of Al–Al_2O_3–complex–Pb tunnel junctions. This is only the second published IETS study of a transition metal–carbonyl complex.[16]

The postulated reaction pathway is illustrated in Figure 4. The dimer adsorbs physically on the surface, but it must dissociate before chemisorption can occur. When the dimer dissociates, the monomers react with surface hydroxyl groups resulting in the formation of HCl gas and allowing the rhodium atom to bond to the resulting surface oxygen. The metal atom can interact further with a neighboring hydroxyl, possibly coordinating with the lone pair of electrons on the oxygen. This is the predominant surface species, consisting of an isolated rhodium atom binding two carbonyl ligands, $Rh(CO)_2$. Some of these groups may lose one of their carbonyls, or, if two rhodium atoms are on adjacent sites, a CO may form a bridge bond between the two. These result in RhCO and Rh_2CO species, respectively. The scism of the dimer appears to be the rate-limiting step. Adsorption at low temperatures results in a multilayer of physically adsorbed $[RhCl(CO)_2]_2$. If this surface is allowed to warm to room temperature, the multilayers desorb, leaving only the chemisorbed monolayer. If, however, Pb is evaporated on the cold surface, the energy released by the condensing Pb is sufficient to dissociate the dimers present in the multilayer. These monomers then lose their chlorine and bind to the surface.

Our spectra indicate that, compared with evaporated Rh, a large proportion of the Rh present on the surface is in the form of $Rh(CO)_2$, indicating almost atomic dispersion of the metal.

Acknowledgment. We wish to thank Dr. John Yates, Jr. for suggesting this study and for valuable discussions and encouragement. We wish to thank also Professor R. H. Grubbs for very helpful discussions on probable surface reactions. We gratefully acknowledge the financial support of the National Science Foundation under Grant No. ENG78-16927. W.H.W. is a Camille and Henry Dreyfus Foundation Teacher-Scholar.

An Interstitial Hydrogen Atom in a Hexanuclear Metal Cluster: X-ray and Neutron Diffraction Analysis of $[(Ph_3P)_2N]^+[HCo_6(CO)_{15}]^-$

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Giuliano Longoni,[1b] Stefano Campanella,[1c] Paolo Chini,*[1c,2] and Thomas F. Koetzle*[1d]

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007, the Centro del CNR per la Sintesi e la Struttura dei Composto dei Metalli di Transizione nei Bassi Stati Di Ossidazione and the Istituto di Chimica Generale dell'Università, 20133 Milano, Italy, and the Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973. Received June 23, 1980

Abstract: A six-coordinate H atom has been found in the octahedral metal cluster complex $[HCo_6(CO)_{15}]^-$ by single-crystal neutron diffraction analysis at 80 K. Within experimental error, the H atom is situated in the geometric center of the cluster, with an average Co–H distance of 1.82 Å. The mean Co–Co distance of 2.58 Å is longer than those in $[Co_6(CO)_{14}]^{4-}$ (2.50 Å) and $[Co_6(CO)_{15}]^{2-}$ (2.51 Å). $[HCo_6(CO)_{15}]^-$ is prepared via the protonation of $[Co_6(CO)_{15}]^{2-}$. The monoanion shows an unusual ^1H NMR chemical shift at τ −13.2 (acetone-h_6 solution, 173 K), which disappears upon warming to room temperature. Experimental evidence seems to point to the existence of some type of exchange of the proton in solution, as $[HCo_6(CO)_{15}]^-$ shows no ^1H NMR signal in acetone-d_6 and is readily deprotonated by water, methanol, and other proton-accepting solvents. $[(Ph_3P)_2N]^+[HCo_6(CO)_{15}]^-$ crystallizes in space group $P2_1/n$, with $Z = 4$ and unit cell constants at 80 K of $a = 17.922$ (3) Å, $b = 17.524$ (4) Å, $c = 16.329$ (8) Å, $\beta = 92.27$ (2)°, and $V = 5124$ (3) Å^3. The conventional R value is 0.071 for 3574 reflections with $I > 3\sigma(I)$. Neutron diffraction data were collected at the Brookhaven high flux beam reactor. The nonhydrogen portion of the structure was originally solved with X-ray data collected at 177 K.

Introduction

The bonding of hydrogen to transition metals has been shown to take a wide variety of forms by means of single-crystal X-ray[3] and neutron diffraction[4] analyses. Besides the terminal M–H bond such as is commonly found in mononuclear complexes,[5] many different types of hydrogen bridge bonds have been discovered. It is now known that metal–metal bonds can be bridged by one $[HW_2(CO)_9(NO)]$,[6] two $[H_2Os_3(CO)_{10}]$,[7] three $[H_3Ir_2(C_5Me_5)_2]^+$,[8] and even four H atoms $[H_8Re_2(PEt_2Ph)_4]$.[9] (Abbreviations used in this paper are as follows: Me = methyl, Et = ethyl, Ph = phenyl, Cp = cyclopentadienyl.) In some clusters, the hydride ligand has been shown to be bonded to three metal atoms on a triangular face of the cluster, as in $H_3Ni_4Cp_4$[10] and $HFeCo_3(CO)_9(P(OMe)_3)_3$.[11] Interstitial H atoms have been

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(2) Deceased February 2, 1980.

(3) For summaries of some of the large amount of X-ray work on transition-metal hydride complexes see, for example: (a) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides", E. L. Muetterties, Ed., Marcel Dekker, New York, 1971, p 33; (b) M. R. Churchill, *Adv. Chem. Ser.*, No. **167**, 36 (1978); (c) J. A. Ibers, *ibid.*, No. **167**, 26 (1978); (d) R. G. Teller and R. Bau, *Struct. Bonding* (*Berlin*), in press.

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characterized by powder neutron diffraction methods in the octahedral cavities of polymeric HNb_6I_{11}[12] and in the multihole polyhedral clusters $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$ by single-crystal diffraction techniques.[13] In this paper we report the first definitive characterization of an H atom located inside a hexanuclear metal polyhedron in a molecular crystal.[14]

We have recently found that protonation of $[Co_6(CO)_{15}]^{2-}$ gives rise to $[HCo_6(CO)_{15}]^-$ (vide infra). Spectroscopic characterization did not provide unambiguous information about the environment of the H atom in the monoanion. The NMR spectrum contains a signal at τ -13.2. This unexpectedly low-field signal (an H atom directly bound to a transition metal would be expected to have a resonance up field from tetramethylsilane) led to the hypothesis that the H atom might be bonded to a carbonyl group instead of to the cobalt core.[15] The recent synthesis of several metal formyl complexes and of complexes containing oxygen-bonded H atoms, all of which show characteristic downfield chemical shifts, provided additional evidence favoring this hypothesis. Examples of such molecules are $[Et_4N]^+[$*trans*-$((PhO)_3P)(CO)_3Fe(CHO)]^-$ (τ -4.82),[16] $CpRe(PPh_3)(NO)(CHO)$ (τ -7.23),[17] $(OC)_4Re[C(CH_3)O\cdots H\cdots OC(CH_3)]$ (τ -11.8),[18] $HFe_3(CO)_{10}(\mu\text{-}COH)$ (τ -5.0),[19] $Co_3(CO)_9(\mu_3\text{-}COH)$ (τ -11.25),[20] and several iridium, ruthenium, and osmium formyl clusters.[21]

Chemical reactivity of the $[HCo_6(CO)_{15}]^-$ ion gives support to a model in which a carbonyl group is protonated. Weak bases, even including acetone or ethanol, will deprotonate the monoanion to reform the parent $[Co_6(CO)_{15}]^{2-}$, suggesting that the H atom is not only rather acidic but also accessible to attack by incoming nucleophiles. The IR spectra of $[HCo_6(CO)_{15}]^-$ salts in solution, however, fail to reveal absorptions that might be attributed to an O–H or a formyl C–H stretching mode.

To provide unambiguous information about the location of the H atom in this system, we carried out single-crystal X-ray and neutron diffraction studies on the $[(Ph_3P)_2N]^+$ salt.

Experimental Section

All operations were carried out in a nitrogen atmosphere (O_2 < 5 ppm).

Synthesis of $K[HCo_6(CO)_{15}]$. A 700-mg sample of $K_2[Co_6(CO)_{15}]$[22] was dissolved in 7 mL of water, and 5 mL of concentrated hydrochloric acid added drop by drop while the solution was stirred vigorously. A black microcrystalline precipitate of the less soluble monoanion appeared; this was filtered off and washed with 10 mL of a 2:1 (by volume) mixture of water/concentrated hydrochloric acid followed by 10 mL of heptane to eliminate traces of $Co_4(CO)_{12}$ which was also formed. The vacuum-dried product gave the following analysis by atomic absorption: potassium, 5.02% (calcd 4.80%); cobalt, 43.00% (calcd 43.50%).

Synthesis of $[H_3O]^+[HCo_6(CO)_{15}]^-$. This particular "salt" was prepared as an intermediate for the synthesis of salts of other cations. The previous procedure was followed up to the step prior to filtration, and then 10 mL of diisopropyl ether was added to the aqueous suspension of $K[HCo_6(CO)_{15}]$ (the black microcrystalline precipitate). Upon vigorous stirring, the ether phase became deep red (due to the formation of $[H_3O]^+[HCo_6(CO)_{15}]^-$) while the aqueous phase became colorless (and contained KCl). The ether phase was dried under vacuum to obtain a black powder. This should be used immediately, as it decomposes in the solid state in 1 or 2 h to give mainly $Co_4(CO)_{12}$. $[H_3O]^+[HCo_6(CO)_{15}]^-$ is stable indefinitely in diisopropyl ether but decomposes in methylene chloride to give primarily $Co_4(CO)_{12}$.

