Synthesis, Structure, and Magnetic Properties of Low-Valent Triangulo Cobalt−Hydride Clusters $[XCo_3(\mu\text{-}CO)_3(PMe_3)_6]$

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Syntheses and properties of low-valent clusters $[X\{Co(\mu\text{-}CO)(PMe_3)_2\}_3]$, X = none (**1**), H (**2**), and H_3 (**3**), are reported. All solids are isostructural as explicitly shown by single-crystal structure data. The molecular structures of $C_{21}H_{54}Co_3O_3P_6$ **(1)** and $C_{21}H_{57}Co_3O_3P_6$ **(3)** contain central Co_3 units which form perfect equilateral triangles with Co−Co distances of 2.4055(5) and 2.432(1) Å, respectively. Both compounds crystallize in trigonal space group $R\bar{3}c$, with $Z = 6$: **1**, $a = 10.678(1)$ Å, $c = 52.298(11)$ Å; **3**, $a = 10.679(2)$ Å, $c = 52.729(12)$ Å. Compounds **1** and **2** form a continuous range of solid solutions. Powder samples exhibit molecular paramagnetism of different extent: At 298 K the effective magnetic moments for **1**−**3** are $\mu_{eff}/\mu_B = 1.9$, 3.1, and 2.7, respectively. The magnetic behavior could be rationalized in terms of the Curie−Weiss law for a one electron system **(1)** and two electron system (**2**). The two electron approximation has been discussed as well for **3** above 6.2 K. A description of the scope of exchange coupling is presented for **1**.

Investigation of metal clusters is interesting, even fascinating, from the view-point of structural chemistry, magnetochemistry, spectroscopy, and general chemistry. These systems, particularly low-valent cobalt clusters, are also promising for homogeneous catalysis.

There are only a few examples of low-valent tricobalt clusters quoted in the literature. Among them the following members span the series of *triangulo*-tris(μ-carbonyl)hexakis(trimethylphosphane)tricobalt clusters $[X\{Co(\mu\text{-}CO)(PMe_3)_2\}_3]$: X = none (**1**), H (**2**), and H_3 (**3**). The X-ray structure determination for **2** confirmed a perfect equilateral triangle formed by three Co atoms.[1]

The first member shows an odd number of electrons, while the other members possess an even number of electrons. Thus the first cluster must be an open shell system, but the clusters **2** and **3** may exist in low-spin as well as high-spin states. Good argument for the latter is that the complexes exhibit either D_{3h} or C_{3v} symmetry and doubly degenerate levels (e′ or e″) appear within their irreducible representations.

Methods

Starting Material. Standard high-vacuum techniques were used in handling volatile and air-sensitive materials.[1] Starting complexes $[CoD(PMe_3)_4]$, $[Co(olefin)(PMe_3)_3]$ and $[Co_2(CO)_4(PMe_3)_4]$ were prepared by published procedures.[2−5]

Analyses. Microanalyses were carried out by Dornis & Kolbe, microanalytical laboratory, Mülheim, FRG. Infrared spectra (4000−400 cm^{-1}), as obtained from Nujol mulls between KBr windows, were recorded on a Perkin-Elmer Model 397 spectrophotometer. Mass spectra were recorded on a Varian MAT Model 311 A spectrometer equipped with an EFD source and SS 100 data system. Decomposition temperatures were determined in open glass capillaries on a Büchi Model 510 apparatus and are uncorrected.

Physical Measurements. Magnetic susceptibility measurements were carried out[6] for **1**−**3** in the temperature range of 4.2−300 K using a Faraday-type magnetic balance at the applied field of $B = 1.56$ T. The molar susceptibility was corrected for diamagnetism using the set of Pascal constants,[7] which yields the correction $\chi_{dia} = -5.516 \times 10^{-9}$ m^3 mol^{-1}. No constitutive corrections have been taken into account either for the Co_3 ring or for the three bridging carbonyl units as those data appear to be absent in the literature. The experimentally determined values for PMe_3 (−0.462), CO (−0.123), and Co (−0.226) yield $\chi_{dia} = -3.823$ (in units of 10^{-9} m^3 mol^{-1}).[8]

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Table 1. Crystal Data, Data Collection, and Refinement of Structures **1** and **3**

