimethylphosphine and Carbonyl Ligands: Syntheses, Properties, and X-ray Structures

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Trinuclear clusters $HCo_3(\mu\text{-}CO)_3(PMe_3)_6$ (1) and $Co_2Ni(\mu\text{-}CO)_3(PMe_3)_6$ (2) are synthesized in high yields from mononuclear precursors by thermal or photochemical activation. X-ray structural data of isostructural 1 and 2 show molecular cores of regular M_3 triangles. 1: trigonal, space group $R\bar{3}c$, $a = 10.685$ (2) Å, $c = 52.496$ (10) Å, and $Z = 6$. 2: trigonal, space group $R\bar{3}c$, $a = 10.689$ (1) Å, $c = 52.778$ (7) Å, and $Z = 6$. While the hydrogen atom of 1 was not located, a positional disorder of metal atoms in 2 gives rise to D_{3h} symmetry of the $M_3(CO)_3P_6$ skeleton in both structures. Calculations of the INDO/1 type support proposals of chemical bonding in 1 and 2.

Introduction

Cobalt and nickel form a variety of homonuclear clusters with carbonyl, isonitrile, and phosphine ligands. But there are very few examples of mixed Co,Ni clusters because a rational syntheses are still lacking.[1,2] In this contribution we describe rational, high-yield syntheses, properties, and X-ray structures of triangulo clusters $HCo_3(\mu\text{-}CO)_3(PMe_3)_6$ (1) and $Co_2Ni(\mu\text{-}CO)_3(PMe_3)_6$ (2).

Belonging to the same structural type (Figure 1), this pair of compounds can serve to demonstrate the different properties of mixed-metal clusters and homonuclear clusters because of an identical framework of phosphine and carbonyl ligands.

As first examples, 3 and 4 (Table I) were reported in 1969 by Pregaglia et al.[3] The X-ray structure of 3 was published in 1983 by Pino's group,[4] and a hydride ligand was then added on the basis of chemical reactions. Similar observations and mass spectrometry had suggested 5 to be a hydrido cluster $HCo_3(CO)_9$ in 1979.[5,6] To our knowledge, mixed Co,Ni clusters of this structural type (Figure 1) have not been described.[7]

Experimental Section

Standard vacuum techniques were used in manipulations of volatile and air-sensitive material. Microanalyses (C and H by combustion, metals by AAS) were obtained from Dornis & Kolbe, Microanalytical Laboratory, D-4330 Mülheim a.d. Ruhr, Germany. Decomposition temperatures were obtained from sealed capillaries under argon and are uncorrected. Starting materials were prepared by literature methods: PMe_3,[8] $Co_2(CO)_4(PMe_3)_4$,[9] $Co(C_2H_4)(PMe_3)_3$,[10] $Ni(CO)_2(PMe)_2$,[11] $Ni(CO)(PMe_3)_3$,[11] and $Co_2(CO)_2(PMe)_6$.[12] Other chemicals (Merck-Schuchardt) were used as purchased. Irradiation was carried out in quartz Schlenk flasks using a mercury lamp (Heraeus, 15 W). Infrared spectra were recorded on a Perkin-Elmer Type 397 spectrometer; ^1H-NMR spectra were obtained at 300 MHz (Bruker WM 300) from benzene solutions at 25 °C with external TMS as reference. X-ray structural measurements were performed at the University of Paderborn, Paderborn, Germany.

Preparations. Preparation of $HCo_3(\mu\text{-}CO)_3(PMe_3)_6$. Method a. $Co_2(CO)_4(PMe_3)_4$ (360 mg, 0.56 mmol) and $Co(C_2H_4)(PMe_3)_3$ (490 mg, 1.55 mmol) in 20 mL of toluene are irradiated in a 70-mL quartz tube (ϕ 30 mm) at a distance of 5 cm, which raised the temperature of the mixture to 80 °C. Within 4 h the dark green solution turned red-brown. Upon slow cooling to 20 °C, dark violet hexagonal crystals separated that were collected by decantation, washing with 5 mL pentane, and drying in vacuo (200 mg, 0.28 mmol, 38% based on carbon monoxide).

Table I. Triangulo Clusters $M^1(M^2)_2(\mu\text{-}CO)_3(L^1)_3(L^2)_3$

compd	M^1	M^2	L^1	L^2	ref
1	Co	Co	PMe_3	PMe_3	*a*
2	Ni	Co	PMe_3	PMe_3	*a*
3	Co	Co	CO	PPh_3	*b*
4	Co	Co	CO	P^nBu_3	*b*
5	Co	Co	CO	CO	*c*

[a] This work. [b] References 3 and 4. [c] References 5 and 6.