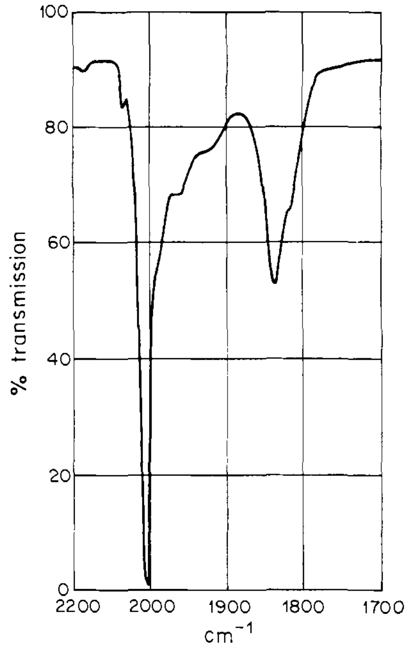

Figure 1. Infrared spectrum of $[PPh_3Me]^+[HCo_6(CO)_{15}]^-$ in diisopropyl ether.

Synthesis of $[Cat]^+[HCo_6(CO)_{15}]^-$ ($[Cat]^+$ = $[NMe_4]^+$, $[NBu_4]^+$, $[PPhMe_3]^+$, $[PPh_4]^+$, $[(Ph_3P)_2N]^+$). The above procedure was followed for the synthesis of $[H_3O]^+[HCo_6(CO)_{15}]^-$. Freshly prepared black powder of the $[H_3O]^+$ salt was dissolved in a solution of CatX (X = halide) in 2-propanol (30 mL, 0.06 M). A 40-mL sample of a mixture of H_2O/concentrated HCl (2:1 in volume) was quickly added to the resulting solution with vigorous stirring, until the precipitation of the salt was complete. A slow deprotonation of the $[HCo_6(CO)_{15}]^-$ anion takes place in 2-propanol solution, but the salts are stable indefinitely in the solid state. After being filtered off, washed, and dried, these salts were recrystallized from methylene chloride/heptane by using the slow diffusion technique. The $[PPh_4]^+[HCo_6(CO)_{15}]^-$ salt gave the following analysis: tetraphenylphosphonium, 31.04% (calcd 30.44%) (by gravimetric determination as the $[BPh_4]^-$ salt); cobalt, 32.10% (calcd 31.75%) (by atomic absorption).

Infrared Spectra. All infrared spectra were taken in the range 2200–1600 cm^{-1} (e.g., Figure 1). Data recorded for the $[PPh_4]^+$ salt in a variety of solvents are summarized (solvent, CO stretching modes (±5 cm^{-1})): diisopropyl ether, 2060 (w), 2005 (s), 1975 (sh), 1830 (ms); methylene chloride, 2070 (w), 2005 (s), 1950 (sh), 1815 (ms); tetrahydrofuran, 2060 (w), 2005 (s), 1920 (sh), 1810 (ms); acetone, 2060 (w), 2005 (s), 1920 (sh), 1810 (ms).

No absorptions could be found that could be attributed to either a formyl group or a hydroxyl group.

^1H NMR Studies. Spectra were recorded in the range τ -20 to +60. At -100 °C, brown solutions of the $[PPh_4]^+[HCo_6(CO)_{15}]^-$ salt in acetone-h_6 (145 mg/mL) or methylene chloride (98 mg/mL) showed a broad, strong peak at τ -13.5. When the temperature was increased, this signal decreased in intensity until it disappeared at -50 °C, but upon being recooled to -100 °C, it reappeared with the same intensity and width. A solution of the same salt in acetone-d_6 (147.9 mg/mL) showed no signal in the range τ -20 to +60 at -100 °C.

Stability of the $[HCo_6(CO)_{15}]^-$ Salts. All salts of $[HCo_6(CO)_{15}]^-$ that were investigated are deprotonated by water (immediately), methanol (in 5–10 min), and 2-propanol (in 1–2 h). The K^+, $[H_3O]^+$, and $[PPh_3Me]^+$ salts are all soluble and stable in diisopropyl ether. All salts are soluble in tetrahydrofuran, acetone, dimethylformamide, and dioxane, but they readily either deprotonate to form $[Co_6(CO)_{15}]^{2-}$, decompose to give $[Co(CO)_4]^-$, or both. However, this decomposition can be slowed markedly by cooling to -70 °C. All salts of $[HCo_6(CO)_{15}]^-$ were also found to be soluble and fairly stable in dichloromethane and therefore could usually be crystallized at low temperature by addition to dichloromethane solutions.

X-ray Data Collection and Structure Analysis. Crystal data and details of the structure refinements are summarized in Table I. A platelike

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Table I. Summary of Crystal Data and Refinement Results for $[(Ph_3P)_2N]^+[HCo_6(CO)_{15}]^-$

	X-ray (177 K)	neutron (80 K)
space group	$P2_1/n$	
Z	4	
mol wt	1313.4	
ρ(obsd), g cm^{-3}	1.65 (at room temp)	
a, Å	17.962 (6)	17.922 (3)
b, Å	17.561 (6)	17.524 (4)
c, Å	16.420 (8)	16.329 (8)
β, deg	92.31 (3)	92.27 (2)
V, Å^3	5175 (4)	5124 (3)
ρ(calcd), g cm^{-3}	1.685	1.702
cryst dimens (mm) along a, b, c, respectively	0.60 × 0.57 × 0.26	3.0 × 2.2 × 0.5
wavelength used, Å	0.71069 (Mo K$\bar{\alpha}$)	1.1622 (1)
abs coeff, cm^{-1}	12.37	1.178
$(\sin\theta)/\lambda$ limit, Å^{-1}	0.538 ($2\theta = 45°$)	0.524 ($2\theta = 75°$)^a
total no. of reflections measd	6440	6510
no. of unique reflections	6207	6069
no. of reflections used in the structural analysis (n_o) [$I > 3\sigma(I)$]	4966	3574
no. of variable parameters (n_v)	244	463
final agreement factors^b		
$R(F)$	0.085	0.071
$R(wF)$	0.078	0.042
$R(F^2)$		0.107
$R(wF^2)$		0.081

^{a} Some strong reflections were sampled out to $2\theta = 85°$. ^{b} $R(F) = \Sigma|F_o - |F_c||/\Sigma F_o$; $R(wF) = \{\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$; $R(F^2) = \Sigma|F_o^2 - |F_c|^2|/\Sigma F_o^2$; $R(wF^2) = \{\Sigma w(F_o^2 - |F_c|^2)^2/\Sigma wF_o^4\}^{1/2}$.

crystal of $[(Ph_3P)_2N]^+[HCo_6(CO)_{15}]^-$ was mounted in a glass capillary and space group $P2_1/n$ assigned on the basis of precession photographs.[23] Data collection was carried out on a Syntex $P2_1$ automated diffractometer equipped with an LT-1 low-temperature attachment. Unit cell constants, based on the accurate centering of 30 reflections at 177 K, are included in Table I together with other crystal data.

Intensities of 7243 reflections were measured in one quadrant of reciprocal space ($h,k,\pm l$) up to a 2θ limit of 45° with graphite-monochromatized Mo Kα radiation and a $\theta/2\theta$ scan technique. Each reflection was scanned from $[2\theta(\text{Mo K}\alpha_1) - 0.6]°$ to $[2\theta(\text{Mo K}\alpha_2) + 0.6]°$, with the scan speed varying between 2.0 and 14.6 deg/min depending upon the intensity of the reflection. Background counts of duration equal to one-fourth of scanning time were taken at the beginning and end of each scan. As a check on experimental stability, intensities of the 2,3,4 and $\bar{3}$,1,7 reflections were monitored at 60-reflection intervals. No systematic variation in these monitor intensities was observed during the entire period of data collection. Averaging of equivalent measurements resulted in a total of 4966 unique reflections having intensities greater than $3\sigma(I)$. The standard deviation of each intensity was estimated by using the expression[24] $\sigma(I) = [(\text{peak + normalized background counts}) + (0.04)^2 (\text{net intensity})^2]^{1/2}$. Intensities were corrected for Lorentz and polarization effects[25] and for absorption by an empirical ψ-scan method.[26]

The coordinates of the Co_6 cluster and the P and N atoms of the cation were obtained by direct methods[27] and those of the other nonhydrogen atoms obtained from subsequent structure factor calculations and difference Fourier syntheses.[28] In the least-squares refinement,[29] which minimized $\sum w(F_o - |F_c|)^2$,[30] the Co and P atoms were assigned anisotropic thermal parameters and the phenyl rings were treated as rigid groups[31] with C–C = 1.394 Å and C–C–C = 120°. Final agreement factors are included in Table I. During structure refinement, the isotropic temperature factor of one oxygen atom [O(15)] became unusually large. A difference Fourier synthesis revealed a peak of height 1.25 e/Å^3 within 0.90 Å of O(15), which was initially assigned as the postulated oxygen-bonded H atom. However, refinement of an H atom at this position gave rise to unreasonable bond distances and angles (O–"H" = 1.33 Å, C–O–"H" = 77°). When this atom was treated as a disordered oxygen [O(15)′], the results were more reasonable [C(15)–O(15) = 1.23 (2) Å, C(15)–O(15)′ = 1.24 (3) Å, Co(6)–C(15)–O(15) = 149 (1)°, Co(6)–C(15)–O(15)′ = 147(2)°; O(15), 75% occupancy; O(15)′, 25% occupancy].