	1	**3**
formula	$C_{21}H_{54}Co_3O_3P_6$	$C_{21}H_{57}Co_3O_3P_6$
fw	717.25	719.3
space group	$R\bar{3}c$	$R\bar{3}c$
a, Å	10.678(1)	10.679(2)
c, Å	52.298(11)	52.729(12)
γ, deg	120	120
V, Å^3	5164(1)	5208(2)
Z	6	6
d(calc), g cm^{-3}	1.384	1.376
μ, mm^{-1}	1.72	1.71
T, °C	293	293
λ, Å	0.710 73	0.710 73
R1/wR2,[a] %	2.25, 4.94	2.41, 5.71

[a] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]^2]^{1/2}$. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

Table 2. Atomic Coordinates ($\times 10^4$ Å) and Equivalent Isotropic Displacement Parameters ($\times 10^3$ Å^2) for **1** and **3**

	x	y	z	U(eq)
		Complex **1**		
Co(1)	1301(1)	0	2500	25(1)
P(1)	2701(1)	73(1)	2813(1)	35(1)
C(1)	0	−2033(2)	2500	32(1)
O(1)	0	−3145(2)	2500	54(1)
C(11)	4660(2)	1235(2)	2786(1)	57(1)
C(12)	2422(3)	770(3)	3113(1)	63(1)
C(13)	2583(3)	−1614(2)	2920(1)	62(1)
		Complex **3**		
Co(1)	1315(1)	0	2500	22(1)
P(1)	2699(1)	70(1)	2816(1)	33(1)
C(1)	0	−2043(2)	2500	36(1)
O(1)	0	−3149(2)	2500	67(1)
C(11)	4655(2)	1239(3)	2786(1)	56(1)
C(12)	2431(3)	765(3)	3115(1)	62(1)
C(13)	2587(3)	−1616(3)	2921(1)	63(1)
H(1)	0	0	2684(9)	80

Sample **3** was reinvestigated using an alternating current (AC) susceptometer (LakeShore, Model 7221) in the temperature range 3.8−123 K. The field parameters were $H_{AC} = 800$ A m^{-1}, $H_{DC} = 800$ A m^{-1}, and $f = 222.2$ s^{-1}. The signal of the free sample holder was subtracted during the data analysis.

X-ray Crystallography. A summary of crystal data and structure refinement on **1** and **3** is given in Table 1. The data sets were collected on a Siemens R3m/V diffractometer, $\omega - 2\theta$ scan mode, graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Variable parameters were used in the full-matrix least-squares refinement on F^2.[9] Methyl hydrogens were refined at idealized positions with a "riding" model. The final atomic coordinates are displayed in Table 2.

Preparations and Reactions. ***triangulo*-[$Co_3(\mu$-CO$)_3(PMe_3)_6$] (1).** A mixture of [$Co(C_2H_4)(PMe_3)_3$] (1.35 g, 4.28 mmol) and [$Co_2(CO)_4(PMe_3)_4$] (1.14 g, 2.13 mmol) in 50 cm^3 of toluene was kept at 80 °C for 4 days.[10] After slow cooling to 20 °C black crystals were isolated by decantation and washing with pentane; yield 1.04 g, 51%.

Anal. Calcd for $C_{21}H_{54}Co_3O_3P_6$: C, 35.16; H, 7.59; P, 25.91. Found: C, 35.03; H, 7.51; P, 25.76. IR (2000−1600 cm^{-1}): KBr disk, 1675 vs, ν(CO); Nujol, 1700 s, 1685 vs, 1660 s, ν(CO).

***triangulo*-[$HCo_3(\mu$-CO$)_3(PMe_3)_6$] (2).** [$CoH(PMe_3)_4$] (2.04 g, 5.60 mmol), [Co(cyclo-C_5H_8)$(PMe_3)_3$] (0.99 g, 2.80 mmol), and [$Co_2(CO)_4(PMe_3)_4$] (2.25 g, 4.20 mmol) in 40 cm^3 of toluene were kept at 100 °C for 9 d. At 20 °C a black solid was isolated by decantation and washing with two 20 cm^3 portions of ether. Drying in vacuo gave shiny black crystals (2.41 g, 60% based on [$CoH(PMe_3)_4$]), dec pt >150 °C. The IR spectrum (Nujol mull) was identical with that of **1**.