Method b. $Ni(CO)(PMe_3)_3$ (331 mg, 1.05 mmol) and $Co(C_2H_4)(PMe_3)_3$ (660 mg, 2.09 mmol) in 30 mL of toluene were irradiated for 3 h as above. Workup gave a 45% yield based on carbon monoxide.

Method c. $Co_2(CO)_2(PMe_3)_6$ (140 mg, 0.22 mmol) and $Co(C_2H_4)(PMe_3)_3$ (227 mg, 0.88 mmol) in 30 mL of toluene were irradiated for 3 h as above (48% yield based on carbon monoxide).

Dec pt: >150 °C. Anal. Calcd for $C_{21}H_{55}Co_3O_3P_6$ (M_r = 718.3): C, 35.11; H, 7.71; P, 25.87. Found: C, 35.27; H, 8.31; P, 24.69. MS: m/e 718 (M^+). ^1H NMR: $\delta(PMe_3)$ 1.18 ppm (s).

Preparation of $Co_2Ni(\mu\text{-}CO)_3(PMe_3)_6$ (2). Method a. $Co(C_2H_4)(PMe_3)_3$ (1.33 g, 4.2 mmol) and $Ni(CO)(PMe_3)_3$ (1.32 g, 4.2 mmol) in 10 mL of toluene are irradiated for 5 h, keeping the temperature of the solution below 50 °C. Slow cooling to 20 °C

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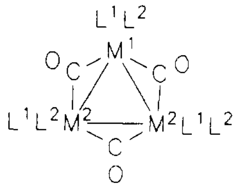


Figure 1. Important structural type of triangulo cluster.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 1

	x	y	z	U_{eq}^{a}
Co(1)	1308 (1)	0	2500	23 (1)
P(1)	2700 (1)	72	2814 (1)	34 (1)
C(1)	0	−2049 (4)	2500	30 (3)
O(1)	0	−3144 (3)	2500	48 (3)
C(2)	2577 (5)	−1612 (4)	2922 (1)	60 (3)
C(3)	4659 (4)	1247 (4)	2787 (1)	52 (3)
C(4)	2431 (5)	766 (5)	3115 (1)	63 (3)

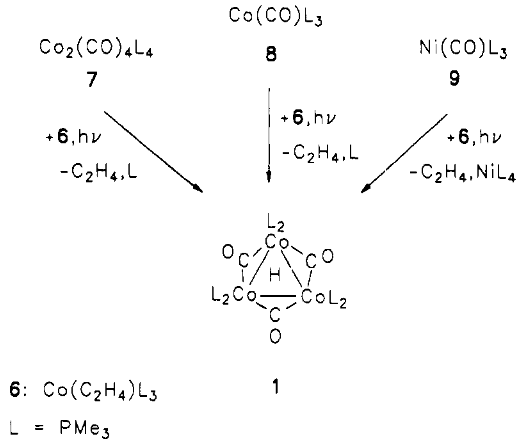
^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 2

	x	y	z	U_{eq}^{a}
M	1317 (1)	0	2500	23 (1)
P(1)	2703 (2)	68 (2)	2817 (1)	34 (1)
C(1)	0	−2030 (7)	2500	36 (3)
O(1)	0	−3142 (5)	2500	54 (3)
C(2)	2577 (7)	−1628 (6)	2925 (1)	64 (4)
C(3)	4668 (5)	1228 (6)	2787 (1)	58 (3)
C(4)	2430 (6)	774 (7)	3116 (1)	61 (4)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor (M = Co, Ni).

Scheme I. Photochemical Routes to 1 in Toluene



completes deposition of dark green hexagonal plates. The crystals are washed with 5 mL pentane and dried in vacuo (700 mg, 0.98 mmol, 70% based on carbon monoxide).

Method b. $Co(C_2H_4)(PMe_3)_3$ (1.85 g, 5.86 mmol) and $Ni(CO)_2(PMe_3)_2$ (780 mg, 2.93 mmol) are dissolved in 40 mL of pentane at −60 °C. The dark green mixture is allowed to warm to 20 °C and after 3 h turns red-brown. After 21 h under 1 bar of argon a dark green solid is isolated by decantation, washed with 20 mL of pentane, and dried in vacuo (1.18 g, 1.65 mmol, 85% yield based on carbon monoxide).

