CF_3NO, $ON(CF_2)_3NO$, NO_x, and unreacted CF_2I_2 and NO, $CF_2(NO)_2$ (~10% yield) was found in a trap at −135 to −140 °C having passed through a trap at −120 °C. It can be handled in a glass vacuum line in diffuse light for brief periods.

Synthesis of II. When the mixture of CF_2I_2, NO, and Hg described for I was photolyzed for longer time periods, e.g., 8 h, the yield of I was reduced to a trace, and $ONCF_2CF_2CF_2NO$ was formed in ~20% yield. This was separated by trap-to-trap distillation (passes a trap at −60 °C and is stopped at −78 °C) and found to be stable at 25 °C for extended periods (dark).

Synthesis of III. In an effort to conclusively confirm the existence of I, p-$O_2NC_6H_4NH_2$ (1.5 mmol) was dissolved in 4 mL of ethanol and I (0.5 mmol) was condensed into the solution. A bright yellow solid (III) began to precipitate immediately. After being stirred for 2 h, the mixture was filtered, and III was washed with ethanol and dried. Mass, ^{19}F and ^1H NMR, and IR spectra confirm the structure. The IR spectrum (KBr disk) has bands at 1710 vw, 1697 vw, 1671 vw, 1650 m, 1591 m, 1516 m, 1480 w, 1449 w, 1407 vw, 1399 s, 1320 s, 1295 s, 1245 vs, 1170 s, 1134 m, 1108 s, 1034 w, 1006 vw, 847 m, 754 m, 692 m, 631 m, 613 m, 561 m, and 486 vw cm^{-1}.

Acknowledgment is made to the Battelle Pacific Northwest Laboratories for financial support.

Registry No. III, 137568-62-8; $CF_2(NO)_2$, 137541-03-8; $ON(CF_2)_3NO$, 137541-04-9; CF_2I_2, 1184-76-5; $(CF_3)_2Hg$, 371-76-6; $CF_2[C(O)ONO]_2$, 137541-05-0; $CF_2[C(O)OAg]_2$, 2624-69-3; CF_2N_2, 814-73-3; CF_3NO, 334-99-6; p-$O_2NC_6H_4NH_2$, 100-01-6; hexafluoropropylene oxide, 428-59-1; perfluoromalonic acid, 1514-85-8.

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Synthesis and Structural Characterization of the Nitrido–Carbonyl Cluster Anion $[Co_7N(CO)_{15}]^{2-}$, Possessing a Carbonyl Stereochemistry Different from That of Its Rhodium Analogue

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Introduction

Nitrido–carbonyl clusters, a class of compounds including today less than 20 species, exhibit interesting structural features both in the metal atom arrays and in the geometries of the cavities containing the interstitial nitrogen atoms. The first examples reported were the trigonal-prismatic species $[M_6N(CO)_{15}]^-$ (M = Co, Rh),[2,3] from which other higher nuclearity species {up to 14 metal atoms, as $[Co_{14}N_3(CO)_{23}]^{3-}$[4] and $[Rh_{14}N_2(CO)_{25}]^{2-}$[5]} were derived. In particular, condensation of the simple anionic carbonylates $[M(CO)_4]^-$ (M = Co, Rh, Ir) on $[Rh_6N(CO)_{15}]^-$ afforded the $[Rh_6MN(CO)_{15}]^{2-}$ species,[6] containing a trigonal-prismatic cluster capped on a square face. In this case the Rh_7 dianion and the two related Rh_6Co and Rh_6Ir mixed-metal species were found to have the same overall ligand geometry.

