# Structural Characterization of $\{[(C_6H_5)_3P]_2N\}[Cr_2(CO)_{10}I]$. Stereochemistry and Bonding of the Bis(triphenylphosphine)iminium Cation and of a Monohalogen-Bridged Dinuclear Metal Carbonyl Anion

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**Abstract:** An X-ray crystallographic analysis of the $[PPN][Cr_2(CO)_{10}I]$ salt (where PPN represents the $[(C_6H_5)_3P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_3]^+$ cation) has provided unequivocal proof that the halodecacarbonyldimetalate anion, $[Cr_2(CO)_{10}I]^-$, possesses a "bent" Cr–I–Cr framework rather than a linear one initially proposed from infrared analysis. Hence, the formal replacement of the bridging hydrogen atom in the $[(OC)_5Cr\text{–}H\text{–}Cr(CO)_5]^-$ anion of $D_{4h}$-4/*m*2/*m*2/*m* geometry, which contains a *linear* Cr–H–Cr segment held together by a three-center electron-pair bond, by a bridging halogen atom results in a drastic geometrical transformation to a configuration containing a Cr–I–Cr bond angle of 117.9 (1)° and equivalent Cr–I bond lengths of 2.789 (4) Å; this Cr–I–Cr linkage may be described simply in terms of localized electron-pair Cr–I $\sigma$ bonds. The now hypothetical $D_{4h}$ configuration is analyzed qualitatively from the same MO model which previously was used to rationalize that the linear Ru–O–Ru segment in the $[Cl_5Ru\text{–}O\text{–}RuCl_5]^{4-}$ anion of $D_{4h}$ symmetry is due to extensive delocalized Ru(d$\pi$)–O(p$\pi$)–Ru(d$\pi$) bonding character. In contrast, these topological symmetry arguments indicate relatively little if any net Cr(d$\pi$)–I(p$\pi$)–Cr(d$\pi$) stability by use of the normally two unshared electron pairs of the bridging iodine atom. This structural study has also established that there are two basic geometrical conformations adopted in the solid state by a $[(ZYX)P\overset{\cdots}{-}N\overset{\cdots}{-}P(X'Y'Z')]^+$ cation (containing a bent central P–N–P fragment) which may be considered to originate from the sharing of the common nitrogen atom between (ZYX)PN and NP(X′Y′Z′) tetrahedra; the two tetrahedra are linked such that for six atomic ligands both conformations may possess $C_2$-2 symmetry (when X = X′, Y = Y′, Z = Z′) or $C_{2v}$-2*mm* symmetry (when X = X′ and Y = Y′ = Z = Z′). One conformation, the particular one retained by the $[(C_6H_5)_3P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_3]^+$ cation whose phenyl rings are approximately disposed in a $C_2$-2 geometry, has the X and X′ ligands (*viz.*, the $P\text{–}C_6H_5$ bonds) nearly oriented in the plane of the bent P–N–P fragment to give a cisoid pentadienyl-type arrangement. The other conformation has the in-plane X and X′ ligands oriented relative to the central bent P–N–P fragment in a transoid pentadienyl-type arrangement; this one is exhibited by the symmetrically substituted $[(NH_2)(C_6H_5)_2P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_2(NH_2)]^+$ cation (X = X′ = Z = Z′ = $C_6H_5$ and Y = Y′ = $NH_2$) of approximately $C_2$-2 geometry and by the unsymmetrically substituted $[(NHCH_3)_2(NH_2)P\overset{\cdots}{-}N\overset{\cdots}{-}P(NH_2)_3]^+$ cation (X = Z = $NHCH_3$ and Y = X′ = Y′ = Z′ = $NH_2$). Comparison of the geometry of the bis(triphenylphosphine)iminium cation in the $[PPN][Cr_2(CO)_{10}I]$ salt with those in four other PPN salts (whose unreported structures were subsequently determined in our laboratories) shows that the $[(C_6H_5)_3P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_3]^+$ cation possesses in the solid state a fairly uniform conformation of phenyl ligands essentially invariant to the different packing and size effects of the anions. Its particular geometry, which appears to be primarily governed by steric effects, is shown to be closely related to the conformation of the $(C_6H_5)_2P\text{–}N\text{–}P(C_6H_5)_2$ segment in the cyclotriphosphazene molecule $N_3P_3Cl_2(C_6H_5)_4$ in which a $N\text{–}P(Cl_2)\text{–}N$ chelating ligand is formally substituted in place of the two in-plane cisoid-oriented phenyl ligands. The two chemically equivalent P–N bond lengths in the P–N–P central fragment of the PPN cation in the five salts have average values all within 0.005 of 1.575 Å; although this value is substantially shorter than the presumed P–N single bond length of 1.77 Å, it compares favorably with the P–N bond lengths of 1.578 (4) Å in $N_3P_3Cl_2(C_6H_5)_4$ and 1.597 (3) Å in $N_3P_3(C_6H_5)_6$. Hence, despite the considerably larger P–N–P bond angles of range 137–142° found in the PPN cation *vs.* those in the cyclically constrained $N_3P_3Cl_2(C_6H_5)_4$ (125°) and $N_3P_3(C_6H_5)_6$ (122°), the essentially unchanged P–N bond lengths in the "open" $(C_6H_5)_2P\text{–}N\text{–}P(C_6H_5)_2$ system compared with the analogous segments of cyclotriphosphazene rings suggest that the composite interdependent effect on P–N contraction of (1) increased P(d$\pi$)–N(p$\pi$)–P(d$\pi$) bonding, (2) stronger P–N $\sigma$-bonding character, and (3) contraction of the phosphorus orbitals due to increased positive charge is not appreciably different in these systems. The $[PPN][Cr_2(CO)_{10}I]$ salt crystallizes in the triclinic system of centrosymmetric symmetry $P\bar{1}$ with cell parameters $a$ = 13.283 (9) Å, $b$ = 11.479 (7) Å, $c$ = 16.259 (10) Å, $\alpha$ = 100.08 (4)°, $\beta$ = 105.20 (6)°, $\gamma$ = 95.65 (2)°. The experimental density of 1.49 g/cm³ is in agreement with the calculated value of 1.50 g/cm³ for two formula species per cell. The structural determination was performed with a Datex-controlled General Electric diffractometer, and anisotropic–isotropic least-squares refinement, which utilized rigid-body constraints on each of the six phenyl rings of the PPN cation, resulted in an unweighted discrepancy factor of $R_1$ = 7.8%.

The X-ray diffraction analysis[3,4] of the $[Cr_2(CO)_{10}H]^-$ anion revealed a prototype structure of $D_{4h}$ geometry containing a bridging hydrogen atom linearly coordinated to the two $Cr(CO)_5$ moieties. This unparalleled example of a linear three-center two-electron X–H–X system kindled our curiosity concerning the stereochemistry of the series of dinuclear chromium carbonyl neutral and anionic species of formula $[Cr_2(CO)_{10}L]^-$ (where L = I, CN, or SCN) originally re-

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[3] L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Amer. Chem. Soc.*, **88**, 366 (1966).

[4] L. B. Handy, J. K. Ruff, and L. F. Dahl, *ibid.*, **92**, 7312 (1970).

ported by Behrens and coworkers,[5,6] and further extended by Ruff[7–9] to include I, Br, Cl, CN, SCN, and RS (R = $CH_3$ and $C_6H_5$) bridging ligands of the anions of chromium and the two congeners, molybdenum and tungsten. Behrens, Lindner, and Birkle[10] also recently reported the preparation (by other methods) of bridging mercapto ligands (R = H, $CH_3$, $C_2H_5$, $C_6H_5$) for the dichromium anion. Our attention was drawn in particular to the $[Cr_2(CO)_{10}I]^-$ anion,[6,7] since structural predictions based on its infrared spectrum were in conflict. Infrared spectral examinations of both $[Cr_2(CO)_{10}I]^-$ and the neutral paramagnetic species $[Cr_2(CO)_{10}I]$[11] and $[Cr_2(CO)_{10}SCN]$[12] together with other mono- and dinuclear chromium carbonyl halo and pseudohalo derivatives were performed by Lindner and Behrens[13] over the range 4000–200 cm$^{-1}$. From the four carbonyl frequencies found for the $[Cr_2(CO)_{10}I]^-$ anion in $CH_2Cl_2$ solution (and the similarity of these frequencies with those of the $[Cr_2(CO)_{10}CN]^-$ anion which no doubt has a linear Cr–CN–Cr system), Lindner and Behrens[13] initially suggested that the $[Cr_2(CO)_{10}I]^-$ anion may have either $D_{4h}$ or $D_{4d}$ symmetry with a linear Cr–I–Cr framework.[14] However, on the basis of a more complex infrared carbonyl spectral pattern of seven discernible bands in THF solution, Ruff[7] concluded that the Cr–I–Cr framework in the $[Cr_2(CO)_{10}I]^-$ anion is nonlinear.[15] Since assignments of probable geometry based on the number of observed infrared carbonyl frequencies have not proven reliable in the past for other well-known metal carbonyl complexes (*e.g.*, $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$) and since no detailed molecular parameters existed for any dinuclear metal carbonyl complexes with singly bridged halogen atoms, the $[Cr_2(CO)_{10}I]^-$ anion was selected for single-crystal X-ray study.

