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## Anharmonic Thermal Motion and Low-Temperature Phase Transition in Tetraethylammonium Octahydrido(triphenylphosphine)rhenate(1–)

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### Abstract

[N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>][ReH<sub>8</sub>{P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}],  $M_r = 586.81$ , orthorhombic with lattice constants at 295 K of  $a = 10.615$  (3),  $b = 25.338$  (7) and  $c = 10.134$  (2) Å,  $V = 2725.6$  (1.2) Å<sup>3</sup> in space group  $P2_12_12_1$  with  $Z = 4$ ; at 163 K, monoclinic with  $a = 10.497$  (3),  $b = 24.970$  (10),  $c = 10.067$  (4) Å and  $\beta = 91.06$  (3)°,  $V = 2638.2$  (1.7) Å<sup>3</sup> in space group  $P2_1$  with  $Z = 4$ .  $F(000) = 1184$ . At 295 K,  $D_m = 1.45$  (8),  $D_x = 1.430$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 0.4587$  cm<sup>-1</sup>; at 163 K,  $D_x = 1.477$  g cm<sup>-3</sup>. Anisotropic damage is suffered by exposure to Mo K $\alpha$  radiation both at 295 and 163 K; correction for this effect results in an internal agreement indicator  $R_{\text{int}}$  on  $F_m$  at 295 K of 0.0187 and, on  $F_m$  at 163 K, 0.0339. The Re atom undergoes such severe anharmonic oscillation at 295 K that P was the only other atom detectable in subsequent analysis without adequate thermal motion modelling. Inclusion of all tensor coefficients to seventh order in the Gram–Charlier expansion for the probability density function led to a final structural solution. Refinement on  $F_m^2$  measured at 295 K by least squares gave the indicators (on  $F_m$ ):  $R = 0.0132$ ,  $wR = 0.0119$  and  $S = 0.902$  for 2391 independent observations (averaged over the full form) with  $F_m^2 \geq 3\sigma(F_m^2)$ . The eight H atoms and one P atom form a distorted equatorially girdled trigonal prism about Re with the P atom occupying a prism corner. The average Re–H

distance is 1.92 (11) Å and Re–P distance is 2.419 (3) Å; the systematic increase in both distances is a function of the Re-atom anharmonic motion. The cation is disordered at 295 K, with local pseudo-inversion through the N atom. The low-temperature phase contains two independent molecules in the asymmetric unit with coordinates related to those of the high-temperature phase by a simple transformation and displacement. The anionic displacements between the phases at 295 and 163 K do not exceed 0.25 Å, but atoms in the cation undergo displacements over this temperature interval as large as 1.8 Å. Refinement on  $F_m^2$  at 163 K gave  $R(F_m) = 0.0645$ ,  $wR = 0.0638$ , and  $S = 2.038$  for 6306  $F_m^2 \geq 3\sigma(F_m^2)$ . Severe anharmonic motion by the two independent Re atoms remains present at 163 K and was fitted to sixth order in the Gram–Charlier expansion. The lower quality data at 163 K did not allow the H atoms to be located. The Re–P distances in the two independent anions at 163 K are 2.397 (10) and 2.422 (11) Å.

### Introduction

The molecular structures of numerous transition-metal polyhydrides have been reported. The first determination of an Re polyhydride was that of K<sub>2</sub>ReH<sub>9</sub>, in which it was shown by neutron diffraction that the ReH<sub>9</sub><sup>2-</sup> anion forms a regular equatorially tricapped

trigonal prism (Abrahams, Ginsberg & Knox, 1964). The Re—H distance averages 1.68 (1) Å at 295 K. Most polyhydride complexes include one or more nonhydride ligands for stability, usually a high-field ligand such as a tertiary phosphine. The  $[\text{Re}_2(\mu\text{-H})_3\text{H}_6\{\text{CH}_3\text{C}(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_3\}]^-$  anion, in which one Re has six terminal and three bridging H atoms forming a tricapped trigonal prism, was studied by neutron diffraction (Abrahams, Ginsberg, Koetzle, Marsh & Sprinkle, 1986). The Re atom in this anion is bound to the second Re by a metal–metal triple bond that caps a deltahedron face. The average bridging Re—H distance in  $[\text{Re}_2(\mu\text{-H})_3\text{H}_6(\text{triphos})]^-$ , where triphos is  $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ , at 80 K is 1.86 (4) Å and the average terminal Re—H distance is 1.66 (6) Å, in excellent agreement with the earlier work.

The octahydrido[triphenylphosphine]rhenate(1−) anion was originally prepared as part of a study of  $\text{ReH}_7^-$  chemistry (Ginsberg, 1968). The possibility of distortion in the expected equatorially tricapped atomic arrangement about Re resulting from the replacement of an Re—H bond by an Re—P ligand led to the present study. The diffraction technique used was necessarily limited to X-rays due to the small size of crystals available, even under conditions of growth lasting for extended periods. The unexpectedly high anharmonic component in the Re atomic thermal vibrations at 295 K led to further study at 163 K and recognition of a phase-transition onset from orthorhombic to monoclinic symmetry between these temperatures. Reduced accuracy in the diffraction measurements at 163 K, together with substantial remaining anharmonicity in the Re atomic vibrations, obscured the scattering information contributed by the H atoms at low temperatures. Despite these difficulties, the results are of crystallographic interest and are reported below.

### Experimental

Small colorless crystals that change color to very pale orange–yellow (*ISCC–NBS Centroid Color Charts*, 1964) on exposure to air grow from 2-propanol at room temperature, see Ginsberg (1968) for preparation details. The crystal used for measurement at 295 K had the typical morphology shown in Fig. 1, with maximum length 0.55 mm and thickness 0.37 mm. The crystal at 163 K had similar morphology with corresponding

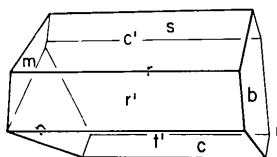


Fig. 1. Morphology of  $[\text{N}(\text{C}_2\text{H}_5)_4]^+[\text{ReH}_8\{\text{P}(\text{C}_6\text{H}_5)_2\}_3]^-$  crystal, where  $b = (010)$ ,  $c = (001)$ ,  $c' = (00\bar{1})$ ,  $m = (0\bar{1}\bar{1})$ ,  $n = (0\bar{1}1)$ ,  $r = (101)$ ,  $r' = (\bar{1}0\bar{1})$ ,  $s = (10\bar{1})$  and  $t = (\bar{1}02)$ .

