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Synthesis and Characterization of the Triangulo Raft Cluster $[(AgCo\{CN(2,6\text{-}C_6H_3Me_2)\}_4)_3]$, a Bimetallic Hexanuclear Isonitrile Cluster

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Summary: The trimer $[\{AgCo(CNPh^*)_4\}_3]$ (1, Ph* = 2,6-$C_6H_3Me_2$) has been established by a single-crystal X-ray diffraction study to have a triangulo raft structure (space group $P\bar{1}$, with a = 14.738 (3) Å, b = 14.717 (3) Å, c = 22.693 (5) Å, α = 84.29 (3)°, β = 81.74 (3)°, γ = 89.55 (3)°, D_c = 1.421 g/mL, Z = 2, and R_F = 5.62%). The raft contains an equilateral triangle of silver nuclei with a "$Co(CNPh^*)_4$" fragment bridging each edge. All of the isonitriles are essentially linear, and each cobalt has one isonitrile ligand radial to the raft and three with close contacts to silver. Structural analysis suggests that these close contacts do not correspond to significant bonding interactions, and that the raft is best described as a cluster of $[Co(CNPh^*)_4]^-$ anions held together by Ag^+ cations.

Introduction

It is well established that homoleptic isonitrile ligand environments[1] can stabilize low-valent transition-metal dimers to give complexes such as $[Co_2(CN^tBu)_8]$[2a,b] and $[Co_2(CNAr)_8]$ (Ar = 2,6-$C_6H_3Me_2$, 2,4,6-$C_6H_2Me_3$, 2,6-Me_2-4-BrC_6H_2)[2c,d] analogs of the well-known carbonyl dimer $[Co_2(CO)_8]$. Reports of higher nuclearity isonitrile clusters have, however, been limited to $[Ni_4(CNR)_7]$ (R = ^tBu, C_6H_{11}),[3,4] $[Ni_8(CNCHMe_2)_{12}]$,[3,4] $[Ni_4(CNCH_2Ph)_4]$,[3,4] $[Pd_3(CNR)_6]$ (R = ^iPr, Ph, p-$CH_3OC_6H_4$, C_6H_{11}),[5] $[Pt_3(CNR)_6]$ (R = Me, Et, ^tBu, Ph*, C_6H_{11}),[6] and $[Pt_7(CNPh^*)_{12}]$ (Ph* = 2,6-$C_6H_3Me_2$).[7] We now report that the bimetallic hexanuclear cluster $[\{AgCo(CNPh^*)_4\}_3]$ (1, Ph* = 2,6-$C_6H_3Me_2$) can be prepared by addition of $AgBF_4$ to $[K(DME)][Co(CNPh^*)_4]$[8] ([K(DME)]2, DME = 1,2-dimethoxyethane), and that 1 adopts a triangulo raft structure of the type first established for $[Fe_3Pt_3(CO)_{15}]^{n-}$ (n = 1, 2).[9]

Experimental Section

General Procedures. Reactions and manipulations were carried out under an inert atmosphere of nitrogen by means of standard Schlenk techniques[10] or in a Vacuum Atmospheres Dry-lab glovebox unless otherwise noted. Glassware was oven dried or flamed under vacuum. Tetrahydrofuran (THF) was distilled from potassium/benzophenone ketyl. Toluene was distilled from potassium and hexane from potassium/benzophenone ketyl. Solvents were deoxygenated immediately prior to use. Silver tetrafluoroborate was purchased from Ozark-Mahoning and used as received. Infrared spectra were recorded on a Perkin-Elmer 783 with polystyrene as an external standard. ^1H NMR spectra were recorded on a Bruker AF300 spectrometer at 300.13 MHz. Deuterated benzene was purchased from Cambridge Isotopes Lab and deoxygenated before use. The microanalysis was performed by Atlantic Microlab, Inc., Norcross, GA. $[K(DME)][Co(CNPh^*)_4]$ was prepared as reported elsewhere.[8]