The bis(triphenylphosphine)iminium cation, $\{[(C_6H_5)_3P]_2N\}^+$ (abbreviated PPN), employed as the counter ion in this investigation is also of considerable structural interest. This unusually bulky cation, first synthesized by Appel and Hauss[16] as a bromide salt, was recently prepared by Ruff and Schlientz[17] by a much simpler chemical route in quantitative yield as a chloride salt (and then converted in a straightforward manner to salts containing other simple inorganic anions such as bromide, iodide, cyanide, cyanate, thiocyanate, azide, nitrate, and nitrite). Ruff[7,18] has shown this cation to impart a remarkable degree of air and moisture stability in the isolation of mono- and polynuclear metal carbonyl anions. Although at the time of this investigation a considerable number of cyclophosphazene complexes[19,20] had been characterized by X-ray investigations,[20–23] there were no literature reports of X-ray work on any noncyclic $[(ZYX)P\overset{\cdots}{-}N\overset{\cdots}{-}P(X'Y'Z')]^+$ system despite extensive chemical and physical studies[20–27] on both cyclic and noncyclic phosphorus–nitrogen complexes. The considerable variations of opinion[23,28] concerning the detailed nature and extent of multiple bonding (including the degree of pseudoaromatic character) in the cyclophosphazene complexes made it particularly desirable to determine the unknown geometry of the bis(triphenylphosphine)iminium cation and thereby to assess from a comparison of P–N bond lengths in this cation with those in the $(C_6H_5)_2P–N–P(C_6H_5)_2$ part of structurally known tricyclophosphazene derivatives the relative degree of multiple bonding character in an open $[(ZYX)P\overset{\cdots}{-}N\overset{\cdots}{-}P(X'Y'Z')]^+$ system.

## Experimental Procedure

**Preparation and X-Ray Data Collection.** The $[(C_6H_5)_3P]_2N[Cr_2(CO)_{10}I]$ salt was prepared by the photolytic reaction of a mixture of $Cr(CO)_6$ and $[(C_6H_5)_3P]_2NI$ in THF solution.[7] Single crystals suitable for an X-ray diffraction study were obtained by slow recrystallization from ether–pentane solutions. A slightly distorted cube approximately 0.15 mm on a side was cemented to a glass fiber and used for all subsequent measurements. Preliminary oscillation and Weissenberg photographs showed the crystal to be triclinic. The crystal was then transferred to a General Electric four-circle automatic diffractometer for the collection of intensity data. Lattice parameters and reflection orientations, based on 21 manually centered reflections, were calculated with a local version of the Argonne National Laboratory orientation and angle-setting program.[29] The $\theta$–$2\theta$ scan technique was employed with symmetric scans of 2° at 4°/min and 15-sec background counts before and after each scan. Zr-filtered Mo K$\alpha$ radiation was used. Intensity data for $2\theta \leq 40°$ were collected for one independent unit: $hkl$ $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$. A set of three standard reflections was measured every 200 reflections as a check on crystal and instrument stability.

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(5) H. Behrens and J. Köhler, *Z. Naturforsch., B*, **14**, 463 (1959); *Z. Anorg. Allg. Chem.*, 306, 94 (1960).

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(8) J. K. Ruff, *ibid.*, 8, 86 (1969).

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(10) H. Behrens, E. Lindner, and S. Birkle, *Z. Anorg. Allg. Chem.*, **369**, 131 (1969).

(11) H. Behrens and R. Schwab, *Z. Naturforsch. B*, **19**, 768 (1964).

(12) H. Behrens, R. Schwab, and D. Herrmann, *ibid.*, *B*, **21**, 590 (1966).

(13) E. Lindner and H. Behrens, *Spectrochim. Acta, Part A*, 23, 3025 (1967).

(14) It was later assessed by E. Lindner (private communication to L. F. D., 1968) from further infrared data in other solvents (unpublished) as well as from comparison with the infrared spectrum of the $[Cr_2(CO)_{10}SH]^-$ anion[10] that the Cr–I–Cr angle in the $[Cr_2(CO)_{10}I]^-$ anion was probably nonlinear.

(15) Resolution of the carbonyl absorption bands in the infrared spectra of the $[Cr_2(CO)_{10}I]^-$ anion was demonstrated by Ruff[7] to be poorer in $CH_2Cl_2$ solution than in THF solution. The complicated effects of different solvents on the infrared spectra of metal carbonyl complexes are well known [*cf.* G. Bor, *Spectrochim. Acta*, 18, 817 (1962); W. Beck and K. Lottes, *Z. Naturforsch. B*, **19**, 987 (1964)] including that of impurities caused by decomposition and that of incomplete dissociation of solvated cations and anions, which, in the case of the $Na_2Cr_2(CO)_{10}$ salt dissolved in THF solution, gives rise to a complex carbonyl spectra pattern caused by breakdown in the symmetry of the anion (for details with references, see footnote 19 in ref 4.

(16) R. Appel and A. Hauss, *Z. Anorg. Allg. Chem.*, **311**, 290 (1961).

(17) J. K. Ruff and W. J. Schlientz, submitted for publication.

(18) J. K. Ruff, *Inorg. Chem.*, 6, 2080 (1967); 7, 1499 1818 (1968).

(19) Although phosphazene is the recommended systematic nomenclature[20] for phosphorus–nitrogen cyclic complexes containing a repeating $\geqslant P{=}N$ unit, other used diverse names include phosphonitrile and azaphosphorine (for six-membered rings); the monomeric unit may be called phosphinimine or phosphinimide. Alternatively, the $[(C_6H_5)_3P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_3]^+$ cation may be called the iminobis(triphenylphosphorus) or bis(triphenylphosphorus)nitride cation.

(20) H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York, N. Y., 1967.

(21) N. L. Paddock, *Quart. Rev., Chem. Soc.*, 18, 168 (1964).

(22) S. Pantel and M. Becke-Goehring, "Sechs- und Achtgliedrige Ringsysteme in der Phosphor-Stickstoff-Chemie," Springer-Verlag, Berlin, 1969.

(23) K. A. R. Mitchell, *Chem. Rev.*, 69, 157 (1969).

(24) E. Fluck, "Topics in Phosphorus Chemistry," Vol. 4, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1967, p 291.

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(26) F. R. Ahmed, P. Singh, and W. H. Barnes, *Acta Crystallogr., Sect. B*, **25**, 316 (1969), and references cited therein.

(27) C. W. Allen, J. B. Faught, T. Moeller, and I. C. Paul, *Inorg. Chem.*, 8, 1719 (1969), and references cited therein.

(28) (a) K. A. R. Mitchell, *J. Chem. Soc. A*, 2683 (1968); (b) D. P. Craig and K. A. R. Mitchell, *ibid.*, 4682 (1965); (c) D. P. Craig and N. L. Paddock, *ibid.*, 4118 (1962); (d) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *ibid.*, 2423 (1960).

(29) Argonne National Laboratory, "Orientation and Angle Setting Generation Program," Program B-101, 1965.

No significant change in the intensity of these standard reflections was observed during the entire data collection. The raw intensity data were converted to $|F_o|$ values with the program DATRED,[30] and $\sigma(I)$'s for each reflection were calculated as previously given.[30,31] Reflections for which $I < 3\sigma(I)$ were considered unobserved and were discarded. A total of 1978 observed independent reflections resulted from this procedure. The linear absorption coefficient for Mo K$\alpha$ radiation is 12.8 cm$^{-1}$; since $\mu r_{max}$ is less than 0.15, no absorption corrections were made. The maximum possible variation in the intensities caused by neglect of absorption corrections was estimated to be 9%. Atomic scattering factors for all atoms were taken from the Hartree-Fock-Slater calculations of Hanson, *et al.*[32-34]

**Crystal Data.** Crystals of [PPN][$Cr_2(CO)_{10}I$] are triclinic with primitive cell parameters (with the estimated precision given in parentheses) of $a$ = 13.283 (9), $b$ = 11.479 (7), $c$ = 16.259 (10) Å, $\alpha$ = 100.08 (4), $\beta$ = 105.20 (6), and $\gamma$ = 95.65 (2)°. The cell volume equals 2327.9 Å$^3$. The observed density, 1.49 g/cm$^3$ (flotation in bromobenzene), is in good agreement with the calculated value of 1.50 g/cm$^3$ for two formula species per cell.

The choice of $P\bar{1}$ as the probable space group was confirmed by the satisfactory refinement of the structure. All atoms occupy the twofold set of general positions ($i$): $\pm(x,y,z)$.[35] Thus, the solution of the structure required the location of 1 iodine, 2 chromium, 2 phosphorus, 10 oxygen, 1 nitrogen, and 46 carbon atoms; the 30 independent hydrogen atoms were added in the least-squares refinements after the coordinates of the carbon atoms in the 6 phenyl groups were found.