Table 1. *Experimental and crystal data for  $[\text{NET}_4]^+[\text{ReH}_8(\text{PPh}_3)]^-$  at 295 and 163 K*

Temperature (K)	295	163
No. of reflections for cell parameters	25	25
Range in $2\theta$ (°)	18.9–29.1	26.1–33.1
$D_m$ (g cm <sup>-3</sup> )	1.45 (8)	—
$D_x$ (g cm <sup>-3</sup> )	1.430	1.477
$\mu(\text{Mo K}\alpha)$ * (mm <sup>-1</sup> )	4.587	4.739
Transmission-factor range (%)	7.74–32.38	26.33–49.12
$F(000)$ (e)	1184	1184
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ Å), graphite monochromator	Mo K $\alpha$ , graphite monochromator
R.l.p. scan: angle† (°)	$\omega - 2\theta = 0.80 + 0.35\tan\theta$	$\omega - 2\theta = 1.31 + 0.30\tan\theta$
R.l.p. range	$-10 \leq h \leq 10, -24 \leq k \leq 24, -9 \leq l \leq 9$	$-10 \leq h \leq 10, -26 \leq k \leq 26, 0 \leq l \leq 11$
Max. $(\sin\theta)/\lambda$ (Å <sup>-1</sup> )	0.481	0.542
Diffractionmeter	CAD-4	Rigaku AFC6R
Control minicomputer‡	PDP 11/24-8e	MicroVAX II
Max. time/r.l.p. (s)	240	18
Total No. of $F_m$	11 069	12 062
No. of independent forms	2571	6981
No. of independent $\langle F_m \rangle \geq 3\sigma\langle F_m \rangle$ §	2391	6306
No. of standard reflections	9	3
Standard reflection measurement interval (h)	6	0.5
Radiation damage¶	Quadratic anisotropic	Linear anisotropic
$R_{\text{int}}^{**}$	0.0187	0.0339
$wR_{\text{int}}^{**}$	0.0146	0.0223

\* Weber (1969).

† R.l.p. = reciprocal lattice point.

‡ See *Enraf–Nonius CAD-4 Operations Manual* (1982).

§  $\langle F_m \rangle$  averaged over form, see text.

¶ Abrahams & Marsh (1987).

\*\*  $R_{\text{int}} = \sum |F_m - \langle F_m \rangle| / \sum F_m$ ,  $wR_{\text{int}} = \sum (|F_m - \langle F_m \rangle|)^2 / \sum wF_m^2$ <sup>1/2</sup>, where  $w = 1/\sigma^2\langle F_m \rangle$ .

dimensions of 0.28 and 0.22 mm. The density at room temperature was measured pycnometrically. The experimental and crystal data are presented in Table 1. X-ray diffraction measurements at 163 K were undertaken by the Molecular Structure Corporation.

The crystal undergoes anisotropic radiation damage at 295 K, with an average decrease of 66.4% in intensity after a maximum exposure of 610.7 h to Mo K $\alpha$  radiation. Application of equation (3) in Abrahams & Marsh (1987) gave a quadratic anisotropic correction; the  $6\alpha_{ij}$  and the 15  $\alpha_{ijkl}$  coefficients are deposited.\* Following correction for radiation damage and Lorentz, polarization, filter-attenuation and absorption effects, the low value of  $wR_{\text{int}}$  suggested that the H-atom scattering component could be extracted from the  $F_m^2$  magnitudes. The variance in  $F_m^2$  [*i.e.*  $\sigma^2(F_m^2)$ ] was taken as the larger of  $V_1$ , the internal variance derived from the differences among the radiation-damage-corrected Bijvoet-equivalent members of the form  $[F^2(hkl), F^2(\bar{h}\bar{k}\bar{l}), F^2(h\bar{k}l)]$  and  $F^2(h\bar{k}\bar{l})$ , or  $V_2$ , the

\* Lists of anisotropic radiation-damage-correction coefficients, anisotropic thermal parameters and anharmonic tensor coefficients, all calculated H-atom coordinates, and structure factors with e.s.d.'s for both temperatures studied have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51330 (54 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

external variance derived from the sum of the variances due to counting statistics, absorption, filter-attenuation effects and variation in the standard reflections following radiation-damage correction. The need for an extinction correction became apparent in course of the refinement, see below. The magnitudes of the 2571 independent  $F_m$  and  $\sigma(F_m)$ , together with the final corresponding  $F_c$  values on the least-squares-derived absolute scale, are deposited,\* see also Table 1.

The crystal measured at 163 K in a stream of flowing N<sub>2</sub> also suffered radiation damage, with an average intensity decrease of 22%, that was corrected for by a linear anisotropic expression; the 6  $\alpha_{ij}$  coefficients are deposited. The change to monoclinic symmetry was initially noted in the course of measuring the unit-cell dimensions at 163 K and the reciprocal lattice was thereupon scanned in accordance with this symmetry. Data collection was interrupted about midway by the failure of a filament in the rotating anode X-ray generator. Measurement of the final 55 reflections in the first set of data was repeated, on replacing the filament, in the second set to provide a common experimental scale factor. Total measurement time was 40.2 h, see also Table 1. The crystal color had turned yellow by the time the filament failed and was very dark brown at the termination of the experiment. The variance in  $F_m^2$  was calculated by the method used for the data measured at 295 K. An extinction correction was also necessary with the 163 K data. The resulting 6981 independent  $F_m$ ,  $\sigma(F_m)$  and final  $F_c$  magnitudes on the absolute scale are deposited.

### Structure determination

The Re- and P-atom locations at 295 K were readily derived by solving the Patterson function. However, following refinement of the position and anisotropic thermal displacement parameters of these two atoms by the method of least squares, assuming simple harmonic motion, the corresponding difference Fourier series failed to reveal the presence of additional atoms. With the largest residual electron density at the Re-atom location, the possibility arose that anharmonic vibrations by this atom should be included in the model. The introduction of all ten symmetry-allowed  $\gamma$ -tensor coefficients in a modified Gram-Charlier expansion for the probability density function (*cf. International Tables for X-ray Crystallography*, 1974) led to least-squares refinement with phases that revealed all three phenyl rings (without H atoms) and the N atom of the cation in the difference Fourier series. Additional atoms were not discernible until the 15  $\delta$ -tensor coefficients were also introduced and varied, whereupon the C atoms in the cation became detectable in difference Fourier series; it may be noted that these cation atoms

are disordered at 295 K, with local pseudo-inversion through the N atom (see discussion below). The occupancy of the two orientations is not identical, hence an occupancy factor was included as an additional variable. A view of the anion, excluding H atoms, is shown in Fig. 2.