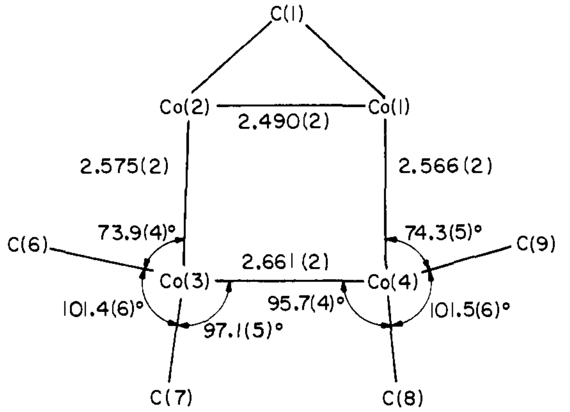

Figure 2. Schematic drawing, showing important bond distances and angles involving atoms Co(3) and Co(4) as determined in the X-ray analysis.

The X-ray analysis showed a Co_6 octahedron surrounded by ten terminal, one symmetrically bridging, and four asymmetrically bridging carbonyl groups. The geometry of the CO groups looked quite normal and gave no indication of a carbonyl-associated H atom. Attention thus shifted to the possibility that the H atom might be situated on the metal cluster itself. Attempts to locate the hydride ligand directly from difference Fourier syntheses were unsuccessful, even upon application of the low-angle data method.[32] However, it was noticed that one of the Co–Co edges [Co(3)–Co(4) = 2.661 (2) Å] was significantly longer than the others [range 2.490 (2)–2.596 (2) Å] and that the CO groups associated with this long edge seemed to be in a "splayed out" configuration. [This is seen in Figure 2: note that the angles C(7)–Co(3)–Co(4) and C(8)–Co(4)–Co(3) are both over 20° larger than C(6)–Co(3)–Co(2) and C(9)–Co(4)–Co(1), suggesting the possibility that C(7) and C(8) are being repelled sterically by an atom bridging the Co(3)–Co(4) bond]. These effects (i.e., bond lengthening coupled with angular deformations) had been utilized by us earlier to deduce the presence of edge-bridging H atoms in the $[H_2Re_3(CO)_{12}]^-$ anion.[33] We therefore suggested[34] that

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(23) $P2_1/n$ is a nonstandard setting of space group $P2_1/c$ (C_{2h}^5, No. 14) with equivalent positions (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$, $(^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$.

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(25) The *Lp* factor was calculated by assuming a polarization term for the graphite monochromator midway between that for a perfect and mosaic crystal. See K. A. Kerr and J. P. Ashmore, *Acta Crystallogr., Sect. A*, **A30**, 176 (1974).

(26) For a description of the empirical ψ-scan absorption correction, see M. R. Churchill, F. J. Hollander and J. P. Hutchinson, *Inorg. Chem.*, **16**, 2697 (1977). In our case, the reflections used to record the ψ-scan data were 3,$\bar{3}$,4 ($2\theta = 14.03°$, $\chi = 73.64°$); 5,$\bar{5}$,4 ($2\theta = 20.67°$, $\chi = 80.77°$), and 6,$\bar{6}$,7 ($2\theta = 26.50°$, $\chi = 77.09°$). The maximum/minimum intensity ratios for the three reflections are 1.38, 1.44, and 1.48, respectively.

(27) MULTAN: A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data [G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **A27**, 368 (1971)].

(28) For the X-ray portion of this work, major computations were performed on the USC IBM 370-158 computer using CRYM, an amalgamated set of crystallographic programs developed by Dr. Richard Marsh's group at the California Institute of Technology. For the neutron diffraction analysis, calculations were performed on CDC 6600 and 7600 computers using programs described by H. M. Berman, F. C. Bernstein, H. J. Bernstein, T. F. Koetzle, and G. J. B. Williams, Brookhaven National Laboratory Informal Report 21714, 1976.

(29) The scattering factors used in the X-ray analysis and the real and imaginary dispersion corrections for the Co atom were taken from Vol. III of the "International Tables for X-ray Crystallography", Kynoch Press, Birmingham, England, 1968.

(30) Weights were taken inversely proportional to the estimated variance for each reflection.

(31) The program used for the rigid-body refinement was UCIGLS, a version of W. R. Busing and H. A. Levy's ORFLS, modified by J. A. Ibers and R. J. Doedens. See R. J. Doedens in "Crystallographic Computing", F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, pp 198–200. Phenyl group positions were defined by three angles which correspond to rotations about the central axes and the coordinates of the group centroid, giving six refined parameters for each phenyl ring.

(32) (a) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965); (b) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.*, **95**, 4532 (1973).

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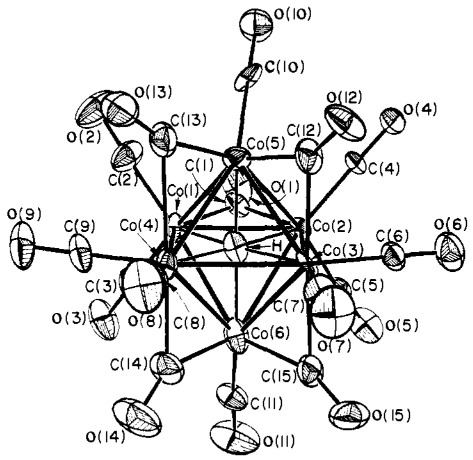

Figure 3. The $[HCo_6(CO)_{15}]^-$ anion with atomic numbering and thermal ellipsoids as determined in the neutron diffraction analysis. In this and all other plots, atoms are shown as 50% probability ellipsoids.

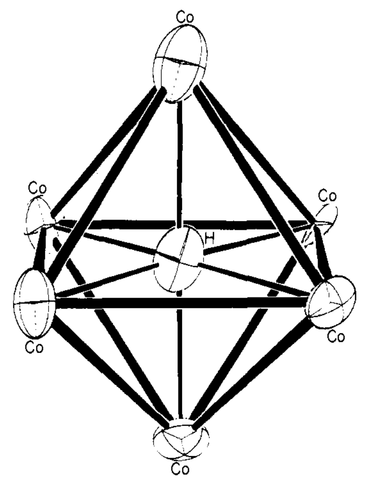

Figure 4. The HCo_6 core of $[HCo_6(CO)_{15}]^-$ (neutron results).

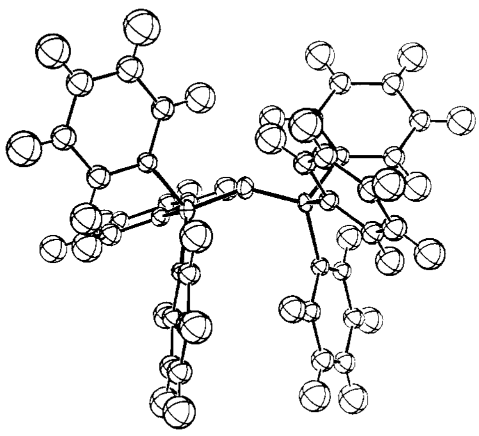

Figure 5. View of the $[(Ph_3P)_2N]^+$ cation (neutron results).

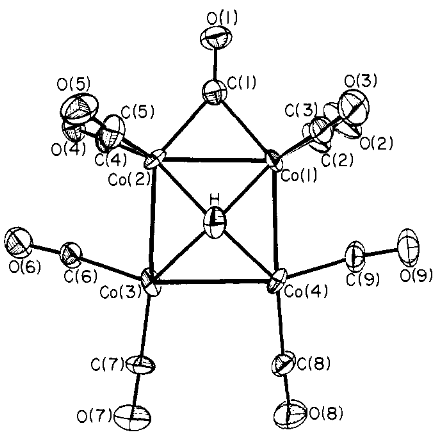

Figure 6. A plot of the central equatorial plane of the $[HCo_6(CO)_{15}]^-$ cluster (neutron results).

the H atom in $[HCo_6(CO)_{15}]^-$ bridged the Co(3)–Co(4) edge. However, this model was shown to be incorrect by the subsequent neutron diffraction analysis.

Neutron Data Collection and Structure Analysis. Neutron diffraction measurements[35] were carried out at the Brookhaven National Laboratory High Flux Beam Reactor. Calibration of the neutron beam from the Ge(220) monochromator with a standard KBr crystal[36] indicated a wavelength of 1.1622 (1) Å and flux at the sample of 3.6×10^6 neutrons $cm^{-2}\ s^{-1}$. The incident and diffracted beams were defined by 0.5-in. diameter apertures, which were found to greatly reduce background levels from the cryostat and incoherent scattering of the sample without measurably influencing the integrated peak intensities.