**Solution of the Structure.** The positions of the iodine and two chromium atoms were determined from a Patterson synthesis. Three successive Fourier difference maps revealed the positions of all remaining nonhydrogen atoms. For least-squares refinement each of the phenyl rings including the hydrogen atoms was geometrically constrained as a rigid body.[4,36] Four cycles of full-matrix least-squares refinement resulted in discrepancy factors of $R_1$ = 7.8 and $R_2$ = 8.0%.[37] The last two cycles included anisotropic thermal parameters for the iodine and chromium atoms and individual isotropic thermal parameters for the phenyl carbons. The isotropic temperature factors for the hydrogen atoms were fixed throughout the refinement at $B$ = 9.0 Å$^2$. Although there were substantial parameter shifts on the last cycle, with values for the shift divided by the estimated error ($\Delta/\sigma$) as high as 6 for thermal parameters and 3 for carbonyl positions, the important chromium and iodine positions all had $\Delta/\sigma \leqslant 0.7$, and cycle times of 37 min on the CDC 3600 computer made further refinement an expensive luxury. A clear indication that the refinement had essentially converged was obtained from the predicted and observed decrease in $R_2$ from one cycle to the next. The final cycle predicted a decrease in $R_2$ of only 0.4%, from 8.4 to 8.0%. This was confirmed when the list of structure factors was calculated for the final Fourier difference map. For the previous cycle, however, a decrease from $R_2$ = 15.9% to 8.5% was predicted and 8.4% was observed. A final Fourier difference map failed to reveal any residual electron density greater than +0.57 or less than −0.52 electron/Å$^3$.

All Patterson and Fourier calculations were carried out with the Blount program,[38] while least-squares refinements were carried out with a local modification of the Busing-Martin-Levy ORFLS program.[39] Interatomic distances and angles with their estimated standard deviations were calculated with the Busing-Martin-Levy ORFFE program[40] from the full inverse matrix (which included the estimated errors in lattice parameters).

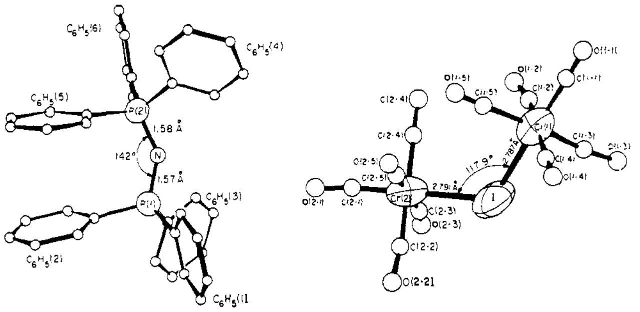

Figure 1. View of the cation and anion as found in the structure of {[$(C_6H_5)_3P]_2N$}[$Cr_2(CO)_{10}I$].

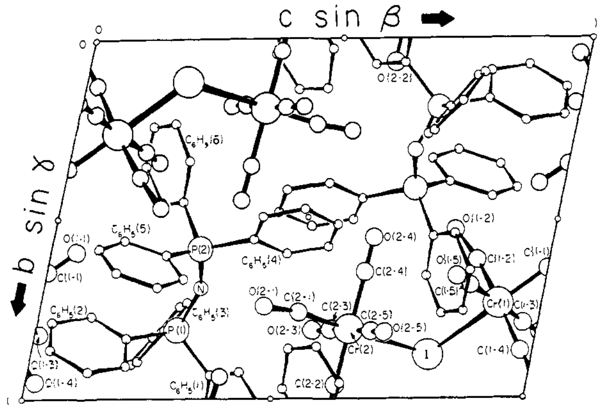

Figure 2. [100] projection of the centrosymmetric triclinic unit cell of {[$(C_6H_5)_3P]_2N$}[$Cr_2(CO)_{10}I$] showing the orientations of the two cations and two anions.

Atomic and rigid-body parameters from the output of the last cycle are given in Table I,[41] while Table II lists selected interatomic distances and angles.

## Results and Discussion

**General Description of the [PPN][$Cr_2(CO)_{10}I$] Crystal Structure..** The crystal structure is comprised of discrete {[$(C_6H_5)_3P]_2N$}$^+$ cations and [$Cr_2(CO)_{10}I$]$^-$ anions with configurations depicted in Figure 1. The orientations of the two cations and two anions in the centrosymmetric triclinic unit cell are shown in Figure 2. Interionic anion···anion contacts are all greater than 3.6 Å, while the shortest interionic distances between the phenyl carbon atoms of different cations are in the range 3.3-3.8 Å. The shortest separations between the phenyl carbon atoms of the cations and the carbonyl oxygen atoms of the anions are all greater than 3.2 Å.

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(30) E. F. Epstein, Ph.D. Thesis, University of Wisconsin, 1968.

(31) V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 3756 (1969); E. F. Epstein and L. F. Dahl, *ibid.*, **92**, 502 (1970).

(32) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(33) No anomalous dispersion corrections were made, since the relatively small corrections (*i.e.*, for Mo K$\alpha$ radiation $\Delta f'$ = −0.5, $\Delta f''$ = 2.4 for iodine; $\Delta f'$ = 0.3, $\Delta f''$ = 0.8 for chromium)[34] have been found in our laboratories not to affect significantly the atomic coordinates of centrosymmetric structures (*cf.* D. H. Templeton, *ibid.*, **8**, 842 (1955)).

(34) D. H. Templeton in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

(35) Reference 34, Vol. I, 1952, p 75.

(36) Each phenyl ring was assumed to possess $D_{6h}$ geometry with carbon-carbon bond lengths of 1.392 Å and carbon-hydrogen bond lengths of 1.08 Å. The orthonormal set ($x',y',z'$) has $x'$ along C(4)-C(1), $y'$ along C(5)-C(3), and $z'$ along ($x'$ cross $y'$). The origin is at the center of the carbon framework.

(37) All least-squares refinements reported in this work were based on the minimization of the quantity $\Sigma w_i(\Delta F_i)^2$; the weights were assigned according to the estimated standard deviations of the structure factors.[30] The discrepancy factors, $R_1$ and $R_2$, are defined as follows: $R_1 = 100[\Sigma||F_o| - |F_c||/\Sigma|F_o|]$; $R_2 = 100[\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$.

(38) J. F. Blount, Ph.D. Thesis University of Wisconsin, 1965.

(39) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

(40) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

(41) Calculated and observed structure factors are deposited as Document No. NAPS-01148 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting \$2.00 for microfiche or \$5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC-NAPS.

**Table I.** Final Parameters for $[PPN][Cr_2(CO)_{10}I]$[a]

| Atom | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| I | 0.0294 (2) | 0.8801 (2) | 0.7949 (1) | *b* |
| Cr(1) | 0.0969 (3) | 0.7385 (3) | 0.9154 (3) | *b* |
| Cr(2) | 0.0486 (3) | 0.8083 (3) | 0.6273 (3) | *b* |
| P(1) | 0.4696 (4) | 0.8097 (5) | 0.2817 (3) | 3.1 (1) |
| P(2) | 0.5581 (4) | 0.5829 (5) | 0.2959 (4) | 3.5 (1) |
| N | 0.494 (1) | 0.690 (1) | 0.312 (1) | 3.4 (4) |
| C(1-1) | 0.144 (2) | 0.645 (2) | 1.001 (2) | 7.2 (7) |
| O(1-1) | 0.179 (1) | 0.593 (2) | 1.050 (1) | 9.3 (5) |
| C(1-2) | 0.001 (3) | 0.615 (3) | 0.853 (2) | 11 (1) |
| O(1-2) | −0.067 (2) | 0.537 (2) | 0.804 (2) | 13.4 (7) |
| C(1-3) | −0.002 (3) | 0.791 (3) | 0.968 (2) | 11.3 (9) |
| O(1-3) | −0.059 (2) | 0.819 (2) | 1.010 (1) | 12.3 (6) |
| C(1-4) | 0.193 (2) | 0.872 (3) | 0.977 (2) | 7.9 (8) |
| O(1-4) | 0.254 (1) | 0.954 (2) | 1.019 (1) | 8.0 (5) |
| C(1-5) | 0.196 (2) | 0.687 (2) | 0.853 (2) | 6.2 (6) |
| O(1-5) | 0.251 (1) | 0.657 (2) | 0.820 (1) | 8.0 (5) |
| C(2-1) | 0.054 (2) | 0.762 (2) | 0.518 (2) | 8.0 (7) |
| O(2-1) | 0.060 (1) | 0.742 (2) | 0.445 (1) | 9.3 (5) |
| C(2-2) | 0.068 (2) | 0.964 (3) | 0.620 (2) | 8.5 (7) |
| O(2-2) | 0.093 (2) | 1.063 (2) | 0.614 (1) | 10.6 (6) |
| C(2-3) | −0.087 (3) | 0.805 (3) | 0.585 (2) | 12 (1) |
| O(2-3) | −0.177 (2) | 0.812 (2) | 0.556 (1) | 12.2 (6) |
| C(2-4) | 0.029 (2) | 0.650 (3) | 0.636 (2) | 9.0 (8) |
| O(2-4) | 0.021 (1) | 0.551 (2) | 0.640 (1) | 8.3 (5) |
| C(2-5) | 0.189 (2) | 0.814 (2) | 0.670 (2) | 5.9 (6) |
| O(2-5) | 0.282 (1) | 0.816 (1) | 0.696 (1) | 7.8 (4) |
| $C_6H_5(1)$ | | | | |
| PC(1-1) | 0.504 | 0.832 | 0.185 | 3.3 (4) |
| PC(1-2) | 0.441 | 0.771 | 0.103 | 4.4 (5) |
| PC(1-3) | 0.471 | 0.786 | 0.029 | 6.3 (6) |
| PC(1-4) | 0.562 | 0.862 | 0.037 | 8.2 (7) |
| PC(1-5) | 0.625 | 0.924 | 0.119 | 10.0 (8) |
| PC(1-6) | 0.595 | 0.908 | 0.193 | 7.3 (7) |
| PH(1-2) | 0.370 | 0.711 | 0.097 | 9[c] |
| PH(1-3) | 0.422 | 0.738 | −0.035 | 9 |
| PH(1-4) | 0.585 | 0.874 | −0.020 | 9 |
| PH(1-5) | 0.696 | 0.983 | 0.125 | 9 |
| PH(1-6) | 0.643 | 0.956 | 0.257 | 9 |
| $C_6H_5(2)$ | | | | |
| PC(2-1) | 0.331 | 0.812 | 0.259 | 3.0 (4) |
| PC(2-2) | 0.285 | 0.897 | 0.216 | 5.4 (5) |
| PC(2-3) | 0.179 | 0.905 | 0.205 | 6.9 (6) |
| PC(2-4) | 0.118 | 0.828 | 0.237 | 6.5 (6) |
| PC(2-5) | 0.164 | 0.744 | 0.280 | 6.0 (6) |
| PC(2-6) | 0.270 | 0.736 | 0.291 | 3.9 (5) |
| PH(2-2) | 0.333 | 0.956 | 0.191 | 9[c] |
| PH(2-3) | 0.144 | 0.970 | 0.171 | 9 |
| PH(2-4) | 0.036 | 0.835 | 0.228 | 9 |
| PH(2-5) | 0.116 | 0.685 | 0.305 | 9 |
| PH(2-6) | 0.305 | 0.670 | 0.325 | 9 |
| $C_6H_5(3)$ | | | | |
| PC(3-1) | 0.537 | 0.933 | 0.368 | 4.1 (5) |
| PC(3-2) | 0.634 | 0.927 | 0.424 | 5.9 (6) |
| PC(3-3) | 0.692 | 1.029 | 0.484 | 6.6 (6) |
| PC(3-4) | 0.652 | 1.137 | 0.488 | 7.0 (6) |
| PC(3-5) | 0.555 | 1.143 | 0.431 | 8.1 (7) |
| PC(3-6) | 0.497 | 1.041 | 0.371 | 6.1 (6) |
| PH(3-2) | 0.665 | 0.843 | 0.421 | 9[c] |
| PH(3-3) | 0.767 | 1.024 | 0.528 | 9 |
| PH(3-4) | 0.697 | 1.216 | 0.534 | 9 |
| PH(3-5) | 0.524 | 1.227 | 0.434 | 9 |
| PH(3-6) | 0.422 | 1.046 | 0.327 | 9 |
| $C_6H_5(4)$ | | | | |
| PC(4-1) | 0.631 | 0.557 | 0.399 | 3.2 (4) |
| PC(4-2) | 0.596 | 0.598 | 0.471 | 5.4 (6) |
| PC(4-3) | 0.648 | 0.579 | 0.553 | 7.3 (7) |
| PC(4-4) | 0.734 | 0.517 | 0.563 | 7.6 (7) |
| PC(4-5) | 0.769 | 0.476 | 0.491 | 7.7 (7) |
| PC(4-6) | 0.717 | 0.495 | 0.409 | 6.0 (6) |
| PH(4-2) | 0.529 | 0.646 | 0.464 | 9[c] |
| PH(4-3) | 0.621 | 0.611 | 0.608 | 9 |
| PH(4-4) | 0.774 | 0.502 | 0.626 | 9 |
| PH(4-5) | 0.836 | 0.428 | 0.498 | 9 |
| PH(4-6) | 0.744 | 0.463 | 0.353 | 9 |