Preparation of $[\{AgCO(CNPh^*)_4\}_3]$. $[K(DME)][Co(CNPh^*)_4]$[8] (0.25 g, 0.35 mmol) was dissolved in THF (30 mL) and cooled to −78 °C. A slurry of silver(I) tetrafluoroborate (0.08 g, 0.41 mmol) in THF (20 mL, ambient temperature) was added via cannula and the mixture stirred. The supernatant became turbid, and the stirred reaction mixture was allowed to warm to room temperature. After $^1/_2$ h, the solution was concentrated to dryness under vacuum and the residue was washed with hexane (3 × 20 mL) and extracted into toluene (3 × 20 mL). The yellow solution was filtered and concentrated to 8 mL to give a red solution, and a layer of hexane (40 mL) was carefully added above the toluene solution. This led to formation of 0.13 g (0.063 mmol, 54%) of red X-ray quality single crystals which were washed with hexane (10 mL) after removal of the supernatant and dried under vacuum. IR (Nujol) $\nu_{C\equiv N}$ 2060 m, 2015 sh, 2002 sh, 1968 s, 1910 sh, 1865 sh cm^{-1}. ^1H NMR (benzene-d_6): δ 6.62 (m, 36 H, C_6H_3), 2.46 (s, 72 H, CH_3). Anal. Calcd for $C_{108}H_{108}Ag_3Co_3N_3$: C, 62.5, H, 5.3, N, 8.1. Found: C, 62.3, H, 5.2, N, 8.0.

X-ray Diffraction Study of $[\{AgCo(CNPh^*)_4\}_3]$. A red crystal of 1 was encased in epoxy cement and attached to a fine glass fiber. Axial photographs confirmed the crystal quality, and systematic absences did not reveal any crystal symmetry higher than triclinic. The centrosymmetric space group $P\bar{1}$ was chosen on the basis of E values and confirmed by the successful solution and refinement of the structure. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with 18° ≤ 2θ ≤ 25°. Diffraction data were collected on a Siemens R3M/E diffractometer. Data collection parameters and other crystallographic data are summarized in Table I. A semiempirical absorption correction was applied to all diffraction data using the program XABS. No decay was observed in three standard reflections during the data collection. The structure was solved using the direct methods program SOLV which located the three Ag and three Co atoms. All remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and were refined anisotropically. Idealized atomic positions were calculated for all hydrogen atoms (d(C–H) = 0.96 Å, U = 1.2(U of the attached carbon atom)). The final difference Fourier synthesis showed only a diffuse background (maximum contour 0.78 e/Å^3). An inspection of F_o vs F_c values and trends based upon sin θ, Miller index, and parity groups failed to reveal any systematic errors in the X-ray data. Selected atomic coordinates are listed in Table

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Table I. Summary of Crystallographic Data for $[\{\mathrm{AgCo(CNPh^*)_4}\}_3]$ (1)

	Crystal Data
formula	$C_{108}H_{108}Ag_3Co_3N_{12}$
crystal size (mm)	0.38 × 0.35 × 0.25
space group	$P\bar{1}$
a (Å)	14.738 (3)
b (Å)	14.717 (3)
c (Å)	22.693 (5)
α (deg)	84.29 (3)
β (deg)	81.74 (3)
γ (deg)	89.55 (3)
V (Å^3)	4847 (2)
Z	2
μ (cm^{-1})	11.41
formula weight	2074.5
D_c (g/mL)	1.421
T (°C)	23
	Data Collection
radiation	Nb-filtered Mo Kα (λ = 0.71073 Å)
scan type	Wyckoff
2θ range (deg)	4.0–50.0
scan range ω (deg)	2.00
scan speed (deg/min)	variable; 5.00–20.00 in ω
reflcns collcd	17793
independent reflcns	17067
obsd reflcns $F > 5.0\sigma(F)$	8172
absorptn correctn	semiempirical
min/max transm	0.3061/0.3324
	Refinement
params refined	1135
data to param ratio	7.2:1
$R_F{}^a$ (%)	5.62
$R_w{}^b$ (%)	6.60
goodness of fit (GOF)^c	1.30
largest difference peak (e Å^{-3})	0.78
largest difference hole (e Å^{-3})	−0.48