H atoms could not be detected in the residual electron density either at this stage or after the 21 independent  $\varepsilon$ -tensor coefficients were included in the expansion for the probability density function. Addition of the 28  $\zeta$ -tensor coefficients, however, clearly gave the location of seven of the H atoms bonded to Re. Inclusion of the 36  $\eta$ -tensor coefficients for Re as variables had the effect of sharply and significantly reducing  $wR$  (by over 30%) and revealing the position of the remaining H(5) atom. In the final model, the phenyl-ring H atoms were constrained to be coplanar with the ring and located 0.95 Å from their bonded C atoms, bisecting the C–C–C angle. The non-terminal H atoms in the tetraethylammonium cation were constrained to form a tetrahedron with C–H = 0.95 Å in a plane normal to and bisecting the C–C–N angle and with H–C–H = 109.4°. The methyl-group H atoms in the final model were taken as rotating freely, with scattering derived from a zero-order Bessel function (Abramowitz & Stegun, 1964). The 15 phenyl-ring H atoms, the 16 partially occupied non-terminal H atoms in the disordered cation, and the 24 partially occupied methyl-group H atoms were assigned the same anisotropic thermal parameters and occupancy factors as their corresponding bonded C atoms, for a total of 478 variables; see deposition footnote.

The final positional coordinates and r.m.s. radial thermal displacements for the 45 independent and unconstrained atoms at 295 K, including the eight hydridic atoms, are given in Table 2. Final agreement indicators are  $R(F_m) = 0.0132$ ,  $wR(F_m) = 0.0119$  and  $S = 0.902$  [see *e.g.* Abrahams, Bernstein & Keve (1971) for definitions]. The corresponding anisotropic

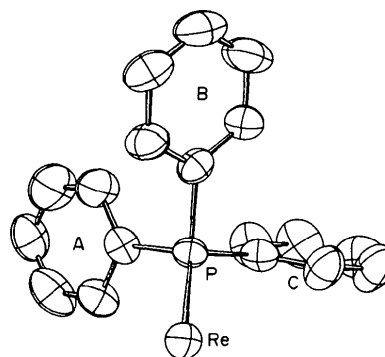


Fig. 2. Perspective view of the anion at 295 K, with atoms illustrated by 50% probability thermal vibration ellipsoids and excluding the eight H atoms bonded to Re.

\* See deposition footnote.

and anharmonic tensor coefficients are deposited. The maximum shift/e.s.d. ratio in the final least-squares refinement cycle was generally well under 5%; coordinate shifts for H(5) were however oscillatory and Table 2 gives average coordinates. Maximum and minimum features in the final Fourier difference maps are smaller than  $+0.25$  and  $-0.19$  e  $\text{\AA}^{-3}$ , integrating to less than  $\pm 0.2$  e. A normal probability plot (Abrahams & Keve, 1971) of the  $\delta R [= (F_m - F_c)/\sigma(F_m)]$  experimental deviates was very nearly linear except for less than about 2% in the extrema which had a slightly larger slope. The overall slope  $S(\delta R) = 0.77$  indicates that the average value of  $\sigma(F_m)$  has been overestimated by about 30%. The linear plot and nearly zero intercept show that both measurement and model are essentially free from systematic error. An isotropic correction for extinction was made (Becker & Coppens, 1974), with spherulite radius refining to  $15.6$  (5)  $\mu\text{m}$ .

Location of the Re and P atoms at 163 K was determined as at 295 K. No evidence of twinning was present although axial reorientation is allowed by the phase transition from point group 222 to point group 2. The lighter atoms could not be determined until both  $\gamma$ - and  $\delta$ -tensor coefficients were introduced in the thermal model for the Re atom. As the determination proceeded, with the  $y$  coordinate of one of the two independent Re atoms placed at zero to establish an origin in the polar low-temperature phase, it became apparent that half the independent atoms present had coordinates related to those in Table 2 by the transformation  $(xyz)_{163\text{ K}} \simeq [x, -(y + 0.41937), (z + \frac{1}{2})]_{295\text{ K}}$ . The other half were related by a pseudo-screw axis to give the transformation  $(xyz)_{163\text{ K}} \simeq [(\frac{1}{2} - x), (y - 0.41937), (z + \frac{1}{2})]_{295\text{ K}}$ ; the common displacement along the polar axis is required in order to maintain the chosen origin. Difference Fourier series gave no indication of disorder in the cation at 163 K, in contrast to that present at 295 K.

Attempts to locate the 16 independent hydridic atoms bonded to the Re atoms at 163 K were unsuccessful, although all tensor coefficients to sixth order were included in the model. The lower quality data, with  $R_{\text{int}} = 0.0339$ , hence do not contain recoverable scattering information from these atoms. The final model at 163 K included the phenyl-ring H atoms, as in the model for the 295 K data, but the total number of parameters was reduced by treating the thermal motion of each ring by a variation of only the librational and translational tensor terms, following Schomaker & Trueblood (1968). The tetraethylammonium ion C atoms were assigned variable isotropic temperature factors and the associated H atoms were not included in the structure-factor calculations. A total of 461 parameters were varied in the final least-squares fit.

The resulting positional coordinates and r.m.s. radial thermal displacements for the 58 independent and unconstrained atoms at 163 K are given in Table 3.

Table 2. Final atomic coordinates ( $\times 10^5$  for Re,  $\times 10^4$  for P, C and N, and  $\times 10^3$  for H) and r.m.s. thermal displacements ( $\times 10^2$   $\text{\AA}$ ) at 295 K