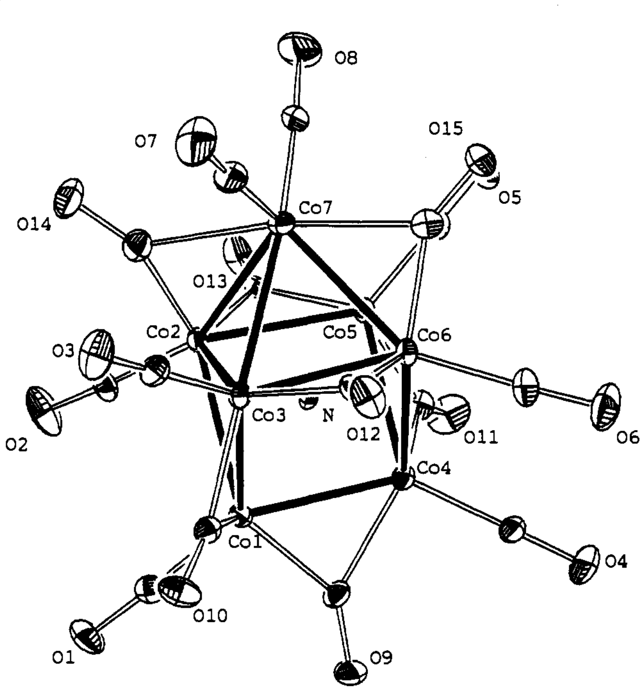

Figure 1. ORTEP drawing of the anion $[Co_7N(CO)_{15}]^{2-}$. For clarity the numbering of the carbonyl groups is indicated only by the labels of their oxygen atoms. Thermal ellipsoids are drawn at the 30% probability level.

We have now studied the analogous condensations starting from $[Co_6N(CO)_{15}]^-$, and we report here on the synthesis and X-ray characterization of the $[Co_7N(CO)_{15}]^{2-}$ anion, which exhibits a carbonyl disposition different from that observed in the rhodium analogue.

Results and Discussion

The anion $[Co_7N(CO)_{15}]^{2-}$ is synthesized by heating at reflux under nitrogen a THF solution containing equimolar amounts of the $[PPh_4]^+$ salts of $[Co_6N(CO)_{15}]^-$ and $[Co(CO)_4]^-$. Close IR monitoring shows that the reaction occurs in two stages. At first there is a decarbonylation of the starting nitride to give the octahedral $[Co_6N(CO)_{13}]^-$[7] (eq 1), followed by a slow condensation

$$[Co_6N(CO)_{15}]^- \rightarrow [Co_6N(CO)_{13}]^- + 2CO \tag{1}$$

$$[Co_6N(CO)_{13}]^- + [Co(CO)_4]^- \rightarrow [Co_7N(CO)_{15}]^{2-} + 2CO \tag{2}$$

of this anion with $[Co(CO)_4]^-$ to give the heptanuclear species (eq 2). Thus the real condensation occurs on $[Co_6N(CO)_{13}]^-$, which is generated "in situ" by reaction 1. It is essential, for the reaction to proceed, to remove the evolved CO. Beside the condensation some decomposition also occurs, and at the end some insoluble black material and a trace of unreacted $[Co(CO)_4]^-$ are present. Separation is achieved by filtration and fractional crystallization.

The IR spectrum of $[PPh_4]_2[Co_7N(CO)_{15}]$ in THF solution shows bands at 2029 w, 1977 vs, 1963 m, 1930 w, 1815 m, 1805 (sh), and 1775 (sh) cm^{-1}. The $[Co_7N(CO)_{15}]^{2-}$ anion reacts immediately with CO giving directly $[Co_6N(CO)_{15}]^-$ and $[Co(CO)_4]^-$ according to the reverse of the synthesis reaction. Partial addition of CO does not give $[Co_6N(CO)_{13}]^-$, as expected from the reverse of reaction 2, but gives again $[Co_6N(CO)_{15}]^-$ and $[Co(CO)_4]^-$, leaving some unreacted $[Co_7N(CO)_{15}]^{2-}$.

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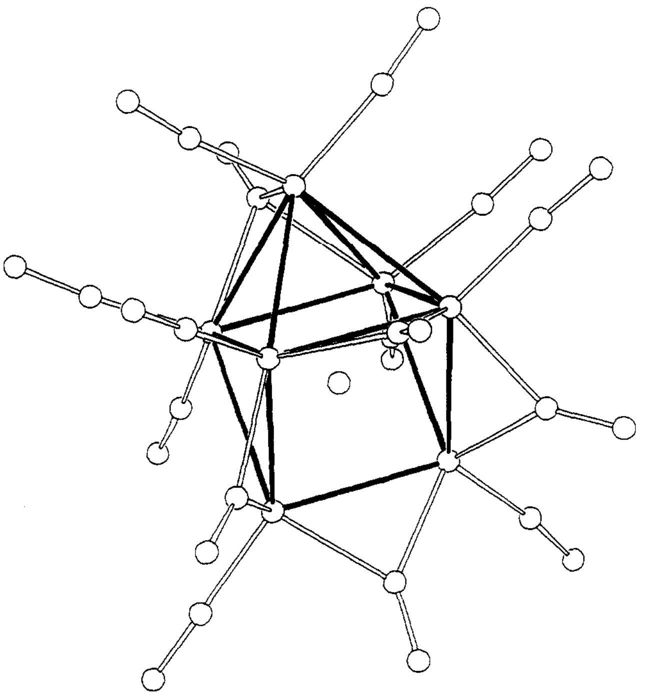

Figure 2. Schematic drawing of the geometry of the anion $[Rh_7N(CO)_{15}]^{2-}$ (see ref 6).