A platelike crystal of $[(Ph_3P)_2N]^+[HCo_6(CO)_{15}]^-$ was mounted approximately along the b axis on a hollow aluminum pin under a quartz cap in a nitrogen atmosphere. The sample was placed in a closed-cycle helium refrigerator[37] and cooled to 80 K. Unit-cell parameters obtained at this temperature are given in Table I. Intensity measurements were carried out with a $\theta/2\theta$ step-scan technique and counts accumulated at each step for approximately 3.3 s, with the exact time interval determined by monitoring the incident neutron flux. The scan width was defined as $\Delta 2\theta = 2.80°$ for $2\theta \leq 50°$, $\Delta 2\theta = 3.20°$ for $50° < 2\theta \leq 65°$, and $\Delta 2\theta = 3.60°$ for $2\theta > 65°$, with 70 steps per scan for $2\theta \leq 50°$, 80 steps for $50 < 2\theta \leq 65°$, and 60 steps for $2\theta > 65°$. One complete asymmetric unit was sampled out to $2\theta = 75°$. In addition, approximately 200 reflections with large $|F_c|$ values were measured in the range $75° < 2\theta < 85°$. Intensities of the 0,0,12 and $\bar{1}\bar{1},\bar{4},\bar{5}$ reflections were monitored at periodic intervals throughout data collection, and no systematic variation in their intensities was observed. Peak profiles were integrated by taking eight points on either end of each scan as a measure of the background. Altogether, 6510 reflections were measured, excluding those systematically absent in space group $P2_1/n$. Values of F_o^2 were calculated as $I(\sin 2\theta)$[38] and averaged for equivalent reflections. Out of 6069 independent reflections, 3574 reflections with $I > 3\sigma(I)$ were used in the subsequent refinements.

Initial positions of all nonhydrogen atoms were taken from the X-ray analysis. The coordinates of the phenyl H atoms were calculated by using a C–H bond length of 1.08 Å. A neutron difference Fourier synthesis[28] contained only one significant peak, located at the center of the Co_6 octahedron. The hydride ligand was placed at this position and subsequently refined in a normal manner. Due to the large number of independent atoms in this structure (106), it was not feasible to carry out full-matrix refinement with individual positional and anisotropic thermal parameters for all atoms. For a reduction in the number of parameters, each of the six phenyl groups was refined as a rigid body[31] and given an idealized geometry as in the X-ray analysis (C–H = 1.080 Å, C–C = 1.396 Å, C–C–C = 120°, C–C–H = 120°). The 11 atoms of each phenyl group were assigned individual isotropic thermal parameters, and all other atoms were assigned anisotropic temperature factors. Least-squares calculations were carried out minimizing $\sum w(F_o^2 - |F_c|^2)^2$ with weights based on counting statistics[30] and about 100 parameters varied at a time. Refinement of the 463 parameters based on 3574 reflections converged to give agreement factors quoted in Table I. After all parameters had converged, two additional cycles were carried out by varying only the atomic positions,[39] in order to prepare the variance–covariance matrix employed to calculate estimated standard deviations of interatomic dis-

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(34) R. Bau, paper presented at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978.

(35) (a) D. G. Dimmler, N. Greenlaw, M. A. Kelley, D. W. Potter, S. Rankowitz, and F. W. Stubblefield, *IEEE Trans. Nucl. Sci.*, **NS-23**, 398 (1976). (b) R. K. McMullan and in part L. C. Andrews, T. F. Koetzle, F. Reidinger, R. Thomas, and G. J. B. Williams, NEXDAS, Neutron and X-ray Data Acquisition System (unpublished).

(36) $a_0 = 6.600$ Å at 295 K.

(37) Air Products and Chemicals Inc., DISPLEX Model CS-202.

(38) No absorption correction was applied because ψ-scan intensity data for the $(1,\bar{8},2)$ reflection indicated that absorption effects were not severe (the mean variation over the scan was 6% and the maximum variation was 9%).

(39) The maximum shift in the last cycle was less than 0.1σ. The standard deviation of an observation of unit weight, $S = \{\sum w(F_o^2 - |F_c|^2)^2/(n_0 - n_v)\}^{1/2} = 2.3$.

Table II

(A) Final Atomic Parameters[a] for $[(Ph_3P)_2N]^+[HCo_6(CO)_{15}]^-$ (Except for Phenyl Groups)

	10^4x	10^4y	10^4z	$10^4\beta_{11}$ [or B]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
H	6566 (5)	3701 (6)	2533 (6)	17 (3)	26 (4)	29 (4)	−6 (3)	−4 (3)	−1 (4)
Co(1)	5639 (6)	3829 (7)	2914 (8)	6 (4)	15 (5)	26 (6)	0 (4)	2 (4)	−1 (5)
	5647 (1)	3821 (1)	2921 (1)	18 (1)	22 (1)	31 (1)	1 (1)	4 (1)	1 (1)
Co(2)	6815 (7)	4625 (7)	3026 (7)	16 (5)	6 (5)	15 (6)	0 (4)	−4 (4)	−3 (4)
	6807 (1)	4598 (1)	3008 (1)	22 (1)	23 (1)	23 (1)	−3 (1)	−3 (1)	−2 (1)
Co(3)	7547 (6)	3615 (8)	2191 (8)	5 (4)	24 (6)	16 (6)	0 (4)	−8 (4)	2 (5)
	7532 (1)	3597 (1)	2213 (1)	17 (1)	34 (1)	27 (1)	−1 (1)	3 (1)	−8 (1)
Co(4)	6283 (7)	2805 (7)	2074 (8)	19 (5)	9 (5)	25 (7)	−6 (4)	0 (5)	−3 (5)
	6285 (1)	2779 (1)	2104 (1)	17 (1)	25 (1)	44 (1)	−2 (1)	−2 (1)	−10 (1)
Co(5)	6861 (8)	3199 (7)	3451 (8)	21 (5)	17 (6)	11 (5)	−1 (4)	2 (4)	−3 (4)
	6861 (1)	3188 (1)	3463 (1)	25 (1)	27 (1)	22 (1)	6 (1)	2 (1)	1 (1)
Co(6)	6328 (7)	4151 (8)	1566 (9)	11 (5)	20 (6)	36 (8)	2 (4)	−1 (5)	−6 (6)
	6325 (1)	4114 (1)	1591 (1)	23 (1)	31 (1)	21 (1)	2 (1)	−3 (1)	0 (1)
N	1055 (2)	4187 (2)	2589 (2)	14 (1)	19 (1)	20 (2)	−2 (1)	−3 (1)	−4 (1)
	1056 (5)	4177 (5)	2590 (5)	19 (4)	26 (4)	24 (4)	−4 (3)	0 (3)	−5 (3)
P(1)	1008 (3)	3593 (3)	1850 (4)	13 (2)	12 (3)	15 (3)	0 (2)	−3 (2)	−2 (2)
	1006 (2)	3594 (2)	1864 (2)	16 (1)	19 (1)	21 (1)	1 (1)	−5 (1)	−1 (1)
P(2)	1566 (3)	4825 (3)	3001 (3)	11 (2)	14 (2)	10 (2)	0 (2)	−4 (2)	−1 (2)
	1565 (2)	4818 (2)	2995 (2)	18 (1)	20 (1)	19 (1)	1 (1)	−5 (1)	−2 (1)
C(1)	5856 (3)	4761 (3)	3495 (3)	14 (2)	20 (2)	21 (2)	2 (2)	−4 (2)	−1 (2)
	5874 (6)	4722 (6)	3480 (6)	[2.7 (2)]					
C(2)	5249 (3)	3364 (3)	3748 (4)	17 (2)	29 (2)	34 (3)	4 (2)	8 (2)	10 (2)
	5248 (8)	3370 (8)	3744 (9)	[5.4 (3)]					
C(3)	4833 (3)	4149 (3)	2333 (3)	11 (2)	20 (2)	37 (3)	2 (2)	−5 (2)	−5 (2)
	4850 (7)	4122 (7)	2362 (7)	[4.1 (3)]					
C(4)	7405 (3)	4819 (3)	3882 (3)	12 (2)	19 (2)	16 (2)	−2 (2)	−6 (2)	1 (2)
	7400 (6)	4798 (6)	3882 (7)	[2.9 (2)]					
C(5)	6836 (3)	5488 (3)	2475 (3)	20 (2)	21 (2)	23 (2)	−4 (2)	−7 (2)	4 (2)
	6838 (7)	5471 (7)	2465 (7)	[4 (3)]					
C(6)	8180 (3)	4367 (3)	2453 (3)	14 (2)	25 (2)	17 (2)	−5 (2)	0 (2)	−5 (2)
	8169 (7)	4330 (7)	2457 (7)	[3.8 (3)]					
C(7)	8103 (3)	3000 (3)	1616 (3)	17 (2)	23 (2)	27 (2)	5 (2)	5 (2)	−10 (2)
	8082 (8)	2979 (8)	1663 (8)	[4.5 (3)]					
C(8)	6713 (3)	1988 (3)	1619 (3)	16 (2)	14 (2)	33 (3)	2 (2)	−5 (2)	−7 (2)
	6685 (7)	1984 (7)	1661 (7)	[3.8 (3)]					
C(9)	5374 (3)	2464 (3)	2200 (3)	14 (2)	22 (2)	40 (3)	−4 (2)	−5 (2)	−3 (2)
	5372 (8)	2469 (8)	2212 (8)	[4.6 (3)]					
C(10)	6880 (3)	3322 (3)	4524 (3)	19 (2)	18 (2)	15 (2)	−1 (2)	0 (2)	−1 (2)
	6870 (7)	3303 (7)	4504 (7)	[3.5 (3)]					
C(11)	5841 (3)	4862 (3)	1005 (3)	23 (2)	19 (2)	24 (2)	6 (2)	−6 (2)	0 (2)
	5856 (7)	4792 (8)	1039 (8)	[4.2 (3)]					
C(12)	7862 (3)	3066 (3)	3298 (3)	10 (2)	26 (2)	33 (3)	2 (2)	0 (2)	1 (2)
	7842 (8)	3042 (7)	3303 (7)	[4.3 (3)]					
C(13)	6569 (3)	2212 (3)	3376 (4)	23 (2)	18 (2)	34 (3)	−5 (2)	−5 (2)	1 (2)
	6551 (7)	2231 (8)	3378 (8)	[4.2 (3)]					
C(14)	6015 (4)	3293 (3)	0968 (3)	38 (3)	21 (2)	26 (3)	−6 (2)	−6 (2)	−5 (2)
	6006 (8)	3299 (8)	1020 (9)	[4.9 (3)]					
C(15)	7217 (3)	4296 (3)	1105 (3)	13 (2)	38 (3)	24 (2)	−5 (2)	3 (2)	−5 (2)
	7179 (8)	4242 (8)	1126 (8)	[4.8 (3)]					
O(1)	5556 (4)	5179 (4)	3932 (4)	23 (2)	29 (3)	39 (4)	5 (2)	−3 (2)	−17 (3)
	5571 (5)	5169 (5)	3904 (5)	[4.8 (2)]					
O(2)	4979 (4)	3096 (5)	4313 (5)	26 (3)	44 (3)	59 (4)	11 (3)	19 (3)	26 (3)
	4989 (6)	3090 (6)	4308 (7)	[7.2 (3)]					
O(3)	4306 (4)	4361 (4)	1991 (5)	19 (2)	31 (3)	58 (4)	4 (2)	−12 (3)	−5 (3)
	4317 (5)	4341 (5)	2023 (5)	[5.5 (2)]					
O(4)	7805 (3)	4942 (3)	4420 (4)	14 (2)	22 (2)	23 (3)	0 (2)	−2 (2)	3 (2)
	7809 (4)	4931 (4)	4407 (5)	[3.6 (2)]					
O(5)	6866 (4)	6081 (4)	2172 (4)	29 (3)	23 (3)	42 (3)	7 (2)	−8 (3)	−6 (3)
	6873 (5)	6053 (5)	2158 (6)	[5.4 (2)]					
O(6)	8634 (4)	4810 (4)	2590 (4)	23 (3)	44 (3)	30 (3)	−9 (2)	4 (3)	−15 (3)
	8641 (5)	4756 (5)	2581 (5)	[5.2 (2)]					
O(7)	8481 (4)	2623 (5)	1260 (5)	33 (3)	38 (3)	53 (4)	4 (3)	13 (3)	−16 (3)
	8472 (6)	2569 (6)	1312 (6)	[7.0 (3)]					
O(8)	6969 (4)	1456 (4)	1358 (5)	29 (3)	21 (3)	63 (5)	7 (2)	1 (3)	−11 (3)
	6950 (5)	1450 (6)	1362 (6)	[5.8 (2)]					
O(9)	4803 (4)	2163 (4)	2261 (5)	16 (2)	27 (3)	66 (5)	−6 (2)	−5 (3)	2 (3)
	4793 (6)	2183 (5)	2264 (5)	[5.7 (2)]					
O(10)	6907 (4)	3395 (4)	5225 (4)	28 (3)	34 (3)	22 (3)	−4 (2)	4 (3)	−6 (3)
	6880 (5)	3400 (5)	5211 (5)	[4.9 (2)]					
O(11)	5593 (5)	5331 (4)	0599 (5)	60 (4)	29 (3)	44 (4)	19 (3)	−15 (3)	8 (3)
	5601 (6)	5298 (6)	0639 (6)	[7.4 (3)]					
O(12)	8433 (4)	2834 (4)	3545 (4)	20 (2)	40 (3)	29 (3)	9 (2)	−8 (2)	−5 (3)
	8412 (5)	2801 (5)	3578 (5)	[5.4 (2)]					
O(13)	6446 (4)	1588 (4)	3543 (4)	41 (3)	18 (3)	36 (3)	−3 (2)	−12 (3)	4 (3)
	6446 (5)	1600 (5)	3562 (5)	[5.1 (2)]					