	x	y	z	$u_{\text{eq}}^*$
Re	53365 (20)	58063 (11)	94041 (27)	25 (4)†
H(1)	454 (6)	513 (3)	980 (6)	32 (2)
H(2)	581 (8)	521 (4)	864 (8)	30 (2)
H(3)	411 (7)	633 (3)	978 (7)	32 (2)
H(4)	391 (6)	568 (3)	816 (8)	31 (2)
H(5)	659 (11)	566 (5)	810 (14)	39 (3)
H(6)	476 (6)	581 (4)	1132 (9)	31 (2)
H(7)	632 (9)	558 (4)	1067 (11)	31 (2)
H(8)	587 (9)	638 (5)	1071 (13)	31 (2)
P	5520 (1)	6466 (1)	7688 (1)	22 (4)
C(1A)	6678 (4)	6996 (2)	7944 (5)	23 (4)
C(2A)	7443 (5)	7177 (3)	6945 (6)	28 (7)
C(3A)	8264 (7)	7593 (4)	7179 (8)	31 (10)
C(4A)	8360 (6)	7816 (3)	8370 (9)	29 (8)
C(5A)	7604 (6)	7649 (3)	9365 (8)	28 (7)
C(6A)	6769 (5)	7234 (2)	9157 (5)	26 (6)
C(1B)	4114 (5)	6853 (3)	7270 (4)	24 (3)
C(2B)	2957 (5)	6598 (3)	7138 (6)	30 (7)
C(3B)	1890 (5)	6879 (4)	6793 (7)	32 (11)
C(4B)	1940 (7)	7407 (4)	6589 (7)	31 (9)
C(5B)	3072 (8)	7664 (3)	6686 (8)	30 (9)
C(6B)	4150 (6)	7396 (3)	7051 (6)	26 (8)
C(1C)	5986 (4)	6216 (2)	6055 (5)	22 (2)
C(2C)	5352 (5)	6342 (2)	4912 (5)	24 (2)
C(3C)	5731 (6)	6141 (3)	3700 (6)	28 (6)
C(4C)	6738 (5)	5815 (3)	3626 (6)	28 (7)
C(5C)	7395 (5)	5686 (3)	4755 (6)	27 (7)
C(6C)	7010 (4)	5887 (3)	5966 (5)	25 (5)
N	4442 (4)	4342 (2)	5523 (5)	27 (8)
C(1)‡	3413 (11)	4090 (6)	6364 (14)	30 (8)
C(2)	5709 (11)	4198 (9)	5923 (16)	31 (8)
C(3)	4101 (10)	4186 (7)	4157 (12)	31 (6)
C(4)	4354 (10)	4959 (5)	5717 (13)	30 (5)
C(5)	3519 (19)	4195 (11)	7777 (20)	38 (12)
C(6)	5967 (13)	3620 (9)	5855 (27)	38 (12)
C(7)	4966 (28)	4535 (17)	2953 (32)	35 (17)
C(8)	3042 (26)	5199 (12)	5807 (28)	30 (18)
C(9)	4287 (12)	3742 (5)	5066 (19)	27 (12)
C(10)	5087 (24)	4329 (8)	6875 (31)	33 (20)
C(11)	3209 (11)	4551 (8)	5550 (23)	29 (11)
C(12)	5282 (15)	4621 (8)	4493 (25)	34 (15)
C(13)	5482 (21)	3429 (9)	4913 (26)	32 (12)
C(14)	4408 (36)	4042 (12)	7992 (22)	39 (25)
C(15)	3268 (31)	5118 (17)	5336 (45)	52 (17)
C(16)	4845 (43)	4501 (18)	3317 (37)	35 (16)

\*  $u_{\text{eq}}$  is the r.m.s. radial amplitude.

† Neglecting the anharmonic tensor coefficients, which are available as deposited material.

‡ C(1)–C(8) sites are 54.4 (2)% occupied, C(9)–C(16) sites are 45.6 (2)% occupied.

Final agreement indicators are  $R(F_m) = 0.0645$ ,  $wR(F_m) = 0.0638$  and  $S = 3.038$ , see deposition footnote. The maximum shift/e.s.d. ratio in the final least-squares refinement cycle was generally well under 20%, the maximum and minimum features in the final difference map were smaller than  $+2.4$ ,  $-1.4$  e  $\text{\AA}^{-3}$ . The spherulite radius from the isotropic extinction correction was  $9.18$  (8)  $\mu\text{m}$ .

The atomic scattering factors used were for neutral atoms, except for  $\text{N}^+$  and hydridic  $\text{H}^{1/8-}$ , of which the latter were interpolated values; these, together with the corresponding values of  $f'$  and  $f''$ , were taken from the *International Tables for X-ray Crystallography* (1974). The least-squares refinement program was a heavily modified local version of *ORFLS* (Busing, Martin & Levy, 1973), run on a VAX 11/750 supermini-computer.

Table 3. Final atomic coordinates and r.m.s. thermal displacements at 163 K (see Table 2 for units)

	x	y	z	u <sub>eq</sub>
Re(1)	53689 (43)	0	69131 (32)	20 (17)
Re(2)	96811 (40)	15942 (22)	19573 (32)	19 (17)
P(1)	5489 (6)	-657 (5)	5183 (6)	19 (2)
P(2)	9459 (6)	2274 (5)	253 (6)	19 (2)
C(1A)	6593 (21)	-1194 (9)	5396 (21)	19 (2)
C(2A)	7357 (27)	-1385 (10)	4389 (25)	24 (7)
C(3A)	8252 (26)	-1806 (10)	4609 (26)	25 (8)
C(4A)	8386 (24)	-2050 (10)	5839 (26)	23 (6)
C(5A)	7462 (27)	-1865 (11)	6852 (24)	25 (5)
C(6A)	6681 (24)	-1453 (9)	6625 (23)	22 (4)
C(1a)	8292 (23)	2797 (9)	502 (21)	20 (4)
C(2a)	7577 (23)	3005 (10)	-479 (25)	24 (11)
C(3a)	6745 (27)	3371 (12)	-307 (30)	28 (8)
C(4a)	6609 (27)	3613 (10)	1006 (26)	24 (7)
C(5a)	7340 (27)	3416 (10)	1943 (26)	25 (9)
C(6a)	8133 (26)	3029 (11)	1730 (14)	24 (7)
C(1B)	4097 (22)	-1037 (10)	4781 (20)	20 (5)
C(2B)	2908 (23)	-762 (10)	4640 (21)	23 (5)
C(3B)	1802 (26)	-1044 (12)	4246 (25)	27 (7)
C(4B)	1811 (26)	-1588 (10)	4005 (26)	25 (7)
C(5B)	2996 (24)	-1844 (11)	4136 (23)	24 (4)
C(6B)	4062 (25)	-1570 (12)	4501 (20)	23 (11)
C(1b)	10869 (22)	2688 (10)	-112 (19)	19 (6)
C(2b)	11995 (23)	2425 (11)	-303 (21)	23 (7)
C(3b)	13091 (25)	2724 (11)	-582 (23)	25 (7)
C(4b)	12981 (24)	3287 (11)	-759 (22)	23 (5)
C(5b)	11872 (24)	3541 (10)	-657 (23)	23 (5)
C(6b)	10809 (22)	3225 (9)	-296 (20)	20 (7)
C(1C)	6012 (20)	-391 (8)	3579 (19)	18 (6)
C(2C)	5291 (22)	-528 (10)	2437 (23)	21 (4)
C(3C)	5662 (26)	-299 (10)	1150 (23)	22 (6)
C(4C)	6778 (23)	44 (11)	1129 (20)	23 (9)
C(5C)	7492 (23)	149 (11)	2308 (23)	24 (8)
C(6C)	7003 (20)	-57 (10)	3466 (21)	21 (2)
C(1c)	9042 (21)	2029 (9)	-1398 (21)	20 (4)
C(2c)	9715 (22)	2146 (10)	-2557 (22)	21 (4)
C(3c)	9344 (25)	1945 (10)	-3812 (23)	22 (5)
C(4c)	8294 (22)	1595 (10)	-3874 (20)	22 (5)
C(5c)	7563 (23)	1490 (10)	-2738 (22)	24 (6)
C(6c)	8007 (20)	1656 (12)	-1522 (21)	23 (5)
N(1)	4437 (19)	1427 (10)	3057 (19)	32 (13)
N(2)	10635 (19)	126 (10)	-1999 (18)	31 (13)
C(1)	3405 (26)	1633 (13)	3836 (26)	28 (1)
C(2)	5752 (23)	1523 (11)	3542 (23)	24 (1)
C(3)	4125 (23)	1631 (12)	1633 (24)	26 (1)
C(4)	4372 (23)	818 (10)	3078 (23)	23 (1)
C(5)	3619 (28)	1600 (15)	5426 (28)	30 (1)
C(6)	5944 (32)	2209 (13)	3521 (31)	30 (2)
C(7)	5092 (34)	1401 (12)	672 (33)	31 (2)
C(8)	3100 (32)	599 (12)	2639 (31)	29 (2)
C(9)	10823 (31)	-463 (12)	-2431 (31)	29 (2)
C(10)	9744 (39)	109 (16)	-782 (38)	34 (2)
C(11)	9786 (34)	415 (12)	-3070 (35)	31 (2)
C(12)	11877 (27)	959 (11)	-1551 (28)	27 (1)
C(13)	10698 (34)	-152 (13)	443 (34)	31 (2)
C(14)	9484 (39)	-765 (13)	-2681 (38)	36 (2)
C(15)	10303 (30)	399 (12)	-4472 (30)	27 (1)
C(16)	11985 (24)	294 (10)	-1840 (25)	32 (1)