Table 3. Reaction of **2** with Protic Acids

2	HA	THF	yield of **3**
	PhCOOH		
0.37 g	0.064 g	50 cm^3	0.18 g
0.52 mmol	0.52 mmol		48%[a]
0.40 g	0.36 g	80 cm^3	0.36 g
0.56 mmol	16.7 mmol		89%
0.74 g	0.25 g	150 cm^3	0.72 g
1.01 mmol	2.06 mmol		97%
	CH_3COOH		
0.41 g	0.034 g	50 cm^3	0.20 g
0.57 mmol	0.57 mmol		49%[b]
	$(CH_3)_3COH$		
0.28 g	0.10 cm^3	50 cm^3	0.22 g
0.39 mmol	11.6 mmol		78%
	$(CH_3)_2CHOH$		
0.32 g	0.44 cm^3	60 cm^3	0.29 g
0.45 mmol	13.3 mmol		89%

[a] 96% based on PhCOOH. [b] 98% based on CH_3COOH.

***triangulo*-[$DCo_3(\mu$-CO$)_3(PMe_3)_6$] (2D).** [$CoD(PMe_3)_4$] (1.94 g, 5.31 mmol) and [$Co_2(CO)_3(PMe_3)_5$] (2.96 g, 5.08 mmol) in 20 cm^3 of THF were kept at 60 °C for 16 h to yield a black precipitate. At 20 °C this was isolated by decantation and washing with 3 cm^3 of cold THF. Recrystallization from THF afforded **2D** (1.35 g, 37%). The IR spectrum (Nujol mull) was identical with those of **1** and **2**.

***triangulo*-[$H_3Co_3(\mu$-CO$)_3(PMe_3)_6$] (3). Method A.**[11] Complex **2** (0.21 g, 0.29 mmol) in 50 cm^3 of tetrahydrofuran under 1 bar of H_2 changed from red violet to orange brown within 13 h depositing a brown solid in quantitative yield, which was analytically pure **3**. Recrystallization from tetrahydrofuran afforded 0.143 g of black crystals suitable for X-ray diffraction; yield 67%.

Method B. In the presence of anhydrous $CoCl_2$ (3.6 g, 27.7 mmol) 60 cm^3 of THF and PMe_3 (4.22 g, 55.5 mmol) were at −70 °C condensed in vacuo. The mixture was kept stirring under 1 bar of CO at 20 °C for 2 h. At −80 °C the CO atmosphere was replaced by argon, and 22.2 cm^3 of 2.5 M *n*-BuLi in hexane (55.5 mmol) was added. Warming to 20 °C and removing the volatiles in vacuo afforded a dark brown oil. This was dissolved in 20 cm^3 of toluene and kept at 100 °C for 4 d. The black precipitate was isolated by decantation, washing with 5 cm^3 of toluene, and recrystallization from toluene; yield 1.36 g (20%).

Anal. Calcd for $C_{21}H_{57}Co_3O_3P_6$: C, 35.02; H, 7.98. Found: C, 34.94; H, 7.50. IR (2000−1600 cm^{-1}): KBr disk, 1762 s, 1732 sh, 1725 vs, 1705 vs, 1683 vs (CO); Nujol 1720 m, 1680 vs (broad) (CO). Dec pt. > 150 °C (open capillary in air).

***triangulo*-[$D_3Co_3(\mu$-CO$)_3(PMe_3)_6$] (3D). Method A.** [$CoD(PMe_3)_4$] (5.54 g, 15.2 mmol) and [$Fe_3(CO)_{12}$] (2.55 g, 4.20 mmol) in 40 cm^3 of toluene were kept stirring at 90 °C for 12 h. The black microcrystals were isolated as in the preceding synthesis; yield 1.20 g (33%).

Method B. Quantitative conversion of **2D** under 1 bar of D_2 proceeded as described for **3** (method A). IR (Nujol mull): weak but characteristic band at 759 cm^{-1}, ν(Co−μ_3-H).

Reaction of 2 with Protic Acids.[12] In a typical experiment a mixture of **2** and benzoic acid in tetrahydrofuran at 20 °C changed from red violet to dark brown within 24 h depositing a brown solid. This was dissolved by keeping the mixture at 60 °C for 3 h. After being filtered, the solution was slowly cooled to yield dark brown crystals of **3**. Scales and yields are given in Table 3.

Results and Discussion

Syntheses and Properties. Thermal activation of a condensation reaction starting from olefin and carbonyl cobalt(0) precursors at a ratio Co/CO = 1 yields crystalline deposits of **1** as the least soluble compound among a multitude of mononuclear complexes (Scheme 1(1)).