Table I (*Continued*)

| Atom | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| $C_6H_5(5)$ | | | | |
| PC(5-1) | 0.646 | 0.602 | 0.230 | 4.6 (5) |
| PC(5-2) | 0.745 | 0.667 | 0.273 | 8.6 (8) |
| PC(5-3) | 0.816 | 0.691 | 0.226 | 11.3 (9) |
| PC(5-4) | 0.786 | 0.649 | 0.136 | 8.8 (8) |
| PC(5-5) | 0.686 | 0.584 | 0.093 | 7.4 (7) |
| PC(5-6) | 0.616 | 0.560 | 0.140 | 5.0 (5) |
| PH(5-2) | 0.768 | 0.699 | 0.343 | 9[c] |
| PH(5-3) | 0.893 | 0.741 | 0.259 | 9 |
| PH(5-4) | 0.840 | 0.668 | 0.099 | 9 |
| PH(5-5) | 0.663 | 0.552 | 0.023 | 9 |
| PH(5-6) | 0.539 | 0.510 | 0.107 | 9 |
| $C_6H_5(6)$ | | | | |
| PC(6-1) | 0.468 | 0.450 | 0.242 | 4.2 (5) |
| PC(6-2) | 0.364 | 0.457 | 0.199 | 5.7 (6) |
| PC(6-3) | 0.294 | 0.353 | 0.155 | 7.7 (7) |
| PC(6-4) | 0.328 | 0.242 | 0.154 | 7.2 (7) |
| PC(6-5) | 0.432 | 0.235 | 0.197 | 6.5 (6) |
| PC(6-6) | 0.502 | 0.339 | 0.241 | 5.1 (5) |
| PH(6-2) | 0.338 | 0.543 | 0.200 | 9[c] |
| PH(6-3) | 0.213 | 0.358 | 0.122 | 9 |
| PH(6-4) | 0.273 | 0.161 | 0.120 | 9 |
| PH(6-5) | 0.458 | 0.149 | 0.196 | 9 |
| PH(6-6) | 0.583 | 0.333 | 0.274 | 9 |

| | | | Rigid-body parameters[4] | | | |
|---|---|---|---|---|---|---|
| Group | $x$ | $y$ | $z$ | $\phi$ | $\theta$ | $\rho$ |
| $C_6H_5(1)$ | 0.5946 (8) | 1.0349 (9) | 0.4276 (6) | 49.4 (5) | 160.4 (5) | 44.7 (5) |
| $C_6H_5(2)$ | 0.5329 (8) | 0.8472 (8) | 0.1109 (7) | −49.6 (6) | −145.0 (6) | −84.7 (6) |
| $C_6H_5(3)$ | 0.2245 (7) | 0.8202 (8) | 0.2481 (5) | −189.4 (6) | −151.3 (4) | −8.1 (5) |
| $C_6H_5(4)$ | 0.6825 (8) | 0.5370 (8) | 0.4809 (7) | −116.0 (5) | 156.8 (5) | 78.2 (5) |
| $C_6H_5(5)$ | 0.7158 (9) | 0.6255 (9) | 0.1830 (8) | 127.3 (9) | 122.5 (6) | −103.8 (9) |
| $C_6H_5(6)$ | 0.3981 (8) | 0.3459 (9) | 0.1979 (6) | −129.7 (5) | −164.6 (5) | −30.0 (5) |

[a] Estimated standard deviation of the last significant figure is given in parentheses. [b] Anisotropic thermal parameters, used for the chromium and iodine atoms, are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The resulting thermal coefficients ($\times 10^4$) are given as follows

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| I | 146 (2) | 157 (2) | 84 (1) | 101 (2) | 35 (1) | 20 (1) |
| Cr(1) | 68 (3) | 96 (4) | 64 (3) | 9 (3) | 21 (2) | −3 (3) |
| Cr(2) | 74 (4) | 75 (4) | 64 (3) | 16 (3) | 1 (2) | 8 (3) |

[c] Thermal parameters for the hydrogen atoms of the phenyl groups were held constant throughout the least-squares refinement.

**Stereochemistry of the $[Cr_2(CO)_{10}I]^-$ Anion.** The geometry of the $[Cr_2(CO)_{10}I]^-$ anion has a nonlinear Cr–I–Cr framework with a bridge angle of 117.9 (1)°. The two independent Cr–I bond lengths are equal within one standard deviation, and the average value of 2.789 (4) Å is close to the value 2.81 Å given by the sum of a chromium covalent radius of 1.48 Å (corresponding to one-half the Cr–Cr bond distance in the $[Cr_2(CO)_{10}]^{2-}$ anion)[4] and Pauling's covalent radius of 1.33 Å[42] for iodine. On the basis of the observed bridge angle in this noncyclic halogen-bridged system being near the regular tetrahedral angle of 109° 28′, it is concluded that the iodine atom utilizes one of its usually unshared electron pairs to form normal electron-pair metal–halogen $\sigma$ bonds without any appreciable involvement of its other two unshared electron pairs in delocalized bonding with the chromium pentacarbonyl moieties. Hence, there is no discernible stereochemical evidence in this halogen-bridged $[(OC)_5Cr\text{–}I\text{–}Cr(CO)_5]^-$ anion for the occurrence of any electron delocalization either of the three-center electron-pair $\sigma$-bonding kind possessed by the *linear* Cr–H–Cr segment of the corresponding hydrido-bridged $[(OC)_5Cr\text{–}H\text{–}Cr(CO)_5]^-$ anion[4] or of the $\pi$-bonding kind described from a qualitative MO representation[43] for the *linear* Ru–O–Ru segment of the $[Cl_5Ru\text{–}O\text{–}RuCl_5]^{4-}$ anion. This latter dinuclear ruthenium anion with five chlorine atoms and the bridging oxygen atom octahedrally coordinated about each ruthenium atom was shown from an X-ray study[44] to have a $D_{4h}$ geometry in the compound $K_4[Ru_2Cl_{10}O]\cdot H_2O$. Of interest is the application of the Dunitz–Orgel MO scheme[43] to rationalize the different geometries of the $[Cr_2(CO)_{10}I]^-$ and $[Ru_2Cl_{10}O]^{4-}$ anions. With the inherent assumption that the Ru–Cl and Ru–O $\sigma$ bonds may be isolated under the perfect-pairing approximation from the bonding in the Ru–O–Ru system, Dunitz and Orgel[43] showed by topological symmetry arguments that the $\pi$ bonding between the 2 ruthenium and oxygen atoms arises from the 12 available electrons (4 from each Ru(IV) and 4 from the degenerate oxygen p$\pi$ set) being placed in localized MO's which, under $D_{4h}$ symmetry, transform to give a diamagnetic ground state described in their notation by the energy level ordering $(e_u{}^b)^4$, $(b_{2g})^2$, $(b_{2u})^2(e_g)^4$, $(e_u{}^a)^0$. Here, the filled $e_u{}^b$ and empty $e_u{}^a$ symbols represent the degenerate bonding and antibonding d$\pi$(Ru)–p$\pi$(O)–d$\pi$(Ru) orbital combinations, respectively.