## Results and discussion

The principal chemical problem initially addressed by this study concerns the determination of the atomic arrangement and possible distortions from regularity of the hydridic atoms about Re. Advantage could not be taken of the higher accuracy attainable by neutron diffraction, as compared with X-ray diffraction methods, since the largest crystals obtained from numerous growth attempts using various solvents had volumes less than about 0.6 mm<sup>3</sup>. The atomic arrangement about the Re atom at 295 K, corresponding to the positional coordinates in Table 2, is illustrated in Fig. 3. The bond lengths within this atomic grouping, as listed

in Table 4, form a distorted equatorially girdled trigonal-prismatic coordination of the eight H atoms and one P atom about the central Re. A view of the coordination polyhedron is presented in Fig. 4.

Atoms H(1), H(7), H(2), H(3), H(8) and P form a distorted trigonal prism, with equatorial atoms H(4), H(5) and H(6) each capping a quadrilateral face. The average Re–H bond length in the equator of 1.98 (7) Å may be compared with the corresponding average Re–H<sub>eq</sub> of 1.71 (14) Å in [Re<sub>2</sub>(μ-H)<sub>3</sub>H<sub>6</sub>(triphos)]<sup>-</sup>, as measured by neutron diffraction at 80 K (Abrahams *et al.*, 1986); the standard deviation in the least significant digit given in parentheses for this and all subsequent average bond lengths is taken as  $\sigma(\langle d \rangle) = \{[\sum_{r=1}^n (d_r - \langle d \rangle)^2] / (n - 1)\}^{1/2}$ , and is probably an underestimate in view of the systematic effect of the Re-atom anharmonicity on Re–H and Re–P bond lengths, see below. All eight H atoms in the present anion may be regarded as terminal with average Re–H<sub>ter</sub> = 1.92 (11) Å. Average Re–H<sub>ter</sub> distances reported in other rhenium hydride crystals by neutron diffraction determination are 1.687 (13) Å in ReH<sub>5</sub>-(PMePh<sub>2</sub>)<sub>3</sub> at 20 K (Emge, Koetzle, Bruno & Caulton, 1984), 1.68 (1) Å in K<sub>2</sub>ReH<sub>9</sub> at 295 K (Abrahams *et al.*, 1964), 1.669 (18) Å in Re<sub>2</sub>H<sub>8</sub>(PEt<sub>2</sub>Ph)<sub>4</sub> at 80 K (Bau, Carroll, Teller & Koetzle, 1977) and 1.66 (6) Å in [Re<sub>2</sub>(μ-H)<sub>3</sub>H<sub>6</sub>(triphos)]<sup>-</sup> at 80 K (Abrahams *et al.*, 1986).

Large deviations from the regular tricapped trigonal prismatic ReH<sub>9</sub><sup>-</sup> ion found in K<sub>2</sub>ReH<sub>9</sub> had previously been noted in the [Re<sub>2</sub>(μ-H)<sub>3</sub>H<sub>6</sub>(triphos)]<sup>-</sup> ion, for which the origin was speculated to be the reduced ability of the bridge-bonding H atoms to form H–H bonds in one of the prism triangular faces (Abrahams *et al.*, 1986). Distortions within the ReH<sub>8</sub>P grouping are even larger, with average H–H distances in the triangular faces of 2.2 (3) Å, in the equator of 3.5 (5) Å, and in the quadrilateral faces of 2.6 (5) Å. The four equatorial atoms depart appreciably from regularity, with H<sub>eq</sub>–Re–H<sub>eq</sub> angles of 103, 120 and 128°. All other angles in the grouping are similarly

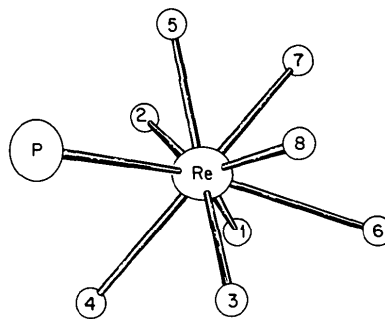


Fig. 3. Arrangement of H and P atoms about Re in the [ReH<sub>8</sub>(PPh<sub>3</sub>)]<sup>-</sup> anion at 295 K.

Table 4. Bond lengths (Å) in the  $\text{ReH}_8\text{P}$  grouping at 295 K

Re-H(7)	1.75 (10)	Re-H(4)	2.00 (7)
Re-H(2)	1.78 (10)	Re-H(6)	2.04 (9)
Re-H(3)	1.90 (8)	Re-H(8)	2.05 (12)
Re-H(5)	1.91 (13)	Re-P	2.419 (3)
Re-H(1)	1.95 (8)		
P-H(5)	2.37 (13)	P-H(4)	2.67 (8)
P-H(3)	2.62 (8)	P-H(8)	3.09 (12)

distorted by comparison with those in the  $\text{ReH}_9^-$  ion. In view of the uncertainty in H-atom positions, due at least partly to the anharmonic motion of the Re atom (see discussion below) and partly to the unfavorable ratio of X-ray scattering by H as compared with that by Re, further consideration of these distortions is best deferred until neutron diffraction results become available.

The Re-atom coordination determined in  $[\text{ReH}_8(\text{PPh}_3)]^-$  at 295 K may be characterized by two observations. All eight Re-H bond lengths and the single Re-P distance (see below) are significantly longer than expected; in addition, the massive Re atom undergoes highly anharmonic displacements both at 295 and 163 K, whereas no evidence exists for comparable anharmonicity in the thermal motion of other atoms in the anion. Even the P-atom displacements are best described in terms of simple harmonic motion.