Table II (*Continued*)

(A) Final Atomic Parameters[a] for $[(Ph_3P)_2N]^+[HCo_6(CO)_{15}]^-$ (Except for Phenyl Groups)

	10^4x	10^4y	10^4z	$10^4\beta_{11}$ [or B]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
O(14)	5817 (5)	3068 (4)	0323 (5)	75 (2)	30 (2)	40 (3)	−6 (2)	−23 (2)	−7 (2)
	5786 (6)	3052 (7)	0381 (7)	[8.3 (3)]					
O(15)[b]	7577 (4)	4542 (5)	0599 (4)	21 (3)	68 (5)	27 (3)	5 (3)	0 (2)	17 (3)
	7554 (7)	4600 (8)	0643 (8)	[4.4 (3)]					
O(15)'[b]	7523 (16)	4202 (17)	0490 (17)	[3.5 (6)]					

(B) Refined Group Parameters of the Phenyl Rings[c]

	group I	group II	group III	group IV	group V	group VI
10^5x	25601 (11)	4534 (11)	−2700 (10)	28483 (10)	5295 (11)	23402 (10)
10^5y	33587 (11)	19926 (12)	40946 (11)	41228 (11)	57961 (11)	59433 (11)
10^5z	9999 (11)	25349 (12)	5563 (11)	41774 (12)	41494 (12)	17320 (11)
ϕ, deg	−146.85 (15)	39.24 (16)	−165.87 (11)	−37.08 (9)	124.26 (9)	44.45 (9)
θ, deg	−127.70 (9)	−127.07 (10)	144.80 (9)	169.25 (9)	162.92 (9)	−168.91 (9)
ρ, deg	46.35 (16)	−34.66 (17)	131.00 (12)	−142.00 (11)	−139.72 (11)	137.77 (11)

[a] For each atom, the neutron diffraction result is given on the first line and the X-ray diffraction result, if available, on the second. The form of the anisotropic Debye-Waller factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] Atom O(15) was found to be disordered in the X-ray analysis. O(15) has 75% occupancy and O(15)' 25% occupancy. [c] x, y, and z are the origin of the rigid body in unit-cell fractional coordinates. (ϕ, θ, ρ) are defined in ref 31. *The actual coordinates of the individual C and H atoms of the phenyl groups are deposited as supplementary material.*

Table III. Interatomic Distances and Angles in the HCo_6 Core[a]

(A) Distances (Å)

	neutron	X-ray		neutron	X-ray
Co(1)–Co(2)[b]	2.527 (16)	2.490 (2)	Co(1)· · ·Co(3)	3.681 (19)	3.646 (2)
Co(1)–Co(4)	2.562 (18)	2.566 (2)	Co(2)· · ·Co(4)	3.658 (19)	3.629 (2)
Co(1)–Co(5)	2.575 (18)	2.575 (2)	Co(5)· · ·Co(6)	3.596 (19)	3.575 (2)
Co(1)–Co(6)	2.626 (19)	2.596 (2)	H–Co(1)	1.810 (15)	
Co(2)–Co(3)	2.619 (17)	2.575 (2)	H–Co(2)	1.854 (15)	
Co(2)–Co(5)	2.593 (17)	2.588 (2)	H–Co(3)	1.872 (16)	
Co(2)–Co(6)	2.639 (18)	2.594 (2)	H–Co(4)	1.805 (16)	
Co(3)–Co(4)	2.675 (17)	2.661 (2)	H–Co(5)	1.799 (17)	
Co(3)–Co(5)[c]	2.544 (18)	2.526 (2)	H–Co(6)	1.800 (18)	
Co(3)–Co(6)[c]	2.554 (17)	2.528 (2)			
Co(4)–Co(5)[c]	2.535 (18)	2.525 (2)	average H–Co	1.823 (13)	
Co(4)–Co(6)[c]	2.502 (19)	2.492 (2)			
overall average Co–Co	2.58	2.56			
bridged Co–Co	2.532 (9)	2.512 (9)			
nonbridged Co–Co	2.613 (15)	2.594 (12)			

(B) Angles (deg)

	neutron		neutron		neutron		neutron
Co(1)–H–Co(2)	87.1 (7)	Co(1)–H–Co(6)	93.3 (7)	Co(2)–H–Co(6)	92.5 (7)	Co(4)–H–Co(5)	89.4 (7)
Co(1)–H–Co(3)	176.2 (8)	Co(2)–H–Co(3)	89.3 (7)	Co(3)–H–Co(4)	93.3 (7)	Co(4)–H–Co(6)	87.9 (7)
Co(1)–H–Co(4)	90.2 (7)	Co(2)–H–Co(4)	177.4 (8)	Co(3)–H–Co(5)	87.7 (7)	Co(5)–H–Co(6)	174.9 (9)
Co(1)–H–Co(5)	91.0 (7)	Co(2)–H–Co(5)	90.4 (7)	Co(3)–H–Co(6)	88.1 (7)		