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(42) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 225.

(43) J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 2594 (1953).

(44) A. McL. Mathieson, D. P. Mellor, and N. C. Stephenson, *Acta Crystallogr.*, 5, 185 (1952).

Table II. Distances (Å) and Angles (deg) for [PPN][$Cr_2(CO)_{10}I$][a]

| | | | |
|---|---|---|---|
| | **A. Lengths** | | |
| | Chromium–Iodine | | |
| Cr(1)–I | 2.787 (5) | Cr(2)–I | 2.791 (5) |
| | Av 2.789 | | |
| | Chromium–Carbon (eq) | | |
| Cr(1)–C(1-2) | 1.77 (4) | Cr(2)–C(2-2) | 1.81 (3) |
| Cr(1)–C(1-3) | 1.84 (3) | Cr(2)–C(2-3) | 1.74 (3) |
| Cr(1)–C(1-4) | 1.84 (3) | Cr(2)–C(2-4) | 1.84 (3) |
| Cr(1)–C(1-5) | 1.94 (3) | Cr(2)–C(2-5) | 1.80 (3) |
| | 1.85 (av) | | 1.80 (av) |
| | Av 1.82 | | |
| | Chromium···Oxygen (eq) | | |
| Cr(1)···O(1-2) | 2.97 (3) | Cr(2)···O(2-2) | 2.99 (2) |
| Cr(1)···O(1-3) | 3.01 (2) | Cr(2)···O(2-3) | 2.93 (2) |
| Cr(1)···O(1-4) | 2.99 (2) | Cr(2)···O(2-4) | 2.98 (2) |
| Cr(1)···O(1-5) | 3.00 (2) | Cr(2)···O(2-5) | 2.99 (2) |
| | 2.99 (av) | | 2.97 (av) |
| | Av 2.98 | | |
| | Chromium–Carbon (ax) | | |
| Cr(1)–C(1-1) | 1.92 (3) | Cr(2)–C(2-1) | 1.79 (3) |
| | Av 1.86 | | |
| | Chromium···Oxygen (axial) | | |
| Cr(1)···O(1-1) | 3.02 (2) | Cr(1)···O(2-1) | 2.98 (2) |
| | Av 3.00 | | |
| | Carbon–Oxygen | | |
| C(1-1)–O(1-1) | 1.11 (2) | C(2-1)–O(2-1) | 1.19 (3) |
| C(1-2)–O(1-2) | 1.21 (3) | C(2-2)–O(2-2) | 1.19 (3) |
| C(1-3)–O(1-3) | 1.17 (3) | C(2-3)–O(2-3) | 1.19 (3) |
| C(1-4)–O(1-4) | 1.16 (3) | C(2-4)–O(2-4) | 1.14 (3) |
| C(1-5)–O(1-5) | 1.06 (2) | C(2-5)–O(2-5) | 1.19 (3) |
| | 1.14 (av) | | 1.18 (av) |
| | Av 1.16 | | |
| | Phosphorus–Nitrogen | | |
| P(1)–N | 1.57 (1) | P(2)–N | 1.58 (1) |
| | Av 1.58 | | |
| | Phosphorus–Phenyl Carbon | | |
| P(1)–PC(1-1) | 1.78 | P(2)–PC(4-1) | 1.80 |
| P(1)–PC(2-1) | 1.80 | P(2)–PC(5-1) | 1.79 |
| P(1)–PC(3-1) | 1.78 | P(2)–PC(6-1) | 1.77 |
| | 1.79 (av) | | 1.79 (av) |
| | Av 1.79 | | |
| | **B. Bond Angles** | | |
| | Chromium–Iodine–Chromium | | |
| | Cr(1)–I–Cr(2) | 117.9 (1) | |
| | Iodine–Chromium–Carbon (eq) | | |
| I–Cr(1)–C(1-2) | 92.2 (10) | I–Cr(2)–C(2-2) | 89.0 (8) |
| I–Cr(1)–C(1-3) | 87.4 (9) | I–Cr(2)–C(2-3) | 89.2 (10) |
| I–Cr(1)–C(1-4) | 85.2 (8) | I–Cr(2)–C(2-4) | 90.5 (8) |
| I–Cr(1)–C(1-5) | 88.9 (7) | I–Cr(2)–C(2-5) | 91.4 (7) |
| | 88.6 (av) | | 90.0 (av) |
| | Av 89.3 | | |
| | Iodine–Chromium–Carbon (ax) | | |
| I–Cr(1)–C(1-1) | 178.4 (7) | I–Cr(2)–C(2-1) | 177.0 (8) |
| | Av 177.7 | | |
| | Carbon (eq)–Chromium–Carbon (eq) | | |
| C(1-2)–Cr(1)–C(1-3) | 88 (1) | C(2-2)–Cr(2)–C(2-3) | 89 (1) |
| C(1-3)–Cr(1)–C(1-4) | 90 (1) | C(2-3)–Cr(2)–C(2-4) | 92 (1) |
| C(1-4)–Cr(1)–C(1-5) | 90 (1) | C(2-4)–Cr(2)–C(2-5) | 90 (1) |
| C(1-5)–Cr(1)–C(1-2) | 91 (1) | C(2-5)–Cr(2)–C(2-2) | 90 (1) |
| | 90 (av) | | 90 (av) |
| | Av 90 | | |

Table II (*Continued*)

| | | | |
|---|---|---|---|
| **B. Bond Angles (*Continued*)** | | | |
| Carbon (ax)–Chromium–Carbon (eq) | | | |
| C(1-1)–Cr(1)–C(1-2) | 89 (1) | C(2-1)–Cr(2)–C(2-2) | 91 (1) |
| C(1-1)–Cr(1)–C(1-3) | 92 (1) | C(2-1)–Cr(2)–C(2-3) | 88 (1) |
| C(1-1)–Cr(1)–C(1-4) | 94 (1) | C(2-1)–Cr(2)–C(2-4) | 89 (1) |
| C(1-1)–Cr(1)–C(1-5) | 92 (1) | C(2-1)–Cr(2)–C(2-5) | 92 (1) |
| | 92 (av) | | 90 (av) |
| | Av 91 | | |
| Chromium–Carbon–Oxygen | | | |
| Cr(1)–C(1-1)–O(1-1) | 174 (2) | Cr(2)–C(2-1)–O(2-1) | 174 (2) |
| Cr(1)–C(1-2)–O(1-2) | 173 (3) | Cr(2)–C(2-2)–O(2-2) | 171 (2) |
| Cr(1)–C(1-3)–O(1-3) | 172 (3) | Cr(2)–C(2-3)–O(2-3) | 174 (3) |
| Cr(1)–C(1-4)–O(1-4) | 177 (2) | Cr(2)–C(2-4)–O(2-4) | 177 (2) |
| Cr(1)–C(1-5)–O(1-5) | 178 (2) | Cr(2)–C(2-5)–O(2-5) | 179 (2) |
| | 175 (av) | | 175 (av) |
| | Av 175 | | |
| Phosphorus–Nitrogen–Phosphorus | | | |
| P(1)–N–P(2) | 142 (1) | | |
| Nitrogen–Phosphorus–Phenyl Carbon | | | |
| N–P(1)–PC(1-1) | 109 | N–P(2)–PC(4-1) | 109 |
| N–P(1)–PC(2-1) | 116 | N–P(2)–PC(5-1) | 115 |
| N–P(1)–PC(3-1) | 108 | N–P(2)–PC(6-1) | 109 |
| Phenyl Carbon–Phosphorus–Phenyl Carbon | | | |
| PC(1-1)–P(1)–PC(2-1) | 108 | PC(4-1)–P(2)–PC(5-1) | 109 |
| PC(1-1)–P(1)–PC(3-1) | 109 | PC(4-1)–P(2)–PC(6-1) | 107 |
| PC(2-1)–P(1)–PC(3-1) | 106 | PC(5-1)–P(2)–PC(6-1) | 106 |
| | 108 (av) | | 107 (av) |
| | Av 108 | | |
| Phosphorus–Phenyl Carbon–Phenyl Carbon | | | |
| P(1)–PC(1-1)–PC(1-4) | 173 | P(2)–PC(4-1)–PC(4-4) | 177 |
| P(1)–PC(2-1)–PC(2-4) | 178 | P(2)–PC(5-1)–PC(5-4) | 176 |
| P(1)–PC(3-1)–PC(3-4) | 175 | P(2)–PC(6-1)–PC(6-4) | 179 |
| | 175 (av) | | 178 (av) |
| | Av 176 | | |
| **C. Nonbonding Distances** | | | |
| Within each Cr(CO)$_5$ fragment | | | |
| C(1-1)···C(1-2) | 2.58 (5) | C(2-1)···C(2-2) | 2.57 (4) |
| C(1-1)···C(1-3) | 2.70 (4) | C(2-1)···C(2-3) | 2.45 (4) |
| C(1-1)...C(1-4) | 2.74 (4) | C(2-1)···C(2-4) | 2.56 (4) |
| C(1-1)···C(1-5) | 2.78 (4) | C(2-1)···C(2-5) | 2.58 (4) |
| C(1-2)···C(1-3) | 2.51 (5) | C(2-2)···C(2-3) | 2.48 (4) |
| C(1-3)···C(1-4) | 2.61 (4) | C(2-3)···C(2-4) | 2.57 (5) |
| C(1-4)···C(1-5) | 2.68 (4) | C(2-4)···C(2-5) | 2.57 (4) |
| C(1-5)···C(1-2) | 2.65 (4) | C(2-5)···C(2-2) | 2.56 (4) |
| Between Cr(CO)$_5$ fragments | | | |
| O(1-2)···O(2-4) | 3.21 (3) | | |
| O(1-5)···O(2-5) | 3.27 (3) | | |
| O(1-5)···O(2-5) | 3.01 (2) | | |

[a] Estimated standard deviation of the last significant figure is given in parentheses.