Dec pt: >150 °C. Anal. Calcd for $C_{21}H_{54}Co_2NiO_3P_6$ (M_r = 717.1): C, 35.17; H, 7.59; Co, 16.43; Ni, 8.18; P, 25.92. Found: C, 35.19; H, 7.42; Co, 15.41; Ni, 7.63; P, 25.11. MS (^{58}Ni): m/e 640 (M − PMe_3^+).

X-ray Crystal Measurement of 1. A red brown single crystal (0.45 × 0.51 × 0.62 mm) of 1 was sealed in a glass capillary under argon. Cell dimensions were obtained on a Nicolet R3m/V four-circle diffractometer (Mo Kα, graphite monochromator, l = 71.073 pm, μ = 1.71 mm^{-1}, $F(000)$ = 2256, T = 296 (1) K) using 25 reflections with $10° \leq 2\theta \leq 30°$: $C_{21}H_{55}Co_3O_3P_6$, M_r = 718.3, trigonal, $R\bar{3}c$ (No. 167), Z = 6; a = 10.685 (2) Å, c = 52.496 (10) Å, V = 5190.5 Å^3, d(calcd) = 1.379 g cm^{-3}. A total of 1568 intensities were measured (ω–2θ scan, scan rate 2.5°/min, $3° \leq 2\theta \leq 55°$, $0 \leq h \leq 13$, $0 \leq k \leq 13$, $0 \leq l \leq 68$, 3 standard reflections every 400 showing statistical deviations). After polarization and Lorentz corrections an empirical absorption correction (ψ scans, minimum/maximum transmissions 0.378/0.401) was introduced. Merging of reflections equivalent by symmetry (R_{int} = 0.020) gave a total of 1340 independent intensities and 948 with $F > 4\sigma(F)$.

Solution and Refinement of the Structure. The structure was solved by using direct and Fourier methods, with full-matrix least-squares refinement based on F and 52 parameters (SHELXTL-PLUS, Nicolet, 1988). Anisotropic refinement proceeded for non-hydrogen atoms (Table II), with H-atoms fixed in an ideal geometry with isotropic thermal parameters U_{iso} = 0.08 Å^2. Refinement converged to R = 0.038 and R_w = 0.032, where $1/w = \sigma^2(F) + 0.0001F^2$, S = 1.358, and $(\Delta/\sigma)_{max}$ = 0.001. A final difference map exhibited minimum/maximum residuals of −0.45/0.50 e Å^{-3}.

X-ray Crystal Measurement of 2. A dark green crystal (0.09 × 0.10 × 0.15 mm) of 2 was sealed in a glass capillary under argon. Cell dimensions were obtained as above (μ = 1.77 mm^{-1}) using 30 reflections with $10° \leq 2\theta \leq 25°$: $C_{21}H_{54}Co_2NiO_3P_6$, M_r = 717.1, trigonal, $R\bar{3}c$, Z = 6; a = 10.689 (1) Å, c = 52.778 (7) Å, V = 5222.2 Å,^{3} d(calcd) = 1.367 g cm^{-3}. A total of 4261 reflections were measured (ω–2θ scan, scan rate 3.5° min^{-1}, $3° \leq 2\theta \leq 55°$, $0 \leq h \leq 13$, $-13 \leq k \leq 13$, $0 \leq l \leq 68$) from which 701 were independent with $F > 4\sigma(F)$. Polarization and Lorentz corrections together with an empirical absorption correction (ψ scans, minimum/maximum transmissions 0.746/0.857) were introduced.

Solution and Refinement of the Structure. The structure was solved by using Patterson and Fourier methods, with full-matrix least-squares refinement of all non-hydrogen atoms (Table III) as above (SHELXTL-PLUS, Siemens, 1990). Refinement (55 parameters) converged to R = 0.0501 and R_w = 0.0336, where $1/w = \sigma^2(F) + 0.0001F^2$, S = 1.130, $(\Delta/\sigma)_{max}$ = 0.001, and there are maximum/minimum residuals of −0.66/0.54 e Å^{-3} in the final difference map. Refinement of metal positions gave no clear distinction between Co or Ni.

Results and Discussion

Both cluster compounds 1 and 2 are formed each in several smooth reactions by virtue of their low solubility. Separation from highly soluble mononuclear byproducts (Scheme I) is in no case a problem.