The Re-P distance at 295 K, see Table 5, is very significantly longer than the corresponding 2.288 (3) Å bond length in  $[\text{Re}_2(\mu\text{-H})_3\text{H}_6(\text{triphos})]^-$  (Abrahams *et al.*, 1986) or the 2.335 (2) Å value reported by Bau *et al.* (1977) in  $\text{Re}_2\text{H}_8(\text{PEt}_2\text{Ph})_4$ . It is also longer than the less-precise values of 2.331 (52) Å (taken from a bond-length range given as a footnote) in  $\text{Re}_2\text{H}_4(\text{PMe}_2\text{Ph})_4[\text{P}(\text{OCH}_2)_3\text{CEt}]_2$  (Green, Huffman & Caulton, 1982), 2.320 (17) Å in  $\text{ReH}_5(\text{PMe}_2\text{Ph})_3$  (Green, Huffman & Caulton, 1981), 2.378 (16) Å in  $[\text{Re}_2\text{H}_5-$

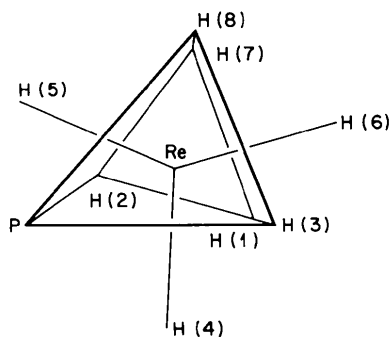


Fig. 4. Distorted equatorially girdled trigonal-prismatic coordination of the eight H atoms and one P atom about Re at 295 K, see also Fig. 3.

Table 5. Principal bond lengths (Å) and angles (°) in the  $\text{Re}(\text{PPh}_3)$  grouping

	295 K	163 K
Re-P	2.419 (3)	2.397 (10)
P-C(1A)	1.839 (5)	2.422 (11)
P-C(1B)	1.837 (6)	1.784 (24)
P-C(1C)	1.840 (5)	1.811 (25)
		1.783 (25)
		1.847 (25)
		1.840 (21)
		1.816 (22)
Re-P-C(1A)	117.2 (2)	118.0 (8)
Re-P-C(1B)	118.0 (2)	117.6 (7)
Re-P-C(1C)	115.5 (2)	118.4 (8)
C(1A)-P-C(1B)	100.7 (3)	117.7 (7)
C(1A)-P-C(1C)	101.4 (2)	114.3 (9)
C(1B)-P-C(1C)	101.2 (2)	115.5 (10)
		98.9 (12)
		99.8 (12)
		100.0 (10)
		102.5 (10)
		104.5 (10)
		100.8 (10)
$(C_{ar}-C_{ar})_{max}$	1.394 (8)	1.458 (38)
$(C_{ar}-C_{ar})_{min}$	1.336 (12)	1.311 (34)
$(C_{ar}-C_{ar})_{av}$	1.375 (16)	1.389 (43)

$(\text{PPh}_3)_4(\text{CN}'\text{Bu})_2\text{PF}_6$  (Allison, Cotton, Powell & Walton, 1984), 2.381 (16) Å in  $\text{ReH}_5(\text{PMePh}_2)_3$  (Emge *et al.*, 1984), and 2.384 (35) Å in  $\text{ReH}_5(\text{PMe}_2\text{Ph})_3(\text{C}_5\text{H}_8)$  (Green, Huffman, Caulton, Rybak & Ziolkowski, 1981). The present value is, however, close to the Re-P mean bond lengths reported by Howard, Mead & Spencer (1983) of 2.413 (2) and 2.423 (2) Å in the two forms of  $\text{ReH}_7[\text{P}(\text{C}_3\text{H}_7)_2\text{Ph}]_2$  and 2.427 (2) Å in  $\text{ReH}_7(\text{PPh}_3)$ , using X-ray diffraction. It may be noted from Table 5 that the average Re-P-C bond angle of 116.9 (1.3)° in  $[\text{ReH}_8(\text{PPh}_3)]^-$  at 295 K is not significantly different from the 118.9 (1.4)° in  $[\text{Re}_2(\mu\text{-H})_3\text{H}_6(\text{triphos})]^-$  at 295 K.

In contrast to the increased Re-H and Re-P bond lengths, the average P-C distance of 1.839 (3) Å at 295 K is not significantly different from the 1.846 (14) Å in  $[\text{Re}_2(\mu\text{-H})_3\text{H}_6(\text{triphos})]^-$  (Abrahams *et al.*, 1986), 1.839 (4) Å in  $\text{ReH}_7(\text{Ph}_3\text{P})_2$  (Howard *et al.*, 1983), or 1.834 (10) Å reported in  $[\text{Re}_2\text{H}_5(\text{PPh}_3)_4(\text{CN}'\text{Bu})_2\text{PF}_6$  (Allison *et al.*, 1984). A stereoview of the content of one unit cell, both at 295 and at 163 K, is shown in Fig. 5.

#### Tetraethylammonium cation

The  $[\text{N}(\text{C}_2\text{H}_5)_4]^+$  cation in the present study is disordered at room temperature. The atoms are numbered so that C(1) through C(4) are bonded to N, C(5) to C(1), C(6) to C(2), C(7) to C(3) and C(8) to C(4); similarly, the disordered atoms C(9) through C(12) are bonded to N, C(13) to C(9), C(14) to C(10), C(15) to C(11) and C(16) to C(12). Atoms C(1)-C(8) are related to atoms C(9)-C(16) by an approximate inversion centered at the N atom. The pseudo-inversion center pairs C(1) with C(12), C(2) with C(11), C(3)

with C(10) and C(4) with C(9). Inversion holds within a maximum deviation of 0.4 Å for the partially occupied set of C(1)–C(4) atom positions in relation to the C(9)–C(12) set, as may be seen by comparing coordinate differences from the N atom using the coordinates in Table 2. The corresponding maximum deviation is 0.6 Å for the partially occupied set of C(5)–C(8) atom positions in relation to the C(13)–C(16) set, with respect to the N atom.

The occupancy of atomic sites C(1)–C(8) is 54.4 (2)% complete, that of the related C(9)–C(16)

sites is 45.6 (2)%. The cationic arrangement in both phases is shown in Fig. 5, with the lower occupancy disordered sites at 295 K removed from Fig. 5(a) for simplicity. The cation is fully ordered at 163 K. The average N–C and C–C distances of 1.51 (6) and 1.49 (3) Å at 295 K, and 1.53 (1) and 1.61 (8) Å respectively at 163 K, are not significantly different from the room-temperature X-ray diffraction values for the  $[\text{N}(\text{C}_2\text{H}_5)_4]^+$  cation in the  $[\text{Re}_2(\mu\text{-H})_3\text{H}_6(\text{triphos})]^-$  salt of 1.44 (11) and 1.51 (3) Å respectively, nor from the corresponding neutron diffraction values at 80 K of 1.55 (2) and 1.54 (2) Å, determined by Abrahams *et al.* (1986).