$^a R_F = \sum|F_o - F_c|/\sum|F_o|$. $^b R_w = \sum|w^{1/2}(F_o - F_c)|/\sum|w^{1/2}F_o$; $w^{-1} = \sigma^2(F_o) + 0.001F_o{}^2$. $^c \mathrm{GOF} = [\sum w(|F_o| - F_c|)^2/(N_o - N_{\mathrm{params}})]^{1/2}$.

II (only the ipso carbons of the aryl groups are included; a full listing of atomic coordinates is given in Table IS of the supplementary material). Selected bond distances and angles are listed in Tables III and IV. All the computer programs used in the data collection and refinement are contained in the Siemens program packages P3 and SHELXTL (Version 5.1).

Results and Discussion

The synthesis of $[\{\mathrm{AgCo(CNPh^*)_4}\}_3]$ resulted from an attempted oxidation of the isonitrilate salt $[\mathrm{K(DME)}][\mathrm{Co(CNPh^*)_4}]$[8] with $AgBF_4$ in tetrahydrofuran (THF) at −78 °C. This resulted in a color change from the blood red characteristic of the $[\mathrm{Co(CNPh^*)_4}]^-$ monoanion in THF to a cherry red color without formation of silver metal. The solvent was removed from the turbid solution under reduced pressure, and the product was crystallized by slow diffusive mixing of hexane into a concentrated toluene extract of the red solid. This gave red, X-ray quality single crystals which were washed with hexane after separation from the supernatant and dried under vacuum to give a 54% yield of a product which analyzed as "$\mathrm{AgCo(CNPh^*)_4}$".

The IR spectrum of $\mathrm{AgCo(CNPh^*)_4}$ in Nujol (see Experimental Section) is more complex than would be anticipated for a monomeric structure, and differs from that of $[\mathrm{K(DME)}][\mathrm{Co(CNPh^*)_4}]$ (2005 vw, 1880 sh, 1815 vs cm^{-1}),[8] which we have established crystallographically contains discrete, tetrahedral $[\mathrm{Co(CNPh^*)_4}]^-$ anions.[8b] The spectrum of the silver compound does contain absorptions attributable to C≡N stretches in a region above 1850 cm^{-1} (consistent with the presence of linear isonitrile ligands), but these bands are at higher frequencies than the corresponding absorptions of $[\mathrm{K(DME)}][\mathrm{Co(CNPh^*)_4}]$. There are no absorptions in the region between 1700 and 1600 cm^{-1} in which stretching bands of bridging isonitrile ligands (such as those of $[\mathrm{Co_2(CNPh^*)_8}]$[8b]) are normally found,[1a] and we resorted to a single-crystal X-ray diffraction study to determine the structure of the compound.

Table II. Selected Fractional Atomic Coordinates (×10^4) and Isotropic Displacement Coefficients (Å^2 × 10^3) for $[\{\mathrm{AgCo(CNPh^*)_4}\}_3]$