Photochemical activation is required in the formation of 1 in all three routes (Scheme I). Cobalt(0) or nickel(0) complexes may serve as sources of carbonyl ligands as long as the ratio Co/CO = 1 is maintained. Starting from 9 and 6 (Scheme I) with Co/CO = 2, no nickel is incorporated in the product. The reaction mixture deposits dark violet hexagonal plates that are very slightly soluble in pentane or ether and only a little soluble in benzene, toluene, or THF. Solutions are rapidly oxidized, while crystals may be safely handled in air for 2 min. Under argon slow decomposition starts above 150 °C.

With excess 9 in toluene under UV light the CoH moiety of 1 is replaced by Ni and 2 is formed in 70% yield. Surprisingly 2 is also formed as a green microcrystalline solid when 10 and 5 dissolved in pentane are allowed to react for 20 h at 20 °C in the dark (Scheme II). This material when dissolved in toluene or THF gives a red solution from which green hexagonal plates of 2 are grown. A red solid could be isolated by concentration of toluene solutions at 20 °C in vacuo with slight decomposition. The red color may be due to dissociation of phosphine in solution (Scheme II). With excess phosphine the red solutions of 2 in toluene or THF turn green, when the phosphine is removed in vacuo at 20 °C the green solution of 2 turns red. At temperatures below −78 °C the equilibrium

Scheme II. Syntheses of 2 in Pentane or Toluene

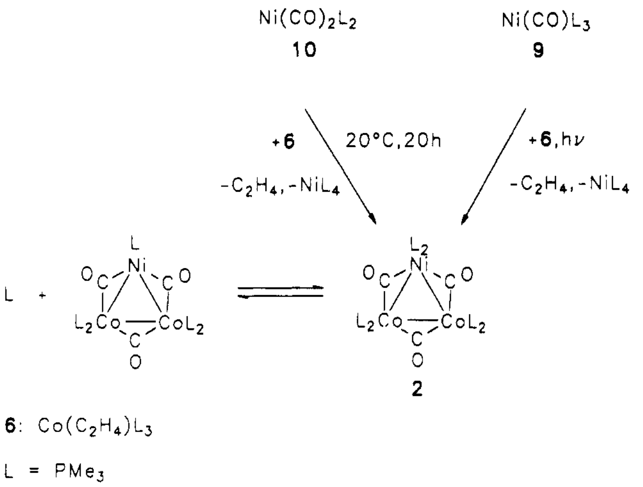


Table IV. Characteristic Infrared Bands (Nujol Mull, 4000–400 cm^{-1}) for 1 and 2

1	2	assgnt
2800 w	2800 w	ν(CH)
1934 w		ν(CoH)
1693 vs	1760 m	ν(CO)
1675 vs	1725 sh	
	1718 s	
	1703 sh	
	1675 vs	
542 w	538 m	δ(CoCO)
510 m		
484 w	475 w	ν(CoC)

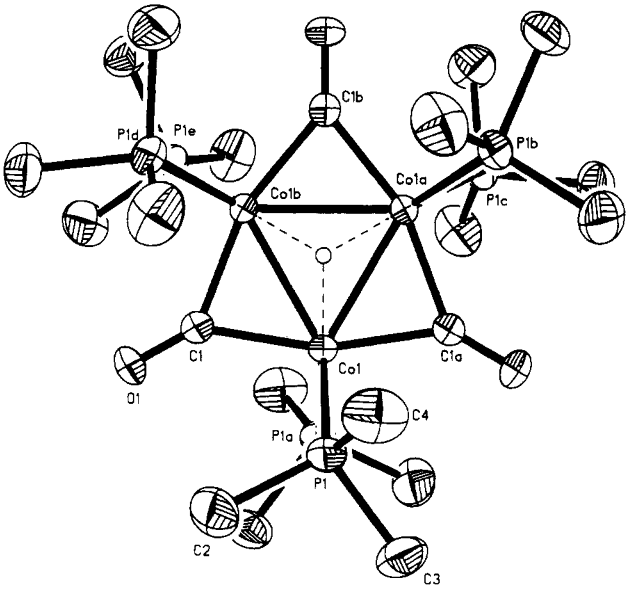


Figure 2. ORTEP drawing of 1.

of phosphine dissociation lies on the right side (Scheme II), visible by the green color of 2 in THF or toluene.

The solubility, thermal stability, and fast reaction of 2 with oxygen almost perfectly match those of 1.