Tetrahedral ions have previously been reported as located at true inversion centers, leading to disorder similar to that found in the present study. Notable examples are provided by the superconducting salts  $(\text{TMTSF})_2\text{X}$ , where TMTSF is tetramethyltetraselenafulvalene and X is  $\text{ReO}_4$  or  $\text{ClO}_4$  (Pouget, Shirane, Bechgaard & Fabre, 1983; Rindorf, Soling & Thorup, 1984). The elimination of the inversion centers on cooling through the low-temperature phase transitions in these salts is comparable with the elimination of the pseudo-inversion center located at the  $[\text{N}(\text{C}_2\text{H}_5)_4]^+$  cation on cooling through the present phase transition.

#### Re–X interatomic distances and anharmonic thermal motion by Re

Interatomic distances calculated from atomic coordinates that are based upon harmonic thermal vibration models tend to decrease with increasing temperature, with measurements at ambient temperature that are often prone to give underestimated bond distances. It has long been customary to make corrections for such thermally affected distances either by assuming that the bonded atoms vibrate independently or that one atom rides on the other, using widely distributed programs such as *ORFFE* (Busing *et al.*, 1973). Atomic positions resulting from refinement of anharmonic thermal motion may differ significantly from those obtained on the basis of harmonic refinement, as discussed by Scheringer (1986). Among the experimental results thus obtained the atomic position of O in the spinel  $\text{MgAl}_2\text{O}_4$  gives, for example, an Al–O distance that is 0.006 (1) Å longer in the anharmonic than in the harmonic case (Yamanaka, Takeuchi & Tokonami, 1984). Larger effects have been noted in  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  by Lundgren, Kvik, Karppinen, Liminga & Abrahams (1984), with shifts of 0.064 (5) Å in the H and O atomic coordinates occurring in the water molecule location on including  $\gamma$ -tensor coefficients in the refinement.

As noted above, the average Re–H bond distance in  $[\text{ReH}_8(\text{PPh}_3)]^-$  is about 15% longer than expected and the Re–P distance is about 6% longer than reported in

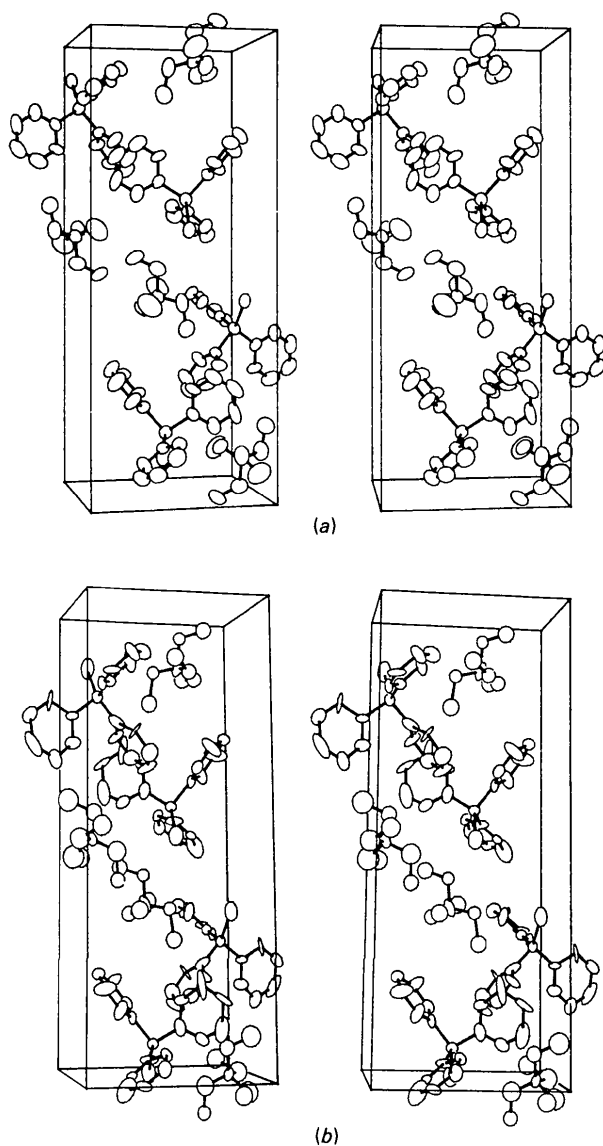


Fig. 5. (a) Stereoview of orthorhombic unit cell and content at 295 K, viewed along  $c$  with  $b$  axis vertical. (b) Stereoview of monoclinic unit cell and content at 163 K, with same aspect as in (a).

Table 6. *Transformed atomic coordinates at 295 K in equivalent cell with space group  $P2_1$  and displacement ( $\text{\AA}$ ) from coordinates of corresponding atoms at 163 K*

Independent atom  $A$  in  $P2_12_12_1$  becomes atoms  $A1$  and  $A2$  in  $P2_1$ , with coordinates:

$$(x'y'z')_{A1} = x, -(y + 0.41937), (z + \frac{1}{2})$$

$$(x'y'z')_{A2} = (\frac{1}{2} - x), (y - 0.41937), (z + \frac{1}{2}).$$

The quantity  $\Delta$  is the displacement between an atom at  $x'y'z'$  in the table below and the same atom in  $P2_1$  at 163 K as given in Table 3.