[a] Esd's of average values have been calculated as $[\Sigma(x_i - \bar{x})^2/n(n-1)]^{1/2}$, for $n > 2$, and set equal to the mean of individual esd's for $n = 2$. [b] Distance associated with the symmetrically bridging CO group. [c] Distances associated with asymmetrically bridging CO groups.

tances and angles. A final difference Fourier synthesis was essentially featureless. The neutron scattering lengths (b × 10^{-12} cm) used in the refinements were $b_{Co} = 0.250$, $b_P = 0.510$, $b_O = 0.5803$, $b_N = 0.940$, $b_C = 0.6648$, $b_H = -0.374$.[40]

Discussion

Figures 3 and 4 show the $[HCo_6(CO)_{15}]^-$ anion and its HCo_6 core together with associated thermal ellipsoids.[41] The $[(Ph_3P)_2N]^+$ cation is displayed in Figure 5, and a plot of the central equatorial plane of the anion is shown in Figure 6. Final atomic coordinates and bond distances and angles from both the X-ray and neutron diffraction analyses are given in Tables II–V.[42] Agreement between the two analyses is, for the most part, quite good; in the following discussion, reference will be made primarily to the generally more precise neutron values.

The most significant result of the neutron diffraction analysis is that the hydride ligand is found inside the Co_6 cluster, in contrast to earlier expectations from solution NMR and X-ray diffraction data. Within experimental error, the H atom lies at the geometric center of the octahedron: the individual Co–H distances [1.799 (17), 1.800 (18), 1.805 (16), 1.810 (15), 1.854 (18), 1.872 (16) Å] agree within 4.5σ, and the trans Co–H–Co angles [174.9 (9), 176.2 (8), 177.4 (8)°] are very nearly linear. The average Co–H distance [1.823 (13) Å] is significantly longer than that found for the face-bridging H atom in $HFeCo_3(CO)_9(P(OMe)_3)_3$ [1.734 (4) Å],[11] indicating that the space inside the octahedral cluster is more than sufficient to accommodate an H atom.

The cobalt and carbonyl positions as determined from the neutron diffraction study at 80 K are essentially the same as those derived from the X-ray analysis at 177 K, with the exception that the oxygen which the X-ray refinement indicated to be disordered [O(15)] is found to be ordered in the neutron analysis. The anion contains ten terminal, one symmetrically bridging [C(1)O(1)], and four asymmetrically bridging [C(12)O(12) through C(15)-O(15)] carbonyl groups. The symmetry is approximately C_{2v}, with

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(40) C. G. Shull, private communication, 1972.

(41) C. K. Johnson, ORTEP-II, Oak Ridge National Laboratory Report ORNL-5138, 1976.

(42) Listings of observed and calculated structure factors are available (see paragraph at the end of the paper for details).

(43) See references in R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, **96**, 7601 (1974).

Table IV. Interatomic Distances (Å) and Angles (Deg) Involving the Carbonyl Groups

	neutron			X-ray		
	C–Co	O–C	O–C–Co	C–Co	O–C	O–C–Co
O(1)–C(1)–Co(1)	1.920 (14)	1.169 (7)	138.2 (6)	1.865 (11)	1.195 (13)	138.4 (9)
O(1)–C(1)–Co(2)	1.923 (13)	1.169 (7)	139.6 (6)	1.887 (11)	1.195 (13)	138.4 (9)
O(2)–C(2)–Co(1)	1.756 (14)	1.158 (8)	176.3 (8)	1.745 (15)	1.164 (18)	177.8 (13)
O(3)–C(3)–Co(1)	1.786 (12)	1.140 (7)	177.3 (8)	1.751 (12)	1.154 (15)	176.8 (11)
O(4)–C(4)–Co(2)	1.754 (12)	1.133 (6)	177.9 (7)	1.787 (11)	1.135 (14)	176.1 (10)
O(5)–C(5)–Co(2)	1.760 (13)	1.154 (8)	174.7 (8)	1.774 (12)	1.144 (15)	175.8 (11)
O(6)–C(6)–Co(3)	1.780 (13)	1.140 (8)	173.7 (7)	1.759 (12)	1.143 (15)	172.5 (11)
O(7)–C(7)–Co(3)	1.762 (14)	1.125 (8)	177.3 (7)	1.744 (14)	1.172 (17)	177.7 (12)
O(8)–C(8)–Co(4)	1.800 (13)	1.130 (8)	176.9 (8)	1.744 (12)	1.169 (16)	179.7 (11)
O(9)–C(9)–Co(4)	1.755 (13)	1.159 (8)	172.7 (7)	1.743 (14)	1.161 (18)	172.6 (12)
O(10)–C(10)–Co(5)	1.765 (13)	1.150 (7)	178.6 (7)	1.721 (12)	1.174 (14)	178.3 (11)
O(11)–C(11)–Co(6)	1.758 (15)	1.136 (8)	172.9 (8)	1.699 (14)	1.186 (17)	173.1 (12)
O(12)–C(12)–Co(3)	2.104 (13)	1.159 (7)	131.4 (6)	2.094 (13)	1.181 (17)	133.6 (11)
O(12)–C(12)–Co(5)	1.835 (14)	1.159 (7)	148.4 (7)	1.810 (14)	1.181 (17)	146.1 (11)
O(13)–C(13)–Co(4)	2.403 (14)	1.150 (8)	125.8 (6)	2.335 (13)	1.167 (16)	126.5 (10)
O(13)–C(13)–Co(5)	1.810 (14)	1.150 (8)	161.8 (7)	1.773 (14)	1.167 (16)	159.0 (11)
O(14)–C(14)–Co(4)	2.038 (14)	1.166 (8)	135.4 (7)	2.045 (15)	1.188 (19)	131.8 (11)
O(14)–C(14)–Co(6)	1.867 (14)	1.166 (8)	144.9 (8)	1.791 (14)	1.188 (19)	147.4 (13)
O(15)–C(15)–Co(3)	2.200 (13)	1.152 (8)	129.9 (6)	2.185 (14)	1.234 (19)	129.9 (11)
O(15)–C(15)–Co(6)	1.809 (14)	1.152 (8)	151.6 (7)	1.755 (14)	1.234 (19)	148.7 (12)
O(15)'–C(15)–Co(3)				2.185 (14)	1.238 (31)	121.5 (16)
O(15)'–C(15)–Co(6)				1.755 (14)	1.238 (31)	146.7 (17)