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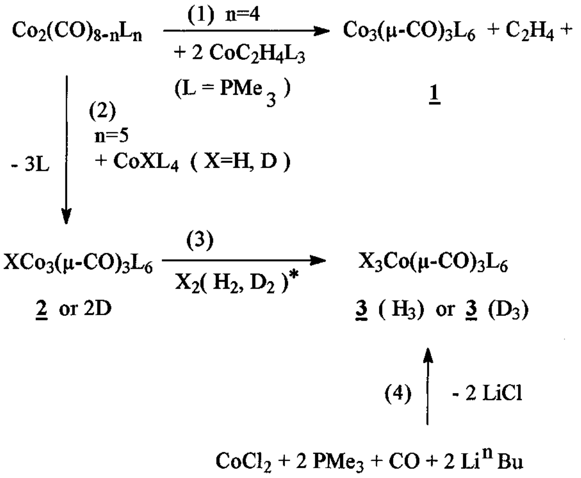
[12] Schlesier, S. Thesis, Technische Hochschule, Darmstadt, 1994.

Scheme 1



* or otherwise protic acids or metal hydride (see text)

Table 4. Infrared Bands of $\tilde{\nu}(Co_3H)$ and $\tilde{\nu}(Co_3D)$ Vibrations (Nujol Mull, 2000−400 cm^{-1})

method of preparation	$\tilde{\nu}(Co_3H)$	$\tilde{\nu}(Co_3D)$
2(H) + H_2 → **3**(H_3)	1036 w	
2(H) + D_2 → **3**(HD_2)		759 w
2(D) + H_2 → **3**(H_2D)	1036 w	
2(D) + D_2 → **3**(D_3)		759 w

UV-induced participation of toluene or tetrahydrofuran solvents as given earlier[1] in the synthesis of **2** is thus excluded, but strictly anhydrous conditions are also necessary in order to suppress formation of **2**. Compounds **1** and **2** form a continuous range of mixed crystals with properties of a solid solution and cannot be separated by recrystallization.

The presence of more than 10% of **2** in solid **1** is best recognized from mass spectra. UV and infrared spectra of **1** and **2** are less reliable due to coinciding absorption bands and an inherently weak Co−H stretching mode in particular.[1] **1** forms dark violet hexagonal crystals which are sparingly soluble in toluene, benzene, or tetrahydrofuran. These solutions instantly deposit violet flakes if air is admitted, while crystals may be safely handled in air at 20 °C for several minutes. Decomposition (open capillary) starts above 150 °C.

A hydride or deuteride ligand is selectively introduced by thermal and stoichiometric control in the synthesis of **2** and **2D**, respectively (Scheme 1(2)). In the absence of UV light no H/D exchange is observed.

Under 1 bar of H_2 in tetrahydrofuran at 20 °C **2** slowly reacts to form the trihydrido cluster **3** (Scheme 1(3)). **3** is collected in quantitative yield as a light brown crystalline solid, which can be recrystallized from large volumes of tetrahydrofuran to give dark brown hexagonal crystals. These are air-stable for several days and are slowly oxidized within 3 weeks at 20 °C. Under argon no loss of dihydrogen is observed prior to thermal decomposition above 160 °C. Mass spectra show the molecular ion and successive loss of three hydrogen atoms suggesting the presence of three CoH functions. Infrared spectra of **3(H_3)** and **3(D_3)** contain bands at 1036 and 759 cm^{-1}, respectively (Table 4), indicating at least one μ^3-H−Co moiety.

However, in tetrahydrofuran under argon or dihydrogen the hydrogen-rich cluster **3** failed to hydrogenate cyclopentene or cyclohexene at 80 °C. Among the products of incipient thermal decomposition of **3** no **2** was detected. Conversely, **3** has been found as the major product in the thermal decomposition of **2**.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg)

	1	**2**[a]	**3**
Co(1)−Co(1)	2.4055(5)	2.420(2)	2.432(1)
Co(1)−H(1)			1.71(3)
Co(1)−C(1)	1.904(2)	1.921(6), 1.913(10)	1.915(2)
C(1)−O(1)	1.188(3)	1.172(11)	1.179(4)
Co(1)−P(1)	2.1929(5)	2.195(2), 2.198(2)	2.202(1)
Co(1A)−Co(1)−Co(1B)	60.0	60.0	60.0
C(1)−Co(1)−Co(1B)	50.82(4)	50.7(3)	50.6(1)
C(1)−Co(1)−Co(1A)	110.82(4)	110.7(3)	110.6(1)
C(1)−Co(1)−C(1A)	161.65(9)	161.7(4)	161.2(1)
Co(1)−C(1)−Co(1B)	78.35(9)	78.3(3)	78.8(1)
Co(1)−C(1)−O(1)	140.82(4)	140.0(7)	140.6(1)
P(1)−Co(1)−Co(1A)	124.06(1)	123.8(1)	123.5(1)
P(1)−Co(1)−Co(1B)	126.21(1)	125.9(1)	125.5(1)
P(1)−Co(1)−C(1)	97.83(3)	97.9(3)	97.8(1)
P(1)−Co(1)−P(1A)	96.72(3)	97.4(1)	98.3(1)
C(1)−Co(1)−P(1A)	94.34(3)	94.4(3)	94.5(1)

[a] After ref 1.