When this MO model is extended to the now *hypothetical* $D_{4h}$ geometry of the $[(OC)_5Cr\text{–}I\text{–}Cr(CO)_5]^-$ anion with the assumption that the $\sigma$- and $\pi$-bonding Cr–CO interactions can likewise be separated to a first approximation from the Cr–I–Cr system, it is found that the 16 available electrons fill both the bonding $e_u^b$ and antibonding $e_u^a$ orbital combinations, $d\pi(Cr)\text{–}p\pi(I)\text{–}d\pi(Cr)$, leading to no net $\pi$-bonding stability unless partial withdrawal occurs from mainly the antibonding $e_u^a$ orbitals by Cr–CO back-bonding involving the empty $\pi_{CO}{}^*$ orbitals. This comparison thus emphasizes the fact that the bent Cr–I–Cr architecture in the $[Cr_2(CO)_{10}I]^-$ anion with the bridge angle of 117.9 (1)° arises from lack of sufficient $\pi$-bonding stability in the Cr–I–Cr system. It is tempting to predict that the neutral paramagnetic analog $[Cr_2(CO)_{10}I]^0$, reported by Behrens and Schwab,[11] should possess markedly increased $\pi$-bonding stability but that this molecule under $D_{4h}$ symmetry[13] would possess an $^2E$ ground electronic state (with three electrons present in the degenerate antibonding $e_u^a$ orbitals) which would lead to a Jahn–Teller distortion.

The octahedral-like coordination of the five carbonyl groups and bridging iodine atom about each chromium atom in the $[Cr_2(CO)_{10}I]^-$ anion is similar to the octahedral-like environment about each chromium atom in the $[Cr_2(CO)_{10}H]^-$ anion rather than in the $[Cr_2(CO)_{10}]^{2-}$ anion in that there is essentially no bending of the

Table III. Selected Parameters for the Bis(triphenylphosphine)iminium Cation, $[(C_6H_5)_3P\overset{..}{-}N\overset{..}{-}P(C_6H_5)_3]^+$

| | P–N bond, Å (mean) | P–C bond, Å (mean) | P–N–P angles, deg | N–P–C(α)[a] angles, deg (av) | N–P–C(β)[b] angles, deg (av) | C–P–C angles, deg (av) |
|---|---|---|---|---|---|---|
| $[PPN][Cr_2(CO)_{10}I]$ | 1.575 (7) | 1.79 | 142 (1) | 115–116<br>(115.5) | 108–109<br>(108.8) | 106–109<br>(107.5) |
| $[PPN]_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$ | 1.570 (15) | 1.78 | 137 (1) | 114–115<br>(114.5) | 109–113<br>(111.0) | 105–108<br>(106.8) |
| $[PPN]_2[Mo_2(CO)_{10}]\cdot CH_2Cl_2$ | 1.570 (15) | 1.81 | 137 (2) | 113–116<br>(114.5) | 108–112<br>(109.8) | 105–109<br>(107.3) |
| $[PPN]_2[Mo_2Ni_3(CO)_{16}]$ | 1.578 (6) | 1.77 | 137.5 (5) | 114.2–115.3<br>(114.8) | 106.7–111.5<br>(109.9) | 106.7–109.3<br>(107.5) |
| $[PPN]_2[W_2Ni_3(CO)_{16}]$ | 1.572 (10) | 1.78 | 139.0 (7) | 113.4–114.4<br>(113.9) | 107.3–111.7<br>(110.2) | 106.8–109.6<br>(107.4) |

[a] Where C(α) represents the phosphorus-attached carbon atom of either the $C_6H_5(2)$ or the $C_6H_5(5)$ phenyl ring (in Figure 1), which occupies the particular coordination site normally occupied by a nitrogen ring atom bonded to a P–N–P segment in an essentially planar cyclotriphosphazene ring. [b] Where C(β) represents the phosphorus-linked carbon atom of either the $C_6H_5(1)$, $C_6H_5(3)$, $C_6H_5(4)$, or the $C_6H_5(6)$ phenyl ring (in Figure 1), which is similarly oriented as a phenyl substituent in a $(C_6H_5)_2P–N–P(C_6H_5)_2$ fragment of the $N_3P_3Cl_2(C_6H_5)_4$ or $N_3P_3(C_6H_5)_6$ molecule.

equatorial carbonyl ligands away from the axial carbonyl ligand. The average $C_{ax}$–Cr–$C_{eq}$ angle is 91°, and the perpendicular displacements from a plane passing through each chromium atom and parallel to the best plane through the four equatorial carbon atoms average 0.02 Å for the carbon atoms and 0.04 Å for the oxygen atoms. These perpendicular displacements are similar to those of 0.03 Å (av) for the equatorial carbon atoms and 0.04 Å (av) for the equatorial oxygen atoms from the analogously defined planes in the $[Cr_2(CO)_{10}H]^-$ anion,[4] but are clearly much less than the corresponding perpendicular deviations of 0.12 Å (av) for the equatorial carbon atoms and 0.29 Å (av) for the equatorial oxygen atoms in the $[Cr_2(CO)_{10}]^{2-}$ anion.[4]

**Stereochemistry of the Bis(triphenylphosphine)iminium Cation. (a) General Description of the $[(C_6H_5)_3P\overset{..}{-}N\overset{..}{-}P(C_6H_5)_3]^+$ Cation and Conformational Similarity with Phenyl-Substituted Cyclotriphosphazene Molecules.** The bis(triphenylphosphine)iminium cation (PPN) in the $[PPN][Cr_2(CO)_{10}I]$ crystalline salt displays an approximate $C_2$-2 geometry (shown in Figure 1), with the noncrystallographic twofold axis passing through the central nitrogen atom and bisecting the P–N–P angle. The three phenyl groups are disposed about each tetrahedral-like phosphorus atom such that two of the six phenyl ligands, $C_6H_5(2)$ and $C_6H_5(5)$, are approximately positioned in coordination sites normally occupied by two ring nitrogen atoms linked to the P–N–P segment of an essentially planar cyclotriphosphazene ring. The other four phenyl groups in the PPN cation are then oriented about the P–N–P fragment in an analogous fashion to the disposition of the phenyl substituents in the $(C_6H_5)_2P–N–P(C_6H_5)_2$ part of 1,1-dichloro-3,3,5,5-tetraphenylcyclotriphosphazene[45] and in hexaphenylcyclotriphosphazene.[26]

This particular configuration for the PPN cation is virtually identical with that later found from the X-ray structural determinations of four other PPN salts, *viz.*, $[PPN]_2[M_2(CO)_{10}]\cdot CH_2Cl_2$ (where M = Cr, Mo)[4] and $[PPN]_2[M_2Ni_3(CO)_{16}]$ (where M = Mo, W).[46] The overall geometrical invariance of the PPN cation to ionic packing influences in three different crystal lattices of the five above-mentioned salts supports the premise that its conformation is primarily dictated by electronic and intra(phenyl ring) steric effects. Table III, which gives selected bond lengths and angles for the PPN cation in the five salts, reveals that the two chemically equivalent P–N bonds of the PPN cation have average lengths within 0.005 of 1.575 Å for all five PPN salts. Although this mean value is substantially shorter than the presumed P–N single-bond length of 1.77 (2) Å found in the $[PO_3NH_3]^-$ anion of the sodium phosphoramidate salt,[47] it is almost the same as the average P–N bond length in the $(C_6H_5)_2P–N–P(C_6H_5)_2$ part of 1,1-dichloro-3,3,5,5-tetraphenylcyclotriphosphazene (1.578 (4) Å)[45] and hexaphenylcyclotriphosphazene (1.597 (3) Å).[26] The chemical equivalence of the phosphorus atoms in the bis(triphenylphosphine)iminium cation is in accord with the $^{31}P$ nmr spectrum of the chloride salt exhibiting a single band at −22.3 ppm *vs.* 85% phosphoric acid.[17]

The conformation of the PPN cation bears an especially close resemblance with that of the corresponding part in the $N_3P_3Cl_2(C_6H_5)_4$ molecule.[45] Their close stereochemical relationship is made apparent from a consideration of a $X(C_6H_5)_2P–N–P(C_6H_5)_2X$ system of a given conformation in which both coordination sites of the two X ligands are occupied by the $C_6H_5(2)$ and $C_6H_5(5)$ phenyl rings in the PPN cation and by the nitrogen atoms of a chelating $NP(Cl_2)N$ ligand in the cyclic $N_3P_3Cl_2(C_6H_5)_4$ complex. This latter molecule has a similarly oriented noncrystallographic twofold axis passing through the central nitrogen atom and the phosphorus atom in the para ring position such that the $N_3P_3$ ring deviates slightly but yet significantly from coplanarity as a puckered boat form with the two P–X bonds (where X represents a nitrogen atom of the N–P($Cl_2$)–N chelating ligand) not exactly parallel but sloping somewhat in opposite directions.[45] Figure 1 shows that the corresponding P–X bonds of the $C_6H_5(2)$ and $C_6H_5(5)$ ligands in the PPN cation are also directed to a similar extent in opposite directions.