The natural-abundance ^{13}C NMR spectrum in THF-d_8 at 24 °C shows a single sharp band at δ = 224.49 ppm indicating complete fluxionality of the carbonyls. At −90 °C a static pattern begins to emerge with several broad bands in the range 199–263 ppm, but due to the low resolution the spectrum could not be assigned. However, the presence of a band at 263 ppm, in a zone typical for triply rather than for double bridging carbonyls, indicates that possibly the solid-state structure is not retained in solution.

Description of the Structure. The structure of the anion $[Co_7N(CO)_{15}]^{2-}$ is illustrated in Figure 1, and relevant bond distances and angles are given in Table I. The overall stereochemistry of the anion shows an idealized C_2 symmetry, different from the C_s symmetry observed in the $[Rh_6MN(CO)_{15}]^{2-}$ family (Figure 2); while in the rhodium cluster anion there are 10 terminal, 4 symmetric edge-bridging, and 1 face-bridging carbonyl groups, in the cobalt species there are 8 terminal, 5 symmetric, and 2 markedly asymmetric edge-bridging CO's.

The metal atom array of $[Co_7N(CO)_{15}]^{2-}$ consists of a trigonal prism capped on one of its square faces by the seventh cobalt atom. The Co–Co bond lengths belong to two distinct classes: carbonyl-bridged edges [seven, range 2.436 (2)–2.555 (2) Å, mean 2.485 Å] and unbridged ones [six, range 2.561 (2)–2.624 (2) Å, mean 2.610 Å]. This is a quite commonly observed feature, and it seems to be the only source of distortion from the strictly ideal regular polyhedron (D_{3h} prism + C_{4v} pyramid). On the other hand, the metal atom array in $[Rh_7N(CO)_{15}]^{2-}$ shows distortions which have suggested an alternative description of the cluster, i.e. a two-layer system consisting of a triangular $Rh_3(\mu_3\text{-}CO)(CO)_6$ moiety and a square Rh_4 $(\mu\text{-}CO)_4(CO)_4$ unit joined only through Rh–N bonds and six long metal–metal bonds.

The interstitial nitrogen atom lies at the center of the trigonal-prismatic moiety, with Co–N bonds in the range 1.903 (6)–1.933 (6) Å, with a mean value (1.920 Å) similar to that observed in the parent $[Co_6N(CO)_{15}]^-$ (1.938 Å). This contrasts with the significant out-of-center displacement of the nitride inside the prism in $[Rh_7N(CO)_{15}]^{2-}$, which is closer to four metal atoms (mean Rh–N = 2.06 Å) than to the others [Rh–N = 2.17 (1) and 2.30 (1) Å].

Table I. Selected Bond Distances (Å) and Angles (deg) within $[Co_7N(CO)_{15}]^{2-}$