	neutron	X-ray		neutron	X-ray
Co(1)–C(1)–Co(2)	82.2 (5)	83.2 (4)	Co(4)–C(14)–Co(6)	79.6 (6)	80.7 (6)
Co(3)–C(12)–Co(5)	80.2 (5)	80.3 (5)	Co(3)–C(15)–Co(6)	78.5 (6)	79.0 (5)
Co(4)–C(13)–Co(5)	72.4 (5)	74.5 (5)			
C(1)–Co(1)–Co(2)	49.0 (4)	48.8 (3)	C(10)–Co(5)–Co(1)	105.6 (7)	105.4 (4)
C(1)–Co(1)–Co(4)	140.7 (7)	140.2 (3)	C(10)–Co(5)–Co(2)	98.5 (6)	99.9 (4)
C(1)–Co(1)–Co(5)	92.5 (5)	91.8 (3)	C(10)–Co(5)–Co(3)	141.0 (7)	142.0 (4)
C(1)–Co(1)–Co(6)	98.0 (7)	98.4 (3)	C(10)–Co(5)–Co(4)	154.9 (8)	153.8 (4)
C(1)–Co(2)–Co(1)	48.9 (4)	48.0 (3)	C(11)–Co(6)–Co(1)	110.4 (7)	110.4 (4)
C(1)–Co(2)–Co(3)	139.9 (6)	139.7 (3)	C(11)–Co(6)–Co(2)	112.8 (7)	112.9 (5)
C(1)–Co(2)–Co(5)	91.9 (6)	90.9 (3)	C(11)–Co(6)–Co(3)	150.2 (8)	149.9 (4)
C(1)–Co(2)–Co(6)	97.5 (5)	97.9 (3)	C(11)–Co(6)–Co(4)	145.0 (8)	145.0 (5)
C(2)–Co(1)–Co(2)	123.8 (7)	125.0 (5)	C(12)–Co(3)–Co(2)	89.1 (5)	90.4 (4)
C(2)–Co(1)–Co(4)	106.9 (7)	106.7 (5)	C(12)–Co(3)–Co(4)	90.9 (6)	90.0 (4)
C(2)–Co(1)–Co(5)	84.0 (6)	84.6 (5)	C(12)–Co(3)–Co(5)	45.3 (4)	44.9 (4)
C(2)–Co(1)–Co(6)	164.6 (8)	164.4 (5)	C(12)–Co(3)–Co(6)	135.0 (7)	135.0 (4)
C(3)–Co(1)–Co(2)	121.3 (7)	122.0 (4)	C(12)–Co(5)–Co(1)	146.2 (7)	145.8 (4)
C(3)–Co(1)–Co(4)	107.9 (7)	108.3 (4)	C(12)–Co(5)–Co(2)	96.2 (6)	96.9 (4)
C(3)–Co(1)–Co(5)	166.9 (8)	167.1 (4)	C(12)–Co(5)–Co(3)	54.6 (5)	54.8 (4)
C(3)–Co(1)–Co(6)	83.4 (6)	84.3 (4)	C(12)–Co(5)–Co(4)	102.2 (6)	101.5 (4)
C(4)–Co(2)–Co(1)	129.8 (7)	128.6 (4)	C(13)–Co(4)–Co(1)	85.1 (5)	84.5 (3)
C(4)–Co(2)–Co(3)	104.3 (6)	104.1 (4)	C(13)–Co(4)–Co(3)	90.9 (5)	91.2 (3)
C(4)–Co(2)–Co(5)	87.8 (5)	86.7 (3)	C(13)–Co(4)–Co(5)	42.9 (4)	42.6 (3)
C(4)–Co(2)–Co(6)	161.6 (7)	162.1 (4)	C(13)–Co(4)–Co(6)	133.7 (6)	133.1 (3)
C(5)–Co(2)–Co(1)	118.2 (6)	119.2 (4)	C(13)–Co(5)–Co(1)	98.4 (6)	97.1 (4)
C(5)–Co(2)–Co(3)	107.1 (6)	107.9 (4)	C(13)–Co(5)–Co(2)	153.7 (7)	151.2 (4)
C(5)–Co(2)–Co(5)	164.4 (7)	165.8 (4)	C(13)–Co(5)–Co(3)	111.5 (7)	111.4 (4)
C(5)–Co(2)–Co(6)	79.8 (5)	81.3 (4)	C(13)–Co(5)–Co(4)	64.7 (5)	63.0 (4)
C(6)–Co(3)–Co(2)	72.6 (5)	73.9 (4)	C(14)–Co(4)–Co(1)	94.9 (6)	92.2 (4)
C(6)–Co(3)–Co(4)	160.1 (8)	161.6 (4)	C(14)–Co(4)–Co(3)	90.6 (5)	89.6 (4)
C(6)–Co(3)–Co(5)	109.9 (7)	110.5 (4)	C(14)–Co(4)–Co(5)	138.2 (7)	136.0 (4)
C(6)–Co(3)–Co(6)	110.5 (7)	111.7 (4)	C(14)–Co(4)–Co(6)	47.2 (4)	45.2 (4)
C(7)–Co(3)–Co(2)	174.7 (8)	175.0 (5)	C(14)–Co(6)–Co(1)	97.2 (7)	97.6 (5)
C(7)–Co(3)–Co(4)	97.6 (6)	97.1 (5)	C(14)–Co(6)–Co(2)	143.9 (8)	145.1 (5)
C(7)–Co(3)–Co(5)	123.9 (7)	122.9 (5)	C(14)–Co(6)–Co(3)	98.5 (7)	100.1 (5)
C(7)–Co(3)–Co(6)	120.3 (7)	120.6 (5)	C(14)–Co(6)–Co(4)	53.2 (5)	54.1 (5)
C(8)–Co(4)–Co(1)	171.0 (8)	171.8 (4)	C(15)–Co(3)–Co(2)	85.9 (5)	85.7 (4)
C(8)–Co(4)–Co(3)	94.3 (6)	95.7 (4)	C(15)–Co(3)–Co(4)	91.8 (5)	90.5 (4)
C(8)–Co(4)–Co(5)	114.6 (7)	115.8 (4)	C(15)–Co(3)–Co(5)	133.2 (6)	132.7 (4)
C(8)–Co(4)–Co(6)	126.3 (7)	126.4 (4)	C(15)–Co(3)–Co(6)	43.9 (4)	43.0 (4)
C(9)–Co(4)–Co(1)	74.7 (6)	74.3 (5)	C(15)–Co(6)–Co(1)	146.2 (8)	147.1 (4)
C(9)–Co(4)–Co(3)	163.8 (8)	162.7 (5)	C(15)–Co(6)–Co(2)	93.8 (6)	94.7 (4)
C(9)–Co(4)–Co(5)	109.7 (7)	110.7 (4)	C(15)–Co(6)–Co(3)	57.6 (5)	58.1 (4)
C(9)–Co(4)–Co(6)	113.7 (7)	111.7 (5)	C(15)–Co(6)–Co(4)	108.2 (7)	107.8 (5)

a noncrystallographic twofold axis passing through atoms H, C(1), and O(1). The asymmetrically bridging carbonyl groups span four contiguous edges of the octahedron [defined by atoms Co(3), Co(4), Co(5), and Co(6)], with the short Co–C distances [range 1.809 (14)–1.867 (14) Å] associated with Co(5) and Co(6) and the long Co–C distances [range 2.038 (14)–2.403 (14) Å] associated with Co(3) and Co(4). A rather striking correlation is seen among the interatomic distances and angles involving the asymmetric carbonyl bridges (see Table IV). As the degree of asymmetry (as expressed in the Co–C bond distances) increases, the C–O bond length becomes shorter. For each CO group, the shorter Co–C distance corresponds to the larger Co–C–O angle.

Table V. Selected Distances (Å) and Angles (Deg) in the $[(Ph_3P)_2N]^+$ Cation

	neutron	X-ray		neutron	X-ray
P(1)-N-P(2)	142.9 (4)	142.9 (6)	N-P(2)	1.579 (7)	1.579 (9)
N-P(1)	1.593 (7)	1.572 (9)			
P(1)-C(101)	1.790 (6)	1.803 (7)	P(2)-C(401)	1.791 (6)	1.809 (7)
P(1)-C(201)	1.800 (6)	1.789 (8)	P(2)-C(501)	1.787 (6)	1.803 (8)
P(1)-C(301)	1.785 (7)	1.800 (8)	P(2)-C(601)	1.812 (6)	1.805 (7)
C(101)-P(1)-C(201)	107.1 (3)	107.2 (6)	C(401)-P(2)-C(501)	107.8 (3)	107.8 (3)
C(101)-P(1)-C(301)	109.0 (3)	108.6 (4)	C(401)-P(2)-C(601)	106.7 (3)	106.3 (4)
C(201)-P(1)-C(301)	107.6 (3)	106.8 (5)	C(501)-P(2)-C(601)	108.7 (3)	108.8 (4)
N-P(1)-C(101)	115.1 (4)	115.1 (5)	N-P(2)-C(401)	112.0 (3)	111.5 (4)
N-P(1)-C(201)	107.8 (4)	108.3 (4)	N-P(2)-C(501)	107.1 (3)	106.6 (4)
N-P(1)-C(301)	109.9 (3)	110.5 (4)	N-P(2)-C(601)	114.3 (3)	115.7 (4)
N-P(av)	1.586 (7)	1.576 (9)	C-P-C(av)	107.8 (4)	107.6 (4)
P-C(av)	1.794 (4)	1.802 (3)	N-P-C(av)	111.0 (14)	111.3 (15)
P-N-P(av)	142.9 (4)	142.9 (6)			

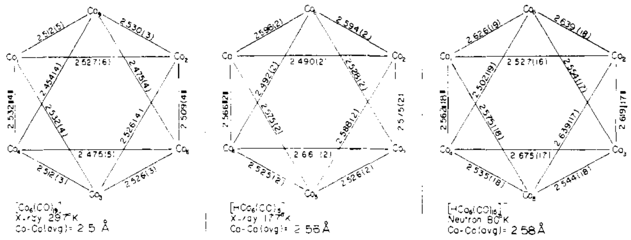

Figure 7. A comparison of the Co_6 cores of $[Co_6(CO)_{15}]^{2-}$ and $[HCo_6(CO)_{15}]^-$.

The structure analysis of $[HCo_6(CO)_{15}]^-$ provides the first example of an interstitial H atom in a hexanuclear metal cluster that has been accurately characterized by single-crystal neutron diffraction techniques. As was mentioned above, earlier powder neutron diffraction studies by Simon[12] showed the existence of this type of structure in polymeric HNb_6I_{11},[44] while more recent single-crystal neutron diffraction work has been carried out on two large clusters, $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$, in which the H atoms were also found to be lodged in octahedral cavities.[13] There are, however, significant differences in the H atom coordination between the Co_6 and Ni_{12} systems. In contrast to the near perfect centering of the H atom in $[HCo_6(CO)_{15}]^-$, those in the Ni_{12} clusters are displaced from the centers of the octahedral holes toward one of the nonequivalent faces. Thus, in a sense the interstitial H atoms in $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$ may be considered pseudo triply bridging, capping a triangular face of an octahedron from within.