	x	y	z	U(eq)^a
Ag(1)	3317 (1)	2228 (1)	1821 (1)	45 (1)
Ag(2)	2048 (1)	2984 (1)	2705 (1)	44 (1)
Ag(3)	3372 (1)	1680 (1)	3045 (1)	48 (1)
Co(1)	4663 (1)	1238 (1)	2192 (1)	36 (1)
Co(2)	2054 (1)	3350 (1)	1504 (1)	35 (1)
Co(3)	2188 (1)	2390 (1)	3830 (1)	39 (1)
C(1)	4238 (7)	933 (7)	1522 (5)	50 (4)
N(1)	4056 (6)	668 (6)	1072 (4)	56 (4)
C(2)	5817 (8)	807 (6)	2027 (4)	48 (4)
N(2)	6526 (6)	472 (6)	1918 (4)	58 (4)
C(3)	4896 (7)	2440 (7)	2276 (4)	42 (4)
N(3)	5081 (6)	3213 (6)	2298 (4)	53 (3)
C(4)	4253 (7)	354 (7)	2799 (5)	46 (4)
N(4)	4104 (6)	−331 (6)	3114 (4)	57 (4)
C(5)	1740 (7)	2189 (7)	1462 (5)	48 (4)
N(5)	1490 (6)	1452 (6)	1357 (4)	59 (4)
C(6)	3217 (7)	3772 (7)	1297 (5)	49 (4)
N(6)	3924 (6)	4169 (6)	1109 (4)	59 (4)
C(7)	1409 (7)	4057 (7)	2012 (5)	47 (4)
N(7)	943 (7)	4624 (6)	2233 (4)	71 (4)
C(8)	1698 (7)	3850 (6)	829 (5)	45 (4)
N(8)	1512 (6)	4193 (6)	363 (4)	52 (3)
C(9)	3324 (7)	2824 (7)	3810 (4)	41 (4)
N(9)	4050 (6)	3100 (6)	3879 (4)	60 (4)
C(10)	2161 (7)	1886 (8)	4577 (5)	54 (4)
N(10)	2262 (7)	1545 (7)	5061 (5)	81 (5)
C(11′)	1399 (8)	3354 (7)	3866 (4)	51 (4)
N(11)	867 (7)	3926 (7)	3971 (4)	65 (4)
C(12′)	1606 (8)	1466 (8)	3581 (5)	57 (4)
N(12)	1144 (7)	846 (7)	3495 (5)	81 (5)
C(16)	3895 (7)	189 (8)	609 (5)	53 (4)
C(26)	7285 (7)	−92 (8)	1799 (5)	51 (4)
C(36)	5512 (8)	4040 (7)	2305 (4)	48 (4)
C(46)	3936 (7)	−974 (8)	3605 (5)	55 (4)
C(56)	1416 (7)	608 (7)	1129 (5)	48 (4)
C(66)	4708 (7)	4693 (8)	913 (4)	51 (4)
C(76)	294 (9)	5257 (8)	2435 (5)	63 (5)
C(86)	1262 (7)	4845 (7)	−91 (5)	47 (4)
C(96)	4767 (7)	3668 (7)	3963 (4)	45 (4)
C(106)	2623 (10)	1052 (10)	5549 (5)	74 (6)
C(116)	124 (8)	4473 (7)	4165 (5)	52 (4)
C(126)	496 (8)	245 (9)	3380 (5)	63 (5)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The diffraction study revealed that the compound is a trimer $[\{\mathrm{AgCo(CNPh^*)_4}\}_3]$ (1), the core of which (Figure 1) is a triangulo raft of Ag and Co atoms similar to the Fe_3Pt_3 rafts observed in $[\mathrm{Fe_3Pt_3(CO)_{15}}]^{2-}$ and $[\mathrm{Fe_3Pt_3(CO)_{15}}]^{-}$[9] and subsequently established for over a dozen other hexanuclear transition-metal clusters.[11] The raft consists of a nearly equilateral triangle of silver nuclei (bond angles at each vertex 59.4 (1), 60.0 (1), and 60.5 (1)°) with a "$\mathrm{Co(CNPh^*)_4}$" fragment bridging each edge. The structure is essentially planar with the cobalt nuclei 0.01–0.4 Å above and below the Ag_3 plane. The silver–silver distances of 2.825 (1), 2.843 (1), and 2.857 (1) Å are shorter than those found in the metal (2.889 Å),[12] but are not unusual for a silver cluster.[13] The Co–C–N and C–N–C angles for the isonitrile ligands (see Table IV) range

Table III. Selected Interatomic Distances (Å)