	Distances		
Co1–Co2	2.624 (2)	Co2–C2	1.719 (10)
Co1–Co3	2.483 (2)	Co2–C13	1.899 (9)
Co1–Co4	2.436 (2)	Co2–C14	1.772 (10)
Co2–Co3	2.617 (2)	Co3–C3	1.730 (10)
Co2–Co5	2.448 (2)	Co3–C10	1.919 (9)
Co2–Co7	2.555 (2)	Co3–C12	1.967 (9)
Co3–Co6	2.450 (2)	Co4–C4	1.729 (10)
Co3–Co7	2.616 (2)	Co4–C9	1.917 (10)
Co4–Co5	2.481 (2)	Co4–C11	1.884 (9)
Co4–Co6	2.616 (2)	Co5–C5	1.744 (10)
Co5–Co6	2.561 (2)	Co5–C11	1.909 (9)
Co5–Co7	2.624 (2)	Co5–C13	1.923 (9)
Co6–Co7	2.543 (2)	Co6–C6	1.735 (10)
Co1–N	1.922 (6)	Co6–C12	1.883 (10)
Co2–N	1.933 (6)	Co6–C15	1.810 (10)
Co3–N	1.915 (6)	Co7–C7	1.760 (12)
Co4–N	1.903 (6)	Co7–C8	1.748 (11)
Co5–N	1.915 (6)	Co7–C14	2.182 (10)
Co6–N	1.929 (6)	Co7–C15	2.092 (10)
Co1–C1	1.730 (11)	av C–O(term)	1.14
Co1–C9	1.877 (9)	av C–O(bridg)	1.17
Co1–C10	1.894 (9)		
	Angles		
C1–Co1–C9	94.8 (4)	C7–Co7–C15	100.4 (4)
C1–Co1–C10	91.3 (4)	C8–Co7–C14	92.6 (4)
C9–Co1–C10	116.7 (4)	C8–Co7–C15	91.6 (4)
C2–Co2–C13	94.4 (4)	C14–Co7–C15	169.8 (4)
C2–Co2–C14	98.7 (5)	av Co–C–O(term)	177.4
C13–Co2–C14	106.0 (4)	Co1–C9–O9	141.8 (8)
C3–Co3–C10	91.6 (4)	Co4–C9–O9	138.3 (7)
C3–Co3–C12	94.7 (4)	Co1–C10–O10	138.1 (7)
C10–Co3–C12	102.7 (4)	Co3–C10–O10	140.6 (7)
C4–Co4–C9	93.8 (4)	Co4–C11–O11	138.9 (8)
C4–Co4–C11	90.7 (4)	Co5–C11–O11	139.4 (8)
C9–Co4–C11	120.1 (4)	Co3–C12–O12	136.6 (7)
C5–Co5–C11	93.1 (4)	Co6–C12–O12	144.1 (7)
C5–Co5–C13	99.0 (4)	Co2–C13–O13	141.6 (7)
C11–Co5–C13	98.3 (4)	Co5–C13–O13	138.6 (7)
C6–Co6–C12	99.8 (4)	Co2–C14–O14	152.5 (9)
C6–Co6–C15	96.8 (5)	Co7–C14–O14	127.7 (8)
C12–Co6–C15	105.9 (4)	Co6–C15–O15	148.6 (8)
C7–Co7–C8	100.1 (5)	Co7–C15–O15	130.3 (8)
C7–Co7–C14	88.0 (4)		

Of the seven edge-bridging carbonyls, those involving the capping Co7 atom are quite asymmetric [Co7–C14 = 2.182 (10) Å, Co2–C14 = 1.772 (10) Å and Co7–C15 = 2.092 (10) Å, Co6–C15 = 1.810 (10) Å]. The mean values of the Co–C and C–O bond lengths for the five symmetric bridging and the eight terminal carbonyl groups are 1.907, 1.17 Å, and 1.737, 1.14 Å, respectively.

The difference in the ligand stereochemistry found for the Co_7 and Rh_7 species is the most outstanding feature of this study. Differences of this type for analogous clusters with metals of the same subgroup were observed in few cases; famous examples are the cobalt and rhodium vs iridium $M_4(CO)_{12}$ and $M_6(CO)_{16}$ species. However, the only previous report of different stereochemistry of analogous compounds of cobalt and rhodium is represented by the $[M_6C(CO)_{13}]^{2-}$ (M = Co, Rh) anions.[8,9] The variation of the properties of the metals in a subgroup can be invoked to account for these differences,[10] and very often indeed metals of the same subgroup display quite different behaviors in cluster chemistry. Furthermore, in the present case the relatively little crowding of the CO groups on the cluster surface is possibly the cause of the extended fluxional behavior of the ligands in

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(10) It is worth noting that not only different stereochemistries but also different numbers of carbonyl ligands were found in higher nuclearity clusters of rhodium and iridium with the same metal cage (Della Pergola, R.; Demartin, F.; Garlaschelli, L.; Manassero, M.; Martinengo, S.; Masciocchi, N.; Strumolo, D. *Inorg. Chem.* **1991**, *30*, 846.