The remarkably similar orientations of two of the three phenyl rings per phosphorus atom in the PPN cation with the corresponding phenyl ring substituents

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(47) D. W. J. Cruickshank, *Acta Crystallogr.*, 17, 671 (1964); E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *ibid.*, 6, 621 (1953).

in the phenyl-substituted cyclotriphosphazene molecules is clearly seen from a detailed comparison of the dihedral angles of corresponding pairs of phenyl rings. In all cases the planes of the two phenyl rings coordinated to the *same* phosphorus atom are nearly perpendicular to each other. The dihedral angles are 64° between $C_6H_5(1)$ and $C_6H_5(3)$ and 73° between $C_6H_5(4)$ and $C_6H_5(6)$ in [PPN][$Cr_2(CO)_{10}I$] (Figure 1), 85 and 79° among the corresponding pairs in $[PPN]_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$,[4] and 80 and 82° among the corresponding pairs in $[PPN]_2[Mo_2(CO)_{10}]\cdot CH_2Cl_2$;[4] the dihedral angles between each pair of phenyl substituents of a given phosphorus atom are 84° in 1,1-diphenyl-3,3,5,5-tetrachlorocyclotriphosphazene,[48] vary from 84.4 to 89.6° in the two molecules of the crystallographically asymmetric unit of 1,1-dichloro-3,3,5,5-tetraphenylcyclotriphosphazene,[45] and vary from 80.9 to 82.3° in the hexaphenylcyclotriphosphazene molecule (for which the $N_3P_3$ ring has an irregular slight chair form).[26]

In the $N_3P_3Cl_2(C_6H_5)_4$ and $N_3P_3(C_6H_5)_6$ molecules the two adjacent phenyl rings which are cis with respect to the $N_3P_3$ ring are also almost at a right angle with each other. Figure 1 clearly illustrates that in [PPN][$Cr_2(CO)_{10}I$] the corresponding adjacent phenyl rings which are cis oriented relative to the P–N–P plane (*viz.*, the $C_6H_5(3)$ and $C_6H_5(6)$ pair and the $C_6H_5(1)$ and $C_6H_5(4)$ pair) are also perpendicularly situated with respect to each other. This stereochemical analysis reinforces the supposition that steric rather than electronic effects are primarily responsible for the particular conformation of the six phenyl rings in the PPN cation.

The P–N–P bond angle, which varies from 137 to 142° in the five PPN salts listed in Table III, is undoubtedly influenced by the steric requirements of the phenyl groups. The nearly parallel $C_6H_5(2)$ and $C_6H_5(5)$ phenyl rings (with a dihedral angle of 10–12°) are particularly important in this regard, as they are separated by approximately 3.5 Å, which is shorter than the known methyl···methyl and methylene···methylene van der Waals contacts of 4.0 Å,[49] but which is close to the separation of 3.4 Å[49] between parallel aromatic rings. The effect of this balance between a smaller P–N–P bond angle and inter(phenyl ring) $\pi$-orbital repulsion is also evident in the N–P–C bond angles. Whereas for the phosphorus-linked carbon atoms of the phenyl rings $C_6H_5(1)$, $C_6H_5(3)$, $C_6H_5(4)$, and $C_6H_5(6)$ the N–P–C angles in the five PPN salts (Table III) are nearly tetrahedral, with average values of range 109–111°, the corresponding N–P–C angles involving the phenyl rings $C_6H_5(2)$ and $C_6H_5(5)$ are larger with an angular variation in the average values of 114° to 115.5°.

The extensive deviation of each of the two triphenylphosphine groups in the bis(triphenylphosphine)iminium cation from localized threefold symmetry is indicated by the considerable variation in the dihedral angles between the three pairs of phenyl rings in a given triphenylphosphine group; the angular ranges are 25 and 28° in [PPN][$Cr_2(CO)_{10}I$], 14 and 27° in $[PPN]_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$,[4] and 15 and 22° in $[PPN]_2[Mo_2(CO)_{10}]\cdot CH_2Cl_2$.[4] Similar deviations of triphenylphosphine ligands from localized threefold symmetry are common, however, in the solid state. La Placa and Ibers[50] reported dihedral angles with maximum differences of 36° for the phenyl rings of a given triphenylphosphine substituent in $Rh(H)(CO)[P(C_6H_5)_3]_3$, while in the triphenylphosphine molecule itself Daly[51] found a difference of 30° from threefold symmetry for one of the phenyl rings.

The average values of the P–C bond lengths of range 1.77–1.81 Å in the five PPN salts (Table III) compare favorably with the corresponding average values (Å) in the cyclotriphosphazenes, *viz.*, 1.789 (7) in $N_3P_3F_4(C_6H_5)_2$,[27] 1.788 (4) in $N_3P_3Cl_4(C_6H_5)_2$,[48] 1.792 (6) in $N_3P_3Cl_2(C_6H_5)_4$,[45] and 1.804 (3) in $N_3P_3(C_6H_5)_6$. In free triphenylphosphine[51] the average value of the P–C distances is 1.828 (3) Å, while for triphenylphosphine as a ligand in transition-metal complexes the average values range from 1.80 to 1.85 Å.[52] The observation that the phenyl $^1H$ nmr resonances in the PPN cation are shifted downfield 15 Hz relative to those in triphenylphosphine is not inconsistent with the slightly shorter P–C bond lengths in the PPN cation, indicating the possibility of some degree of electron delocalization over the entire ion (with the inherent assumption that the bond shortening is not due to bond polarity differences). It should be noted that similar P–C distances have been found in the triphenylmethylphosphonium cation [1.799 (6) Å (av)][53] and in the tetraphenylphosphonium cation [1.792 (3) Å (av), uncorrected, and 1.796 (3) Å, corrected for librational motion].[54]

**(b) Basic Conformational Difference between the $[(C_6H_5)_3P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_3]^+$ Cation and Two Other Homologous $[(ZYX)P\overset{\cdots}{-}N\overset{\cdots}{-}P(X'Y'Z')]^+$ Cations Containing Amino Substituents.** Of prime interest is a comparison of this conformation of the PPN cation with those of the homologous cations in the $\{[(NH_2)(C_6H_5)_2P]_2N\}Cl$ and $\{[(NHCH_3)_2(NH_2)P][(NH_2)_3P]N\}I$ salts whose structures were recently ascertained from X-ray studies.[55,56] The former $[(NH_2)(C_6H_5)_2P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_2(NH_2)]^+$ cation was shown by Cox and Corey[55] to possess an approximate $C_2$-2 geometry with a P–N–P bond angle of 136 (1)°, bridging P–N bond lengths of 1.57 (1) and 1.58 (1) Å, and terminal P–N bond lengths of 1.64 (1) and 1.66 (1) Å; the latter $[(NHCH_3)_2(NH_2)P\overset{\cdots}{-}N\overset{\cdots}{-}P(NH_2)_3]^+$ cation was found by Ziegler[56] to be an unsymmetrically substituted isomer with a P–N–P bond angle of 129°, bridging P–N bond lengths of 1.539 (20) and 1.583 (13) Å,[57] terminal P–N bond lengths of range 1.604 (23)–1.665 (11) Å with a mean value of 1.645 Å, and P–$NHCH_3$ bond lengths of 1.589 (16) and 1.620 (14) Å.

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(57) Although these P–N bond lengths are not significantly different from each other in terms of their esd's, it should be pointed out that the P–N bonds in the analogously substituted $N_3P_3F_4(C_6H_5)_2$[22] and $N_3P_3Cl_4(C_6H_5)_2$[48] molecules show in a parallel fashion three different sets of lengths which have been correlated[22] with expected changes in $\pi$-bond character in a cyclotriphosphazene ring containing these mixed substituents.