Ag(1)-Ag(2)	2.843 (1)	Ag(1)-Co(1)	2.638 (2)	Ag(2)-Co(3)	2.651 (2)
Ag(2)-Ag(3)	2.857 (1)	Ag(1)-Co(2)	2.609 (2)	Ag(3)-Co(3)	2.600 (2)
Ag(1)-Ag(3)	2.825 (1)	Ag(2)-Co(2)	2.724 (2)	Ag(3)-Co(1)	2.639 (2)
Co(1)-C(1)	1.822 (12)	Co(2)-C(5)	1.789 (10)	Co(3)-C(9)	1.791 (11)
Co(1)-C(2)	1.811 (11)	Co(2)-C(6)	1.808 (11)	Co(3)-C(10)	1.777 (11)
Co(1)-C(3)	1.839 (11)	Co(2)-C(7)	1.839 (11)	Co(3)-C(11′)	1.827 (11)
Co(1)-C(4)	1.835 (10)	Co(2)-C(8)	1.778 (11)	Co(3)-C(12′)	1.793 (12)
C(1)-N(1)	1.194 (15)	C(5)-N(5)	1.205 (14)	C(9)-N(9)	1.183 (15)
C(2)-N(2)	1.156 (14)	C(6)-N(6)	1.201 (13)	C(10)-N(10)	1.190 (15)
C(3)-N(3)	1.179 (14)	C(7)-N(7)	1.181 (14)	C(11′)-N(11)	1.165 (15)
C(4)-N(4)	1.180 (13)	C(8)-N(8)	1.193 (13)	C(12′)-N(12)	1.190 (16)

Table IV. Selected Bond Angles (deg)

Ag(2)-Ag(1)-Ag(3)	60.5 (1)	Ag(1)-Ag(2)-Ag(3)	59.4 (1)
Ag(1)-Ag(3)-Ag(2)	60.0 (1)		
Ag(1)-Co(1)-Ag(3)	64.7 (1)	Ag(1)-Co(2)-Ag(2)	64.4 (1)
Ag(2)-Co(3)-Ag(3)	65.9 (1)		
C(1)-Co(1)-C(2)	97.7 (5)	C(2)-Co(1)-C(3)	101.0 (4)
C(1)-Co(1)-C(3)	120.0 (4)	C(2)-Co(1)-C(4)	97.0 (4)
C(1)-Co(1)-C(4)	107.0 (5)	C(3)-Co(1)-C(4)	126.1 (4)
C(5)-Co(2)-C(6)	122.8 (5)	C(6)-Co(2)-C(7)	110.6 (5)
C(5)-Co(2)-C(7)	122.1 (4)	C(6)-Co(2)-C(8)	93.4 (5)
C(5)-Co(2)-C(8)	99.1 (5)	C(7)-Co(2)-C(8)	98.3 (5)
C(9)-Co(3)-C(10)	91.9 (5)	C(10)-Co(3)-C(11′)	106.3 (5)
C(9)-Co(3)-C(11′)	107.9 (5)	C(10)-Co(3)-C(12′)	95.5 (5)
C(9)-Co(3)-C(12′)	140.1 (5)	C(11)-Co(3)-C(12′)	107.5 (5)
Co(1)-C(1)-N(1)	171.7 (9)	C(1)-N(1)-C(16)	168.1 (10)
Co(1)-C(2)-N(2)	175.1 (9)	C(2)-N(2)-C(26)	168.8 (10)
Co(1)-C(3)-N(3)	176.0 (8)	C(3)-N(3)-C(36)	166.1 (10)
Co(1)-C(4)-N(4)	165.9 (9)	C(4)-N(4)-C(46)	164.2 (11)
Co(2)-C(5)-N(5)	170.7 (9)	C(5)-N(5)-C(56)	164.8 (9)
Co(2)-C(6)-N(6)	169.2 (9)	C(6)-N(6)-C(66)	175.0 (11)
Co(2)-C(7)-N(7)	165.5 (9)	C(7)-N(7)-C(76)	171.0 (12)
Co(2)-C(8)-N(8)	176.1 (9)	C(8)-N(8)-C(86)	162.1 (10)
Co(3)-C(9)-N(9)	171.1 (8)	C(9)-N(9)-C(96)	163.1 (10)
Co(3)-C(10)-N(10)	171.6 (10)	C(10)-N(10)-C(106)	163.6 (11)
Co(3)-C(11′)-N(11)	170.7 (9)	C(11′)-N(11)-C(116)	168.6 (10)
Co(3)-C(12′)-N(12)	170.5 (10)	C(12′)-N(12)-C(126)	169.9 (12)