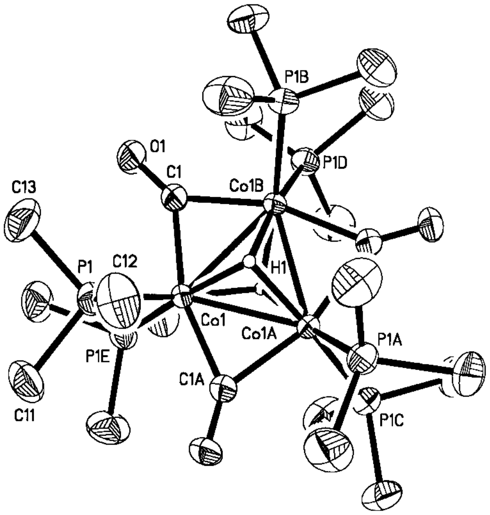


Figure 1. Geometry of the $[H_3(Co(CO)(PMe_3)_2)_3]$ cluster. Hydrogen atoms of methyl groups are omitted for clarity. Thermal ellipsoids are plotted at the 50% probability level.

In the presence of protic acids or any metal hydride **2** is readily transformed to **3**. These observations led us to develop a convenient synthesis of **3** via alkylation of $[CoCl_2(CO)(PMe_3)_3]$ (Scheme 1(4)). Thermally induced condensation of *n*-butyl and hydrido carbonyl cobalt intermediates in toluene or tetrahydrofuran affords constant yields of almost insoluble cluster among highly soluble byproducts.

In another convenient synthesis of **3** [**3D**] CoH(Pme$_3$)$_4$ [CoD(PMe$_3$)$_4$] is reacted with $Fe_3(CO)_{12}$ as a source of carbonyl ligands.

Solid-State Structures of 1 and 3. Both crystals belong to the trigonal space group $R\bar{3}c$ (No. 167). In spite of different compositions **1**−**3** are isostructural.[1] The list of selected bond lengths and angles is given in Table 5. The numbering of atoms is according to Figure 1.

Crystals of **3** exclusively consist of cluster molecules, which display longer Co−Co bonds than in **2** as expected for two additional metal hydride functions. Co−P bonds are not sensitive to missing or added hydride ligands, but the angles PCoP, which are largest for **3** (98.3°), reflect the reduced Co−Co bond order as hydride ligands are added.

The single hydride ligand attached to the cluster core of **2** was not detected by X-ray diffraction.[1] However, in a final difference Fourier map of **3** clear maxima of electron density could be assigned to the presence of the μ_3-H ligand. The refinement led to two symmetrically equivalent positions above and below the center of the Co_3 triangle with Co−H 1.71(3) Å.

The third hydride ligand was not detected but is assumed to be located along the Co−Co vectors of the Co_3 plane.

The Question of $[H_2Co_3(CO)_3(PMe_3)_6]$. A hypothetical dihydrido cluster of the triangulo type is again expected to be isostructural with **2** and **3**. Exchange of hydride ligands between **2** and **3** in equilibria could involve this odd-electron species and provide a remote chance to isolate the compound.

Fractionate crystallization of 1:1 mixtures of **2** and **3** from toluene or tetrahydrofuran gave crystalline solids with properties of both starting materials. Mass spectra contained the parent peak of **3.** Infrared spectra failed to show bands that could be attributed to a third species.

Stoichiometric control in a synthesis directed to yield a dihydrido cluster resulted in the formation of **3**:

$$8[CoH(PMe_3)_4] + 3[Co_2(CO)_4(PMe_3)_4] \rightarrow \mathbf{3} \qquad (5)$$

Infrared spectra of the dark brown crystals showed none of the bands characteristic for **2**.

From these experiments the existence of a dihydrido species appears doubtful.