Infrared spectra of 1 and 2 show the expected bands of coordinated phosphine ligands and only a few CO and CoC bands due to an effective D_{3h} symmetry of the $M_3(CO)_3P_6$ skeleton that is only slightly disturbed in 2 (Table IV).

In the mass spectrum of 1 CoH fragments have higher intensities than those without additional hydrogen atoms, while Co_2Ni fragments of 2 with the correct isotopic pattern outnumber those containing Co_2 and Ni or Co. The highest m/e intensity for 2 corresponds with $M^+ - PMe_3$.

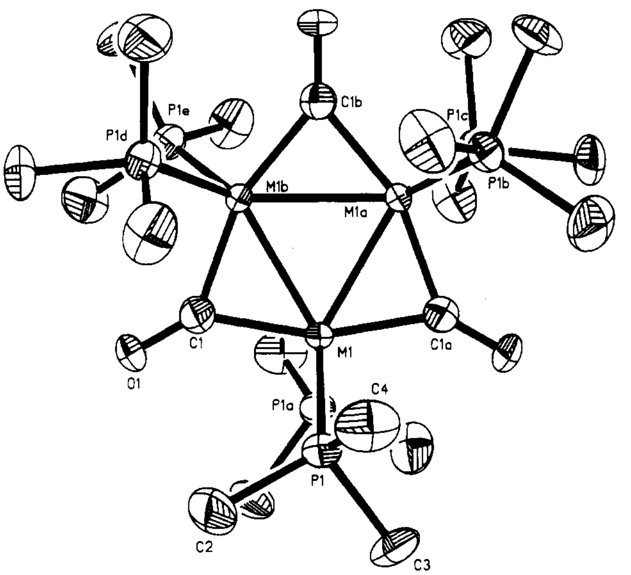


Figure 3. ORTEP drawing of 2 without hydrogen atoms (M(1a) = M(1b) = Co; M(1) = Ni).

Table V. Bond Lengths (Å) and Angles (deg) for 1

Co(1)–Co(1A)	2.421 (1)	Co(1)–P(1)	2.197 (1)
Co(1)–C(1)	1.920 (5)	P(1)–C(2)	1.827 (5)
P(1)–C(3)	1.830 (5)	P(1)–C(4)	1.826 (6)
C(1)–O(1)	1.170 (7)		
Co(1A)–Co(1)–Co(1B)	60.0 (1)	P(1)–Co(1)–Co(1B)	125.9 (1)
C(1)–Co(1)–Co(1A)	110.9 (2)	Co(1)–P(1)–C(2)	118.9 (2)
Co(1)–P(1)–C(3)	119.1 (2)	Co(1)–P(1)–C(4)	114.9 (3)
P(1)–Co(1)–C(1)	97.7 (2)	C(1)–Co(1)–C(1A)	161.9 (3)
Co(1)–C(1)–Co(1B)	78.1 (2)	Co(1)–C(1)–O(1)	140.9 (5)
C(2)–P(1)–C(3)	101.2 (4)	C(2)–P(1)–C(4)	100.7 (4)
C(3)–P(1)–C(4)	98.6 (3)		

Table VI. Bond Lengths (Å) and Angles (deg) for 2

M–M	2.438 (2)	M–P(1)	2.211 (2)
M–C(1)	1.906 (6)	P(1)–C(2)	1.840 (7)
P(1)–C(3)	1.835 (5)	P(1)–C(4)	1.834 (7)
C(1)–O(1)	1.189 (9)		
M–M–M	60.0 (1)	M–M–P(1)	125.5 (1)
M–M–C(1)	110.2 (3)	M–P(1)–C(2)	119.0 (4)
M–P(1)–C(3)	118.6 (4)	M–P(1)–C(4)	114.9 (4)
P(1)–M–C(1)	98.0 (2)	C(1)–M–C(1)	160.5 (4)
M–C(1)–M	110.2 (4)	M–C(1)–O(1)	140.2 (6)
C(2)–P(1)–C(3)	100.8 (3)	C(2)–P(1)–C(4)	101.0 (3)
C(3)–P(1)–C(4)	99.2 (3)		

Table VII. Metal to Metal Bonds and Angles between Terminal Ligands and the M_3 Plane

triangulo clusters	*d*(MM) (pm)	MMP (deg)	MMC (deg)
$HCo_3(CO)_3(PMe_3)_6$ (1)	242.1 (1)	125.9 (1)	
$Co_2Ni(CO)_3(PMe_3)_6$ (2)	243.8 (2)	125.5 (1)	
$HCo_3(CO)_6(PPh_3)_3$ (3)[a]	247.3 (3)	121.30/	128.22/
	245.3 (3)	120.61	126.29
	249.0 (3)	123.85/	121.31/
		118.80	122.80
		131.65/	118.79/
		125.92	123.67
$HCo_3(CO)_9$ (5)[b]	245.9 (8)	c	c

[a] Reference 4. [b] Reference 5. [c] Not given.