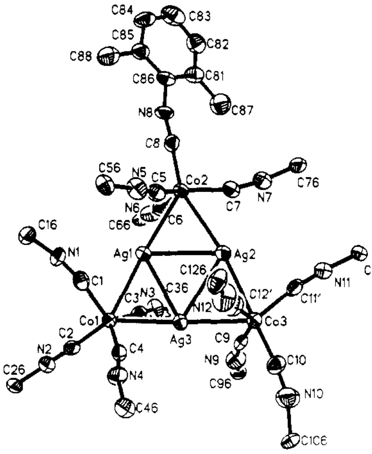

Figure 1. Molecular structure of [{AgCo(CNPh*)$_4$}$_3$] (40% probability ellipsoids). All carbon atoms of one aryl group are included to illustrate the numbering scheme; for clarity only the ipso carbon atoms of the remaining aryl groups are shown.

from 165.9 to 176.1° and 164.2 to 175.0°, respectively; these are within the ranges observed for linear isonitrile ligands, which readily distort as a consequence of packing interactions.

Each of the three cobalt atoms has one unique isonitrile ligand radial to the raft (the C(2), C(8) and C(10) isonitriles), and three isonitriles with close C–Ag contacts and small C–Co–Ag angles suggestive of bridging interactions with the silver atoms (Table V). Since these ligands are not, however, bent, these data invite comparison with linear semibridging carbonyl ligands. The controversial literature on this subclass of bridging carbonyl ligands[14-18] has been largely resolved by a recent structural analysis by Crabtree[19] which established that there are three classes of linear semibridging carbonyls which differ in the extent to which the carbonyls bend back toward the second metal ("ψ" angle) and in the characteristic distance between the carbon atom and the first metal ("*a*").

Comparison of the data in Tables III and V with the ψ vs *a* plot in Figure 7 of ref 19 suggests that the "semibridging" isonitrile ligands are analogous to type III linear semibridging carbonyl ligands, and we would propose, as Crabtree has suggested for the C≡O systems, that the close contact isonitriles in 1 are linear isonitriles which happen to point close to Ag. The Co to C distances for the three radial isonitrile ligands within 1 are comparable with the Co to C distances for the ligands with close approaches to silver, consistent with minimal perturbation of the ligands by the silver atoms. The surprisingly close nonbonding interactions between the isonitrile ligands within 1 and the Ag atoms are consistent with a model in which 1 is regarded as a cluster of tetrahedral [Co(CNPh*)$_4$]$^-$ anions[8b] held together by Ag$^+$ cations.

The unusual two-dimensional structure of triangulo raft clusters has stimulated theoretical interest in their elec-

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Table V. Selected Interatomic Distances (Å) and Angles (deg) Illustrating Close Approaches of the Isonitrile Ligands to the Silver Atoms