	$x'$	$y'$	$z'$	$\Delta$
Re(1)	53365	0	69041	0.04
Re(2)	96635	16126	19041	0.07
P(1)	5520	-660	5188	0.06
P(2)	9480	2272	188	0.07
C(1A)	6678	-1190	5444	0.10
C(2A)	7443	-1371	4445	0.11
C(3A)	8264	-1787	4679	0.09
C(4A)	8360	-2010	5870	0.11
C(5A)	7604	-1843	6865	0.16
C(6A)	6769	-1428	6657	0.12
C(1a)	8322	2802	444	0.07
C(2a)	7557	2983	-555	0.10
C(3a)	6736	3399	-321	0.07
C(4a)	6640	3622	870	0.14
C(5a)	7396	3455	1865	0.14
C(6a)	8231	3040	1657	0.13
C(1B)	4114	-1047	4770	0.03
C(2B)	2957	-792	4638	0.09
C(3B)	1890	-1073	4293	0.13
C(4B)	1940	-1601	4089	0.16
C(5B)	3072	-1858	4186	0.10
C(6B)	4150	-1590	4551	0.12
C(1b)	10886	2659	-230	0.14
C(2b)	12043	2404	-362	0.09
C(3b)	13110	2685	-707	0.16
C(4b)	13060	3213	-911	0.25
C(5b)	11928	3470	-814	0.25
C(6b)	10850	3202	-449	0.17
C(1C)	5986	-410	3555	0.06
C(2C)	5352	-536	2412	0.07
C(3C)	5731	-335	1200	0.13
C(4C)	6738	-9	1126	0.14
C(5C)	7395	120	2255	0.14
C(6C)	7010	-81	3466	0.06
C(1c)	9014	2022	-1445	0.06
C(2c)	9648	2148	-2588	0.08
C(3c)	9269	1947	-3800	0.08
C(4c)	8262	1621	-3874	0.07
C(5c)	7605	1492	-2745	0.05
C(6c)	7990	1693	-1534	0.10
N(1)	4442	1464	3023	0.10
N(2)	10558	148	-1977	0.10
C(1)	3413	1716	3864	0.21
C(2)	5709	1608	3423	0.25
C(3)	4101	1620	1657	0.04
C(4)	4354	847	3211	0.16
C(5)	3519	1611	5277	0.19
C(6)	5967	2186	3355	0.18
C(7)	4966	1271	453	0.41
C(8)	3042	607	3307	0.68
C(9)	11587	-104	-1136	1.77
C(10)	9291	4	-1577	0.97
C(11)	10899	-8	-3343	1.60
C(12)	10646	765	-1783	1.40
C(13)	11481	1	277	0.92
C(14)	9033	-523	-1645	1.30
C(15)	10034	341	-4547	0.33
C(16)	11958	1005	-1693	1.81

many comparable compounds, whereas interatomic separations not involving the anharmonic Re atom are normal at both temperatures. It may hence be assumed that these differences, if significant, are related to the strongly anharmonic motion of the Re atom at the two temperatures and that correction for the effect should await further study.

### Structural rearrangement at the phase transition

Consideration of the detailed structural rearrangement at the phase transition from space group  $P2_12_12_1$  to  $P2_1$  is facilitated if the origin in the orthorhombic unit cell is first translated  $3c/4$  from the normal midpoint between the three non-intersecting screw axes so as to locate it on the  $b$  screw axis. A further translation along the  $b$  axis that places one Re  $y$  coordinate at zero completes the transformation, thus giving the equivalent atomic coordinates presented in Table 6. The difference between these coordinates and the experimental values at 163 K presented in Table 3 represents the displacement required of each atom on cooling a unit cell through the temperature interval 295 to 163 K. It may be emphasized that these displacements give no information concerning the *locus* traced by each atom over this interval, only the overall *change* in position.

It is apparent from Table 6 that the displacement  $\Delta$  for the Re( $\text{PPh}_3$ ) group is no larger than 0.25  $\text{\AA}$  for any constituent atom (excluding H which is not considered here). The barrier to such small displacements, which are comparable with the r.m.s. radial amplitudes (see Table 2), is expected to be small. Similarly, the atomic displacements associated with the  $[\text{N}(\text{C}_2\text{H}_5)_4]^+$  cation atoms N(1), C(1)–C(8) are also relatively small, with maximum rotation by some terminal methyl groups of about  $25^\circ$  resulting in movements of 0.68  $\text{\AA}$  or less.

The major deviation from the higher temperature phase is associated with the rearrangement of the N(2), C(9)–C(16) cation. The disorder present above the phase transition is not detectable at lower temperatures. The atomic displacements from the transposed 295 K positions are as large as 1.81  $\text{\AA}$  at 163 K (see Table 6), the entire cation rotating about  $50^\circ$  between the two temperatures. The heat capacity of this phase transition, the study of which is expected to provide revealing insight into the nature of the transition, has not yet been measured owing to the scarcity of pure material.

It is a pleasure to thank A. P. Ginsberg for bringing this material to our attention, for providing the crystals used in the present study and for his repeated attempts to grow single crystals large enough for a neutron diffraction study, and also T. F. Koetzle for helpful comments on a draft of this manuscript.

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## Steric and Electronic Effects on the Structural Parameters of the Dianions [M<sub>6</sub>C(CO)<sub>15</sub>]<sup>2-</sup> (M = Co, Rh). An Accurate Analysis

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### Abstract

The structures of the carbido-carbonyl cluster species [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[Co<sub>6</sub>C(CO)<sub>15</sub>] and [PPh<sub>4</sub>]<sub>2</sub>[Rh<sub>6</sub>C(CO)<sub>15</sub>] are examined and compared with the results of the previous determinations of the two anions as their isomorphous salts of [N(CH<sub>2</sub>Ph)(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. A 'sliding effect', similar to that observed on passing from isotropic to anisotropic refinement of the C- and O-atom thermal parameters of terminally bound CO groups, is found to occur for μ<sub>2</sub>-bridging CO ligands. M–M bonds within the trigonal prismatic cores of the two species are shown to be significantly affected by changes in the crystal packing, and to depend strongly on the interplay of steric and electronic factors such as CO...CO nonbonding intra- and intermolecular interactions, and bonding M–CO and M–C(carbide) interactions. Crystal data: bis(tetraethylammonium) μ<sub>6</sub>-carbido-nona-μ<sub>2</sub>-carbonyl-hexacarbonyl-triprismo-hexacobaltate(2-), [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[Co<sub>6</sub>C(CO)<sub>15</sub>], M<sub>r</sub> = 1046.3, monoclinic, P2<sub>1</sub>/n, a = 8.890 (2), b = 22.790 (10), c = 20.545 (6) Å, β = 96.00 (1)°, U =

4139.72 Å<sup>3</sup>, Z = 4, D<sub>x</sub> = 1.68 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, μ = 23.14 cm<sup>-1</sup>, F(000) = 2112, R = 0.060 for 5929 observed reflections; bis(tetraphenylphosphonium) μ<sub>6</sub>-carbido-nona-μ<sub>2</sub>-carbonyl-hexacarbonyl-triprismo-hexarhodate(2-), [PPh<sub>4</sub>]<sub>2</sub>[Rh<sub>6</sub>C(CO)<sub>15</sub>], M<sub>r</sub> = 1728.4, triclinic, P1̄, a = 14.784 (8), b = 18.796 (13), c = 11.339 (7) Å, α = 96.50 (5), β = 90.78 (5), γ = 86.35 (5)°, U = 3124.23 Å<sup>3</sup>, Z = 2, D<sub>x</sub> = 1.84 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, μ = 22.30 cm<sup>-1</sup>, F(000) = 1688, R = 0.052 for 5582 observed reflections.

### Introduction

There is an increasing awareness that a better understanding of the relationships between metal–metal, metal–ligand and ligand–ligand interactions (whether bonding or nonbonding) in transition-metal clusters can be gained if more accurate and reliable structural information is available. The problem is not trivial and it has recently been shown that systematic errors are made, even in the evaluation of some of the most basic structural parameters (such as M–C and C–O bond lengths of terminally bound CO groups), if the

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