Table II. Crystal Data for $[PPh_4]_2[Co_7N(CO)_{15}]$

formula	$C_{63}H_{40}Co_7NO_{15}P_2$
fw	1525.50
system	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	14.895 (5)
b, Å	18.945 (5)
c, Å	12.974 (3)
α, deg	105.93 (2)
β, deg	115.21 (3)
γ, deg	96.07 (3)
V, Å^3	3079 (4)
D_c, g cm^{-3}	1.645
Z	2
radiation (λ, Å)	Mo Kα (0.71073)
obsd reflcns/refined params	3331/553
final R and R_w indices^a	0.034, 0.039
temp, °C	22 ± 2

$^a R = \sum(|F_o| - k|F_c|)/\sum|F_o|$. $R_w = [\sum w(|F_o| - k|F_c|)^2/\sum wF_o^2]^{1/2}$. $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}/L_p$.

solution, with easy interconversions involving different almost isoenergetic minima. Bookkeeping of the local electron counts suggests that both carbonyl geometries might produce efficient charge equalization on all metal atoms. Therefore, other non-negligible minor factors, both electronic and steric (for example, the smaller covalent radius of cobalt vs rhodium and/or the central position of the nitride inside the prismatic hole, compared to the out-of-center displacement observed in the rhodium analogue) might cause the different ligand geometries observed in the solid state.

Experimental Section

All the operations are carried out under nitrogen atmosphere using the Schlenk tube technique. $[PPh_4][Co_6N(CO)_{15}]$ is prepared as described,[2] and $[PPh_4][Co(CO)_4]$ is prepared by metathesis of $Na[Co(CO)_4]$ with $[PPh_4]Br$.

Synthesis of $[PPh_4]_2[Co_7N(CO)_{15}]$. A stirred solution of $[PPh_4][Co_6N(CO)_{15}]$ (0.25 g, 0.22 mmol) and $[PPh_4][Co(CO)_4]$ (0.113 g, 0.22 mmol) in THF (30 mL) is heated at reflux in an oil bath at 80 °C until the strongest of the IR bands of the intermediate anion $[Co_6N(CO)_{13}]^-$ at 1999 cm^{-1} completely disappears. During the reaction the evolved CO is eliminated every 2–3 h by brief pumping in vacuum and restoring the nitrogen atmosphere. At the end (12–14 h) the solution is filtered from some black material and, after concentration in vacuum to about 15 mL, is cautiously layered with 2-propanol (50 mL). When the diffusion of the solvents is complete (about 4–6 days), the slightly brown mother liquor is syringed off and the black crystals are washed with 2-propanol and vacuum dried. Should the product contain traces of $[PPh_4][Co(CO)_4]$ (IR band at 1886 cm^{-1}), the crystallization is repeated. Yields: 0.21–0.25 g, 65–75%.

Anal. Found (calcd) for $C_{63}H_{40}Co_7NO_{15}P_2$: C, 49.10 (49.60); H, 2.63 (2.64); N, 0.96 (0.92).

Crystals suitable for the X-ray analysis were obtained from THF/*n*-hexane by the slow-diffusion technique.

X-ray Analysis of $[PPh_4]_2[Co_7N(CO)_{15}]$. Crystal data are reported in Table II. The crystal sample was mounted on a glass fiber in the air. The intensity data were collected on an Enraf-Nonius CAD4 automated diffractometer using graphite-monochromatized Mo Kα radiation. The setting angles of 25 random intense reflections (16° < 2θ < 25°) were used to determine by least-squares fit accurate cell constants and orientation matrix. The collection was performed by the ω-scan method, within the limits 6° < 2θ < 48°. A variable scan speed and a variable scan range were used, with a 25% extension at each end of the scan range for background determination. Three standard intense reflections, monitored every 2 h, showed some crystal decay, of ca. 10% at the end of the collection. The intensities were corrected for Lorentz, polarization, and decay effects. An empirical absorption correction[11] was applied to the data, based on ψ scans (ψ 0–360° every 10°) of three suitable reflections with χ values close to 90°. A set of 3331 significant $[I > 3\sigma(I)]$ independent reflections were used in the structure solution and refinement.