Ag(1)–C(1)	2.427 (10)	Ag(2)–C(5)	3.249 (10)	Ag(3)–C(3)	2.805 (10)
Ag(1)–C(3)	2.709 (10)	Ag(2)–C(7)	2.401 (10)	Ag(3)–C(4)	2.403 (10)
Ag(1)–C(5)	2.573 (11)	Ag(2)–C(11′)	2.776 (10)	Ag(3)–C(9)	2.530 (10)
Ag(1)–C(6)	2.472 (10)	Ag(2)–C(12′)	2.851 (10)	Ag(3)–C(12′)	2.716 (10)
C(1)–Co(1)–Ag(1)	62.8 (3)	C(5)–Co(2)–Ag(1)	68.7 (3)	C(9)–Co(3)–Ag(3)	67.5 (3)
C(3)–Co(1)–Ag(1)	72.0 (3)	C(5)–Co(2)–Ag(2)	89.7 (3)	C(11′)–Co(3)–Ag(2)	74.1 (3)
C(3)–Co(1)–Ag(3)	75.2 (3)	C(6)–Co(2)–Ag(1)	65.1 (3)	C(12′)–Co(3)–Ag(2)	77.2 (3)
C(4)–Co(1)–Ag(3)	61.9 (3)	C(7)–Co(2)–Ag(2)	60.1 (3)	C(12′)–Co(3)–Ag(3)	73.8 (3)

tronic structure,[20] and it has been pointed out that polyhedral skeletal electron pair theory (PSEPT)[21] predicts that hexanuclear raft structures should result in 90-electron clusters if the metals utilize 9 valence orbitals in skeletal bonding and 86-electron clusters if they only utilize 8 valence orbitals.[20] In the case of 1 the 84-electron count differs markedly from the predictions of PSEPT; this is consistent with the [Co(CNPh*)$_4$]$^-$ anion/Ag$^+$ cation model proposed above, but it should be recognized that a number of other triangulo raft clusters are also 84-electron clusters.[11c,e–m]

It is interesting to compare the reaction of [K(DME)][Co(CNPh*)$_4$] with AgBF$_4$ with that of [Co(CO)$_4$]$^-$ with Ag(I) salts; the latter gives a planar tetramer in which there is an approximately square array of silver atoms with "Co(CO)$_4$" fragments bridging each edge.[22] The geometry about each Co atom is approximately octahedral (with four sites occupied by carbonyls and two by silver atoms), suggesting that an anion/cation model is less applicable in this case. This would be consistent with a reduction in the effective electron density on the Co centers as a consequence of the better π-acceptor ability of the carbonyl ligand.

Conclusion

The characterization of [{AgCo(CNPh*)$_4$}$_3$] provides the first example of a hexanuclear cluster with a homoleptic isonitrile ligand environment. The triangulo raft structure adopted by 1 is unusual, and only a few other examples are known of triangulo raft complexes which are not carbonyl complexes or carbonylmetalates.[11j–m] The bonding parameters for the isonitrile ligands, and the close analogy between the parameters for the nine isonitriles with close approaches to Ag and those established as characteristic of type III linear semibridging carbonyl ligands,[19] suggest that the cluster is best regarded as containing [Co(CNPh*)$_4$]$^-$ anions held together by Ag$^+$ cations.

The facility with which Crabtree's structural analysis of linear semibridging carbonyls[19] can be applied to 1 reinforces the close parallels between the ligand characteristics of C≡O and those of isonitriles, and suggests that there should be an extensive chemistry of isonitrile clusters analogous to that of carbonyl clusters. The specific contrast between the structure of 1 and that of [{AgCo(CO)$_4$}$_4$],[22] however, also reminds us that the unique electronic characteristics of isonitriles will result in significant variations from the models established by carbonyl chemistry, and that these variations are likely to be more marked in complexes of metals in extreme oxidation states.

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Registry No. [{AgCo(CNPh*)$_4$}$_3$], 144346-24-7; [K(DME)][Co(CNPh*)$_4$], 121232-44-8; silver(I) tetrafluoroborate, 14104-20-2.

Supplementary Material Available: Table IS, fractional atomic coordinates and isotropic thermal parameters, Table IIS, bond lengths, Table IIIS, bond angles, Table IVS, anisotropic displacement coefficients, and Table VS, hydrogen atom parameters (13 pages). Ordering information is given on any current masthead page.

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