Molecular Structure and Bonding in 1 and 2. Both structures are built up from trinuclear cluster entities (Figures 2 and 3). The cores of the isolated molecules are regular triangles of metal atoms. The metal to metal bond (Table V) in 1 is shorter than in 2 (Table VI), and both values fall below those reported for CO-richer triangulo

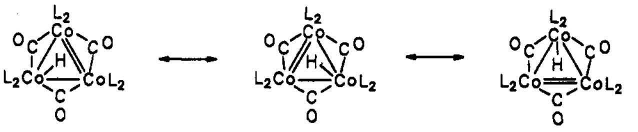


Figure 4. Valence bond description of bonding in 1.

Table VIII. Electronic Characteristics of $M^1M_2^2(CO)_3(PMe_3)_6^q$ Clusters Obtained by the QR/INDO/1 Method[a]

		Cluster		
M^1	Co	Co	Co	Ni
M^2	Co	Co	Co	Co
q	0	+1	−1	0
m	2	1	1	1
		E^b (eV)		
	0.00	−7.66	−7.71	−257.53
		Charges (−e)		
M^1	−0.57	−1.01	−1.07	−0.85
M^2	−1.08 (2×)	−1.01 (2×)	−1.04 (2×)	−1.01 (2×)
$(C{=}O)_3$	+1.59	+1.70	+1.56	+1.46
P_6	+1.80	+2.18	+2.20	+2.06
		Spin Density		
M^1	+0.89			
M^2	−0.11			
	+0.30			
$(C{=}O)_3$	−0.26			
		Wiberg (Bond Strength) Indices (Averaged)		
M^1–M^2	0.65 (2×)	0.66 (2×)	0.69 (2×)	0.66 (2×)
M^2–M^2	0.64	0.66	0.67	0.68
M^1–$C_{C=O}$	0.53 (2×)	0.65 (2×)	0.67 (2×)	0.59 (2×)
M^2–$C_{C=O}$	0.62 (4×)	0.66 (4×)	0.66 (4×)	0.66 (4×)
C–O	2.05 (3×)	2.08 (3×)	2.01 (3×)	2.02 (3×)
M^1–P	0.32 (2×)	0.38 (2×)	0.33 (2×)	0.39 (2×)
M^2–P	0.35 (4×)	0.38 (4×)	0.35 (4×)	0.38 (4×)

[a] q = the total charge of the complex; m = spin multiplicity. [b] Related to the total energy of neutral $Co_3(CO)_3(PMe_3)_6$.

clusters (Table VII) and that of cobalt metal (d(CoCo) = 250.6 pm[13]).

A diamagnetic behavior is expected for 2, but the core of non-hydrogen atoms in 1 should provide at least one unpaired electron. Although residual electron densities in the final difference map do not support its presence, a central bonding situation inside the D_{3h} core seems likely giving a total of 46 valence electrons as in carbonyl compounds 3 and 5. A valence bond representation of the bonding links the short CoCo distance with some double-bond character in a set of three equivalent resonance formulas, where each metal atom attains an 18-electron valence shell (Figure 4).

Either rapid fluctuation of bonds between tautomers or hydrogen tunneling would be consistent with overall D_{3h} symmetry and time-averaged μ_3-H coordination (Figure 2).

The observed D_{3h} molecular symmetry of 2 seems to be more a result of orientational disorder of the Co_2Ni triangles than of insufficient resolution of X-ray data. A 46-electron count of the cluster valence electrons is complete without a hydride ligand.

QR/INDO/1 Calculations on Triangular Cluster Geometries. The electronic structures of $^m[Co_3(CO)_3(PMe_3)_6]^q$ (q = 0, +1, −1; m = spin multiplicity), $HCo_3(CO)_3(PMe_3)_6$ with various H locations, and $Co_2Ni(CO)_3(PMe_3)_6$ clusters have been studied by the nonempirical quasi-relativistic QR/INDO/1 method.[14] According to our results a neutral complex $Co_3(CO)_3(PMe_3)_6$ is only slightly less stable than a complex ion (Table VIII).