Table III. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z
Co1	0.16053 (8)	0.34202 (6)	0.04687 (9)
Co2	0.30056 (8)	0.33194 (6)	−0.02468 (9)
Co3	0.32734 (8)	0.32549 (6)	0.18510 (9)
Co4	0.09175 (8)	0.20525 (6)	−0.05854 (9)
Co5	0.22832 (8)	0.19423 (6)	−0.11898 (9)
Co6	0.26596 (8)	0.18696 (6)	0.08922 (9)
Co7	0.41340 (8)	0.25010 (7)	0.0681 (1)
O1	0.1066 (5)	0.4841 (3)	0.0492 (6)
O2	0.2609 (6)	0.4605 (3)	−0.0966 (5)
O3	0.5030 (5)	0.4330 (4)	0.4016 (6)
O4	−0.0784 (5)	0.0842 (4)	−0.1243 (6)
O5	0.2489 (6)	0.0624 (4)	−0.2737 (6)
O6	0.1481 (5)	0.0533 (4)	0.0829 (6)
O7	0.6060 (6)	0.3100 (4)	0.2917 (7)
O8	0.4936 (5)	0.1884 (5)	−0.0924 (7)
O9	−0.0582 (4)	0.2885 (4)	−0.0435 (6)
O10	0.2280 (4)	0.4176 (4)	0.3018 (5)
O11	0.0189 (5)	0.1382 (4)	−0.3161 (5)
O12	0.3552 (5)	0.2437 (3)	0.3529 (5)
O13	0.2559 (5)	0.2670 (3)	−0.2771 (4)
O14	0.5157 (5)	0.4033 (4)	0.0809 (6)
O15	0.3989 (5)	0.0911 (3)	0.0659 (6)
N	0.2298 (4)	0.2643 (3)	0.0201 (5)
C1	0.1263 (6)	0.4265 (5)	0.0471 (7)
C2	0.2754 (6)	0.4096 (5)	−0.0651 (7)
C3	0.4328 (6)	0.3895 (5)	0.3148 (7)
C4	−0.0111 (6)	0.1322 (5)	−0.1001 (7)
C5	0.2413 (7)	0.1339 (5)	−0.2110 (7)
C6	0.1934 (7)	0.1075 (5)	0.0855 (8)
C7	0.5288 (7)	0.2869 (5)	0.2065 (9)
C8	0.4598 (6)	0.2107 (5)	−0.0319 (8)
C9	0.0254 (6)	0.2832 (5)	−0.0243 (7)
C10	0.2353 (6)	0.3794 (5)	0.2193 (6)
C11	0.0823 (6)	0.1664 (5)	−0.2140 (7)
C12	0.3251 (6)	0.2462 (4)	0.2558 (7)
C13	0.2590 (6)	0.2666 (4)	−0.1859 (6)
C14	0.4365 (7)	0.3605 (5)	0.0489 (8)
C15	0.3635 (6)	0.1437 (5)	0.0713 (7)

The structure was solved by Patterson and Fourier methods, which revealed the locations of all the non-hydrogen atoms. The refinements were carried out by full-matrix least squares, with anisotropic thermal parameters assigned to all atoms except to the carbon atoms of the cations. Weights were assigned according to the formula $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma(F_o^2) = [\sigma^2(\mathrm{I}) + (pI)^2]^{1/2}/L_p$ (I and $\mathrm{L_p}$ being the integrated intensity and the Lorentz–polarization correction, respectively); p was optimized to 0.030. The hydrogen atoms of the phenyl groups were located in ideal positions (C–H = 0.95 Å, with B = 5.0 Å^2) after each cycle of refinement, and their contribution to the structure factors was kept into account. The final difference-Fourier map showed residual peaks not exceeding ca. 0.5 e Å^{-3}. The final values of R and R_w are given in Table II. The final positional parameters for the atoms of the anion are given in Table III. All computations were performed on a PDP 11/73 computer, using the Enraf-Nonius Structure Determination Package (SDP)[12] and the physical constants tabulated therein.

Registry No. $[PPh_4]_2[Co_7N(CO)_{15}]$, 137916-85-9; $[PPh_4][Co_6N(CO)_{15}]$, 137916-83-7; $[PPh_4][Co(CO)_4]$, 95661-79-3.

Supplementary Material Available: An extended list of crystallographic data (Table S1), anisotropic thermal factors (Table S2), calculated fractional coordinates of the hydrogen atoms (Table S3), a complete set of fractional coordinates (Table S5), and bond parameters (Table S6) (14 pages); a listing of observed and calculated structure factor moduli (Table S4) (23 pages). Ordering information is given on any current masthead page.

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