In comparing $[HCo_6(CO)_{15}]^-$ with its deprotonated precursor, $[Co_6(CO)_{15}]^{2-}$,[45] one also finds significant differences. The arrangement of carbonyl groups in the two clusters is markedly different: $[Co_6(CO)_{15}]^{2-}$ has approximate C_{3v} symmetry, with nine terminal, three bridging, and three triply bridging carbonyl groups, while $[HCo_6(CO)_{15}]^-$ has approximate C_{2v} symmetry, with a completely different carbonyl group arrangement as described earlier. Thus, it is seen that the simple act of protonation has exerted a profound effect on the arrangement of ligands around the cluster. A comparison of the metal-metal distances in $[Co_6(CO)_{15}]^{2-}$ and $[HCo_6(CO)_{15}]^-$ (see Figure 7) shows that there is a small but significant expansion of the octahedral core upon insertion of the proton: the average Co–Co distance increases from 2.51 Å in $[Co_6(CO)_{15}]^{2-}$ to 2.58 Å in $[HCo_6(CO)_{15}]^-$.[46] This is similar to the situation in $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$, where Ni–Ni distances associated with H-filled octahedral cavities are 0.02–0.07 Å longer than those associated with empty cavities.[13] In the case of octahedral ruthenium clusters, metal–metal bond distances in $[Ru_6(CO)_{18}]^{2-}$, which contains both μ- and μ_3-bridging carbonyl groups, range from 2.80 to 2.89 Å.[47] In $[HRu_6(CO)_{18}]^-$ with only terminal carbonyls, the average Ru–Ru distance is found to be 2.87 (1) Å.[48] Very recent neutron diffraction results[49] on $[Ph_4As]^+[HRu_6(CO)_{18}]^-$ confirm that the octahedral cavity is occupied. A Ru–H distance of 2.04 (1) Å was measured for that compound.

As described in the Experimental Section, the observation of distortions of the anion in the X-ray analysis (Figure 2) led us to the incorrect conclusion that an edge-bridging H atom was present. With hindsight, the elongation of the Co(3)–Co(4) bond[50] (and the distortion of the Co–Co–C angles around that bond) may be ascribed to steric interaction between the coplanar C(7)O(7) and C(8)O(8) carbonyl groups, which are at van der Waals contact distances apart [C(7)···C(8) = 3.04 Å] (Figure 6). The distortion of the Co(1)Co(2)Co(3)Co(4) square is further exaggerated by the presence of the symmetrically bridging carbonyl group C(1)O(1) which shortens[51] the Co(1)–Co(2) distance. In the future, it would seem prudent to examine the arrangement of carbonyl groups very carefully before invoking molecular distortion arguments to locate H atoms based on X-ray data.

The interpretation of the solution NMR data remains puzzling. On one hand, one could argue that the low-field NMR signal represents a proton that is predominantly associated with the carbonyl ligands in solution. The fact that $[HCo_6(CO)_{15}]^-$ is deprotonated readily by weak bases such as water, methanol, and even tetrahydrofuran, and the similarity of the ^1H NMR chemical shift of $[HCo_6(CO)_{15}]^-$ with those of $H_2Fe_3(CO)_{10}(\mu\text{-COH})$[19] and $(OC)_4Re[C(CH_3)O\cdots H\cdots OC(CH_3)]$[18] argue for the presence of a carbonyl-associated H atom in solution. The disappearance of the ^1H NMR signal of $[HCo_6(CO)_{15}]^-$ when the compound is dissolved in acetone-d_6 also seems to support this point of view.[52]

On the other hand, one could also make a plausible argument that the ^1H NMR chemical shift of τ −13.2 in $[HCo_6(CO)_{15}]^-$ does represent an H atom that remains predominantly in the cluster in solution. The low-field resonance of the interstitial H

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[44] The analysis is of rather low precision, and detailed information such as Nb–H bond lengths were not given (see ref 12).

[45] V. Albano, P. Chini, and V. Scatturin, *J. Organomet. Chem.*, **15**, 423 (1968).

[46] However, it should be pointed out that the difference in Co–Co lengths between $[Co_6(CO)_{15}]^{2-}$ and $[HCo_6(CO)_{15}]^-$ might be partly accounted for by the fact that the two ions do not have the same number and type of bridging carbonyl groups and by the change in overall charge. For purposes of comparison, the average Co–Co distance is 2.49 Å in $Co_4(CO)_{12}$ [C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966)], 2.50 Å in $[Co_6(CO)_{14}]^{4-}$ [V. G. Albano, P. L. Bellon, P. Chini, and V. Scatturin, *J. Organomet. Chem.*, **16**, 461 (1969)], and 2.66 Å in $[Co_6(CO)_{14}C]^-$ [V. G. Albano, P. Chini, G. Ciani, M. Sansoni, D. Strumolo, B. T. Heaton, and S. Martinengo, *J. Am. Chem. Soc.*, **98**, 5027 (1976)].

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[50] The Co(3)–Co(4) distance, which was found to be the longest Co–Co bond in the X-ray study [2.661 (2) Å], is also the longest in the neutron study [2.675 (17) Å].

[51] Carbonyl-bridged metal–metal bonds are known to be significantly shorter than unbridged metal–metal bonds.

[52] It should be noted that the ^1H NMR signal of $[HRu_6(CO)_{18}]^-$ (τ −6.4), which is also known[49] to contain an interstitial H atom, does not indicate exchange with solvent.[48] However, the NMR data for $[HRu_6(CO)_{18}]^-$ were recorded in CD_2Cl_2 solution, whereas the proton exchange of $[HCo_6(CO)_{15}]^-$ was observed to take place in $(CD_3)_2CO$ solution.

atom in $[HRu_6(CO)_{18}]^-$ (τ -6.4) supports this point of view.[52] Although attempts have been made in the past to calculate the chemical shifts of hydride ligands,[53] it is generally acknowledged that this is a difficult problem and that the calculations are subject to wide uncertainties. "Normal" hydridic resonances are usually found in the range τ +10 to +50,[54] and the chemical shifts generally move to more positive τ values as the coordination number of hydrogen increases (i.e., along the series: terminal, bridging, triply bridging). Most interstitial hydride complexes follow this trend {e.g., $[HNi_{12}(CO)_{21}]^{3-}$ (τ 34),[13] $[H_2Ni_{12}(CO)_{21}]^{2-}$ (τ 28),[13] $[H_2Rh_{13}(CO)_{24}]^{3-}$ (τ 36.7),[55] and $[H_3Rh_{13}(CO)_{24}]^{2-}$ (τ 39.3)[55]}, but the two hexanuclear hydride complexes $[HCo_6(CO)_{15}]^-$ and $[HRu_6(CO)_{18}]^-$ are obviously exceptions to this rule. There are also a small number of hydride complexes involving the early transition metals and actinides with anomalously low τ values [e.g., $H_2Zr(C_5Me_5)_2$ (τ 2.54)[56] and $H_4Th_2(C_5Me_5)_2$ (τ -9.25)[57]]. Finally, it should be noted that the chemical shifts of most other interstitial atoms such as C, N, P, or Rh have been found at low fields.[58]

Concluding Remarks

Hydrides now join carbides,[59] nitrides,[60] phosphides,[61] and sulfides[62] as classes of compounds in which small atoms can be found embedded within metal clusters. There are, however, profound differences between the chemical behavior of interstitial H and other atoms. In particular, the easy exchange of protons between the cluster and its surroundings, as we seem to be observing in $[HCo_6(CO)_{15}]^-$, is not found in other interstitial complexes. For example, mass spectral evidence[63] indicates that interstitial C atoms are held very tightly within metal clusters and are released only when the metal aggregate itself is broken apart.

Now that one-, two-, three-, and six-coordinate H atoms have been definitively characterized by neutron diffraction, one wonders whether complexes of four- or five-coordinate H atoms can also be found. The possible existence of interstitial H atoms in tetrahedral metal clusters is an intriguing question. Carbide complexes with tetrahedral clusters are unknown. Earlier speculation[64] that an interstitial H atom might exist in $HFeCo_3(CO)_{12}$ has been essentially disproved by recent X-ray[65] and neutron[11] diffraction experiments on the closely related compound $HFeCo_3(CO)_9(P(OMe)_3)_3$, which unambiguously showed the H atom to be outside the M_4 tetrahedron in a face-bridging position. We recently pointed out, in analyzing the dimensions of the $FeCo_3$ core in $HFeCo_3(CO)_9(P(OMe)_3)_3$, that there is insufficient room in that cluster to accommodate an H atom.[11] Although there is ample space for H atom to "rattle around" in an octahedral cavity (as evidenced by the off-center location of the H atoms in $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$),[13] it is unclear if a tetrahedral cluster would be able to accommodate an H atom in its interior without substantial "swelling" (and hence destabilization). For binary metal hydrides, in which the occupation of tetrahedral holes is a well-documented phenomenon,[66] the lattice itself provides the stabilizing force that keeps the structure intact. The same argument might be made for large metal clusters (e.g., with 12 atoms or more). For small molecular complexes, however, there are no such stabilizing factors, and thus interstitial hydride complexes involving tetrahedral metal clusters probably could not exist, except perhaps if external bridging ligands were present to provide added stability.

The chances of finding five-coordinate H atoms seem more promising. Although a trigonal bipyramid contains no more interior space than a tetrahedron with edges of the same length, a square pyramid has a cavity size which is essentially the same as that of an octahedron. Indeed, carbide clusters are known with square-pyramidal geometry,[67] and so it is reasonable to expect five-coordinate H atoms to exist in square-pyramidal clusters or in larger metal clusters that contain square-pyramidal cavities.[68]

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Supplementary Material Available: Listings of structure factor amplitudes for the X-ray and neutron diffraction analyses and a table of the coordinates of the C and H atoms of the phenyl groups (17 pages). Ordering information is given on any current masthead page.

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