Table IX. Electronic Characteristics of $HCo_3(CO)_3(PMe_3)_6$ Clusters Obtained by the QR/INDO/1 Method

	model[a]			
	A	B	C	D
		Energy Difference		
E^b (eV)	−7.73	−2.43	−0.83	−16.58
		Charges (−e)		
Co	−1.04 (3×)	−1.06 −1.08 (2×)	−1.05 −1.10 (2×)	−1.00 (3×)
$(C{=}O)_3$	+1.50	+1.54	+1.48	+1.50
H_{centr}	+0.48	+0.52	+0.52	+0.35
		Wiberg (Bond Strength) Indices (Averaged)		
Co–Co	0.63 (3×)	0.62 (3×)	0.61 0.65 (2×)	0.64 (3×)
Co–$C_{C=O}$	0.62 (6×)	0.61 (4×) 0.66 (2×)	0.54 (2×) 0.64 (4×)	0.63 (6×)
C–O	2.08 (3×)	1.96 2.08 (2×)	1.87 2.07 (2×)	2.07 (3×)
Co–P	0.34 (6×)	0.37 (2×) 0.34 (4×)	0.38 (2×) 0.34 (4×)	0.36 (3×)
Co–H	0.23 (3×)	0.07 0.26 (2×)	0.02 0.17 (2×)	0.21 (3×)
$C_{C=O}$–H	0.01 (3×)	0.28 0.04 (2×)	0.29 0.01 (2×)	0.21 (3×)

[a] Models are as follows: (A) H is in the center of the Co_3 triangle ($d_{Co-H} = 1.4 \times 10^{-10}$ m). (B) H is in the center of the Co–Co bond ($d_{Co-H} = 1.21 \times 10^{-10}$ m). (C) H is in the center of the Co–$C_{C=O}$–Co triangle ($d_{H-C} = 1 \times 10^{-10}$ m). (D) H is 1.3×10^{-10} m above the center of the Co_3 triangle ($d_{Co-H} = 1.9 \times 10^{-10}$ m). [b] Related to the total energy of neutral $Co_3(CO)_3(PMe_3)_6$.

$$^1[Co_3(CO)_3(PMe_3)_6]^- \approx {}^1[Co_3(CO)_3(PMe_3)_6]^+ > {}^2[Co_3(CO)_3(PMe_3)_6]$$

The unpaired electron of the uncharged system is located predominantly at Co. As the spin density is concentrated in the center of the cluster, the steric factors render intermolecular spin interactions improbable. Relatively high electron density is concentrated at the Co atoms. The Co–Co bond strength is comparable with that of Co–$C_{C=O}$. Wiberg (bond strength) indices indicate CO double bonds. The electronic structures of all the systems considered are very similar.

Replacing one Co by a Ni atom leads to minimal changes in electronic structure (Table VIII). Our calculations give a slightly higher electron density at the Ni atom and a lower density at the carbonyl groups.

Assuming a high similarity for the Co_3 and $NiCo_2$ complexes, the total energies (Table VIII) indicate an order of stabilities

$$^2Co_3(CO)_3(PMe_3)_6 < {}^1Co_2Ni(CO)_3(PMe_3)_6$$

According to our calculations (Table IX), the additional H atom in $HCo_3(CO)_3(PMe_3)_6$ is most probably located 1.3 × 10^{-10} m over the center of the Co_3 triangle (model D). This atom causes no significant changes of electronic structure but accepts a charge of 0.5–0.7 electron. If this atom cannot be observed by X-ray diffraction, either hydrogen migration between stable configurations or positional disorder in the crystal is possible. Our results indicate a very low energy gradient for the D model. For example, an increase in energy of 0.5 eV over the minimum is connected with 0.6 × 10^{-10} m uncertainty of H localization. Consequently, in this case the H electron density could not be observed even in precise x-ray experiments at low temperatures.

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The relative thermodynamic stabilities of $^2Co_3(CO)_3(PMe_3)_6$ and $^1HCo_3(CO)_3(PMe_3)_6$ complexes may be connected by an equilibrium

$$^2H + {}^2Co_3(CO)_3(PMe_3)_6 \rightleftharpoons {}^1HCo_3(CO)_3(PMe_3)_6$$

Our results (Table IX) indicate that only the D model of $^1HCo_3(CO)_3(PMe_3)_6$ is significantly more stable than $^2Co_3(CO)_3(PMe_3)_6$.