Reaction of 2 with Protic Acids. Hydrogen when attached to low-valent cobalt in a trimetal frame supported by electron-donating trimethylphosphines is expected to be much less acidic than in $[CoH(CO)_4]$. In reactions it could prove to be a hydride function. In order to test this possibility some carbonic acids and alcohols were reacted with **2** in a Co/OH ratio 3:1, 3:2, 1:1, or less. Regardless of the proton source additional hydride ligands were generated by reduction in order to form high yields of **3**:

$$\mathbf{2} + 2HOR + 2e^- \rightarrow \mathbf{3} + 2OR^- \qquad (6)$$

The electrons are asssumed to arise from an oxidative cluster degradation reaction involving the metal and the phosphine ligands, although pertinent products were not detected.

Magnetic Studies. For **1** the effective magnetic moment μ_{eff} slowly decreases from 1.9 μ_B at 290 K to ~1.7 μ_B at ~30 K and then rapidly to 1.3 μ_B at 4 K. Complex **1** may thus possess a ground state of S_{total} (S_t) = $^1/_2$ with essentially no thermally accessible $S_t = {}^3/_2$ state and behaves as a normal Curie−Weiss paramagnet for one unpaired electron. The deviation below ~30 K from the theoretical spin-only value of 1.73 μ_B for an $S_t = {}^1/_2$ may be the result of weak antiferromagnetic interactions between neighboring trinuclear complexes. Alternatively the data were fitted by means of least-squares using the Heisenberg−Dirac−van Vleck Hamiltonian $\hat{H}$ for isotropic exchange interaction with $S_1 = S_2 = S_3 = {}^1/_2$,

$$\hat{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_3)$$

where 1−3 stand for the three cobalt centers and J is the Co−Co spin−spin coupling constant.

The solid line in Figure 2 represents the best fit with the fitting parameters $J_{Co-Co} = -453$ cm^{-1} and $g_{Co} = 2.12$ including a molecular field parameter $Y = -2.91$ cm^{-1} reflecting the molecular interaction.

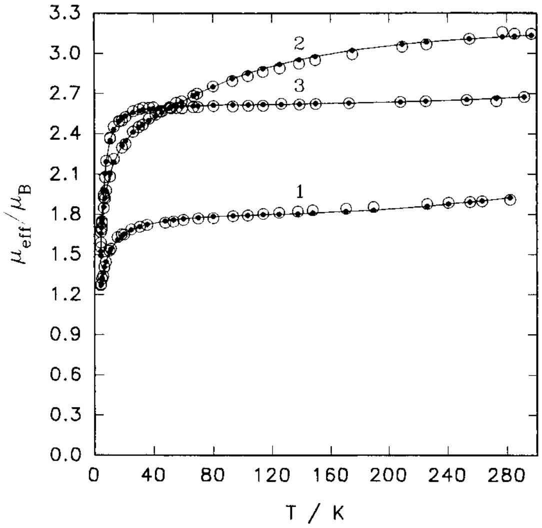


Figure 2. Temperature dependence of effective magnetic moments for $[X\{Co(CO)(PMe_3)_2\}_3]$ clusters, where X = none (**1**), H (**2**), and H_3 (**3**). Observed, open circles; calculated, filled circles and full lines.

For cluster **2** μ_{eff} decreases from 3.1 μ_B at ~300 K to ~2.5 μ_B at ~30 K and then rapidly drops to 1.7 μ_B at 4 K. Qualitatively this behavior is consistent with a Curie−Weiss paramagnet bearing two unpaired electrons per cluster; i.e. $S_t = 1$. On a molecular level this agrees with the assumption of antiferromagnetic coupling in the Co_3 unit and a ferromagnetic coupling between each of the three Co−H pairs. The decrease below 30 K is most probably due to the zero-field splitting of the $S_t = 1$ state or/and the antiferromagnetic intermolecular interaction. Maybe a tendency to reach $S_t = 0$ at lowest temperatures is indicated.

For **3**, μ_{eff} per molecule is essentially temperature-independent at higher temperatures, very slowly decreasing from 2.60 μ_B at ~20 K and then decreasing more rapidly to 1.59 μ_B at 4 K (Figure 2). These data are again consistent with an $S_t = 1$ spin system arising from the doubly degenerate HOMO with no thermally accessible excited spin states in the range 20−300 K. The drop in μ_{eff} below ~20 K might be due to the zero-field splitting of the integer spin state $S_t = 1$.

On a molecular level, the magnetic behavior can be interpreted similar to **2**. For **3**, however, the maximum in $\chi(T)$ at 6.2 K clearly indicates an antiferromagnetic ground state $S_t = 0$. Strong intramolecular exchange coupling through hydride ions has recently been observed in a chromium cluster.[13]

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

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