Conclusions

Formation of triangulo clusters of cobalt and nickel in directed syntheses may be initiated photochemically or thermally depending on the reactants. For the heteronuclear species **2** a unique feature emerges: If two mononuclear complexes, **6** and **10**, each perfectly stable at room temperature, are brought together in a hydrocarbon solvent, they undergo a spontaneous condensation reaction to form the triangulo cluster exclusively.

1 and **2** are not cleaved by phosphine ligands and may be recrystallized without decomposition. However, a 46-electron count is maintained together with unsaturation and high reactivity. The structures of **1** and **2** show tight metal to metal bonds involving CoH or Ni fragments. **1** and **2** also serve to demonstrate the differences in chemical properties of two isoelectronic triangulo clusters.

1 appears to have a pseudo-D_{3h} core that is mainly held together by carbonyl bridges. If allowance is made for some out of plane CoH stretching, its center is the most probable hydrogen position. As a result of molecular dynamics such as hydrogen tunneling, the hydride ligand resides at both sides of the Co_3 triangle.

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Supplementary Material Available: Listings of crystallographic details, atomic positional parameters, anisotropic thermal parameters, and hydrogen positional and thermal parameters for 1 and 2 (3 pages). Ordering information is given on any current masthead page.

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Trinuclear and Dinuclear Fluorinated Ferroles by Cluster Rearrangement and Degradation Reactions

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Thermolysis of the diferraallyl clusters $Fe_3(CO)_8(\mu_3\text{-}CF)(\mu_3\text{-}CFCRCR')$ (**1a–d**) (**a**, R = R′ = H; **b**, R = R′ = CH_3; **c**, R = CH_3, R′ = C_6H_5; **d**, R = H, R′ = CH_3) in hexane yields the isomeric trinuclear ferroles $Fe_2(CO)_8(FeCFCRCR'CF)$ (**2a–d**) and $Fe_2(CO)_8(FeCFCFCRCR')$ (**3a–c**) and the corresponding dinuclear species $Fe(CO)_6(FeCFCRCR'CF)$ (**4a–d**) and $Fe(CO)_6(FeCFCFCRCR')$ (**5a–c**), respectively. The ratio of the products and small amounts of minor products depends on the substituents. The structures of $Fe_2(CO)_8(FeCFCHCHCF)$ (**2a**), $Fe_2(CO)_8(FeCFCFCHCH)$ (**3a**), and $Fe_2(CO)_8(FeCFCCH_3CC_6H_5CF)$ (**2c**) have been established by X-ray crystal structure determinations: **2a**, orthorhombic, *Pcab*, $a = 11.416$ (4) Å, $b = 15.748$ (4) Å, $c = 16.129$ (5) Å, $R = 0.040$, $R_w = 0.040$; **3a**, orthorhombic, *Pnma*, $a = 11.524$ (9) Å, $b = 10.994$ (9) Å, $c = 11.42$ (2) Å, $R = 0.040$, $R_w = 0.041$; **2c**, monoclinic, $P2_1/c$, $a = 18..214$ (6) Å, $b = 7.035$ (3) Å, $c = 17.845$ (6) Å, $\beta = 117.37$ (3)°, $R = 0.105$, $R_w = 0.080$.

Introduction

Ferroles have been first isolated and characterized among the complicated mixture of products obtained by the reaction of dodecacarbonyltriiron and alkynes.[1] Many dinuclear[2] and trinuclear[3] ferroles have been synthesized. However, only one fluorinated ferrole, which is formed in a unknown way from $Fe(CO)_5$ and $CFBr_3$,[4] has been reported thus far, whereas the second example[5] has proved to the erroneous.[6] Difluoroethyne cannot be used as a starting material due to its extreme instability,[7] and only two difluoroethyne complexes have been reported thus far, which have been prepared in an indirect way.[8]

Mathieu et al. reported the formation of ferroles on the thermal reaction of $Fe_3(CO)_9(\mu_3\text{-}CCH_3)$ $(\mu_3\text{-}COC_2H_5)$ with alkynes.[9] The presence of several isomers has been explained by a complicated mechanism, which postulated the formation of intermediate diferraallyl clusters. However, on the photolytic reaction of $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ with alkynes we obtained diferrallyl clusters in a very regioselective reaction.[10] In the single case of the phosphaalkyne $t\text{-}C_4H_9\text{–}C{\equiv}P$ a phosphaferrole type cluster was obtained.[11]

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