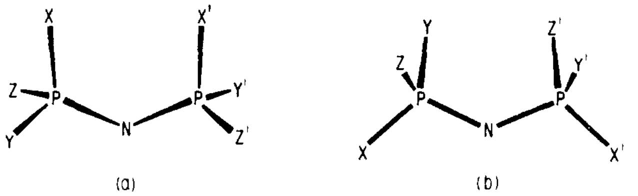

Figure 3. Comparison of the (a) cisoid and (b) transoid pentadienyl-type conformations of the X and X' ligands relative to the "bent" P–N–P fragment in the $[(ZYX)P\overset{\cdots}{-}N\overset{\cdots}{-}P(X'Y'Z')]^+$ cation. For six atomic ligands, both conformations may possess $C_2$-2 symmetry (when X = X', Y = Y', Z = Z') or $C_{2v}$-2*mm* symmetry (when X = X' and Y = Y' = Z = Z'). The $[(C_6H_5)_3P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_3]^+$ cation of approximate $C_2$-2 geometry possesses the cisoid pentadienyl-type conformation, while the symmetrically substituted $[(NH_2)(C_6H_5)_2P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_2(NH_2)]^+$ cation (X = X' = Z = Z' = $C_6H_5$ and Y = Y' = $NH_2$) of approximate $C_2$-2 geometry and the unsymmetrically substituted $[(NHCH_3)_2(NH_2)P\overset{\cdots}{-}N\overset{\cdots}{-}P(NH_2)_3]^+$ cation (X = Z = $NHCH_3$ and Y = X' = Y' = Z' = $NH_2$) have the transoid pentadienyl-type conformation.

The open bent $[(ZYX)P\overset{\cdots}{-}N\overset{\cdots}{-}P(X'Y'Z')]^+$ system exemplified by these two cations (as well as by the PPN cation) may be considered to arise from the common sharing of the nitrogen atom between the (ZYX)PN and (X'Y'Z')PN tetrahedra. An inspection reveals a fundamental conformational difference between the similar geometries of these two cations and that of the PPN cation with respect to the steric disposition of the six phosphorus-coordinated terminal substituents (*viz.*, X, Y, Z and X', Y', Z'). In the one conformational isomer (Figure 3a) represented by the PPN cation, the tetrahedra are linked such that the X and X' ligands (*i.e.*, corresponding to the phosphorus-attached carbon atoms of the $C_6H_5(2)$ and $C_6H_5(5)$ rings of the PPN cation) are approximately coplanar and oriented in a cisoid pentadienyl-type arrangement with respect to the bent P–N–P system. As noted previously, the polymeric extension of such a conformation involving substitution of nitrogen atoms at the X and X' positions gives rise to the cyclotriphosphazenes. The other conformational isomer represented by the $[(NH_2)(C_6H_5)_2P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_2(NH_2)]^+$ and $[(NHCH_3)_2(NH_2)P\overset{\cdots}{-}N\overset{\cdots}{-}P(NH_2)_3]^+$ cations has the X and X' ligands (corresponding to two phenyl rings in the former cation and one methylamino and one amino group in the latter cation) in a transoid pentadienyl-type location relative to the bent P–N–P system (Figure 3b). An extension of this monomeric conformation by replacement of the X and X' ligands with bridging atoms leads to an "open" chain complex. It is noteworthy that the $[Cl_3P\overset{\cdots}{-}N\overset{\cdots}{-}PCl_3]^+$ cation, which was characterized by a vibrational analysis[58] of the infrared and Raman spectra of two salts on the basis that this latter conformation, possesses $C_{2v}$-2*mm* symmetry for atomic ligands with an assumed P–N–P bond angle of 140° for the hexachloro derivative. It is presumed that nonbonding steric interactions account for the PPN cation (with its six phenyl substituents) adopting its particular conformation in preference to this latter conformation.

The closeness of the P–N–P bond angle of 136 (1)° in the $[(NH_2)(C_6H_5)_2P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_2(NH_2)]^+$ cation to the P–N–P angular range of 137–142° found for the $[(C_6H_5)_3P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_3]^+$ cation in the five [PPN] salts, together with the essentially identical values of the P–N bond lengths in the two cations, indicates that the change of $P(d\pi)$–$N(p\pi)$–$P(d\pi)$ bonding (involving participation of both lone-pair electrons of the nitrogen atom) in the P–N–P system due to the substitution of an amino ligand in place of a phenyl one on each phosphorus atom is small. Electronegativity considerations would predict for a more electron-donating ligand (*e.g.*, an amino one compared to a phenyl one) on a phosphorus atom a greater energy separation between the $3d\pi$ phosphorus and $2p\pi$ nitrogen orbitals; increased electron density on the phosphorus atom should also cause a relative expansion of its $3d\pi$ orbitals, thereby resulting in less efficient overlap with the nitrogen orbitals. Both of these interdependent electronic factors should lead to less $\pi$-electron delocalization between the $3d\pi$ phosphorus and $2p\pi$ nitrogen orbitals and consequently, in the absence of nonbonding electrostatic interactions, to longer P–N bond lengths and a smaller P–N–P bond angle. Furthermore, this trend should be enhanced by the much greater $\pi$ bonding between the $3d\pi$ orbitals of each phosphorus atom and the $2p\pi$ orbital of its amino substituent than that between a phosphorus atom and a phenyl substituent; this competitive $\pi$ bonding of the terminal amino substituents should increase the electron density on the phosphorus atom, thereby decreasing the $\pi$ bonding in the P–N–P system. The degree of $\pi$ bonding involving the substituent amino group is indicated by the lengths of the terminal P–amino bonds being appreciably shorter than that of a P–N single bond but still significantly greater than the lengths of the central P–N bonds. Similar arguments would predict still longer P–N bond lengths and a smaller P–N–P bond angle in the $[(NHCH_3)_2(NH_2)P\overset{\cdots}{-}N\overset{\cdots}{-}P(NH_2)_3]^+$ cation. It is apparent that in the P–N–P systems of these cations the P–N bond length changes reflecting the above-cited electronic factors are small (~0.01 Å or even less). The greater sensitivity of the P–N–P bond angle as an index of the degree of $\pi$-electron delocalization in the P–N–P system is indicated by the detectably smaller P–N–P bond angle of 129° in the $[(NHCH_3)_2(NH_2)P\overset{\cdots}{-}N\overset{\cdots}{-}P(NH_2)_3]^+$ cation (in accord with the above electronic arguments), but the inseparability of electronic and nonbonding repulsion effects in these cases makes it difficult to ascribe the larger P–N–P angles in the $[(C_6H_5)_3P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_3]^+$ and $[(NH_2)(C_6H_5)_2P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_2(NH_2)]^+$ cations simply to greater $\pi$-bond formation.

**(c) Geometrical Distinctions between the $[(C_6H_5)_3P\overset{\cdots}{-}N\overset{\cdots}{-}P(C_6H_5)_3]^+$ Cation and Cyclophosphazene Molecules and Resulting Bonding Implications.** The participation of the phosphorus $3d\pi$ orbitals in $\pi$-bond formation with $2p\pi$ orbitals of the nitrogen atoms in the cyclophosphazenes with greater $\pi$ bonding occurring within a P–N–P unit when electron-withdrawing substituents are attached to the phosphorus atom has been widely accepted in accounting for their physical and chemical differences, but both experimental studies and theoretical MO treatments have differed with regard to the importance of "pseudoaromaticity" involving the extent of $\pi$-electron delocalization between fused P–N–P repeating units in the formation of cyclophosphazenes.[20–23,28]

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An assessment may be made of the geometrical differences between an "open" P–N–P system and a "closed" one that is part of a cyclic ring by comparison of the corresponding parameters in the $[(C_6H_5)_3P\stackrel{\cdots}{-}N\stackrel{\cdots}{-}P(C_6H_5)_3]^+$ cation with those in the cyclotriphosphazene molecules, $N_3P_3Cl_2(C_6H_5)_4$ and $N_3P_3(C_6H_5)_6$, containing $(C_6H_5)_2P$–N–$P(C_6H_5)_2$ segments. Despite the considerably larger P–N–P bond angles of range 137–142° found in the PPN cation *vs.* those of 124.9 (5)° and 122.1 (3)° in the geometrically constrained $N_3P_3Cl_2(C_6H_5)_4$ and $N_3P_3(C_6H_5)_6$ rings, respectively, the essential invariance of the P–N bond lengths is indicative that the composite effect of inductive $\sigma$-bonding and $\pi$-bonding character is not appreciably altered in these open and closed P–N–P systems.

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# Organometallic Pnicogen Complexes. V. Preparation, Structure, and Bonding of the Tetrameric Antimony–Cobalt Cluster System, $Co_4(CO)_{12}Sb_4$: The First Known (Main Group Element)–(Metal Carbonyl) Cubane-Type Structure[1]

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**Abstract:** An attempt to prepare the unknown $Co_2(CO)_6Sb_2$ complex (as a pnicogen analog of the recently synthesized $Co_2(CO)_6As_2$) has led instead to the isolation of a new cobalt–antimony cluster $Co_4(CO)_{12}Sb_4$ molecule. Black crystals of this air-stable, insoluble compound were synthesized by the reaction of $Co(OAc)_2\cdot 4H_2O$ with $SbCl_3$ in methanol (or pentane) solution at 150° under a high-pressure mixture of carbon monoxide and hydrogen. Characterization of this complex by a three-dimensional X-ray diffractometry study revealed a cubane-like architecture comprised of two interpenetrating, concentric nonbonded tetrahedra of cobalt and antimony atoms with the four $Co(CO)_3$ fragments interconnected by triply bridging antimony atoms. The determined structure ideally displays cubic $T_d$-$\bar{4}3m$ geometry with an average electron-pair Co–Sb distance of 2.614 (2) Å and with acute Sb–Co–Sb and obtuse Co–Sb–Co angles of average values 74.3 (1) and 103.8 (1)°, respectively. This molecule and the related cyclopentadienyliron tetramers, $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ and $Fe_4(h^5\text{-}C_5H_5)_4S_4$, are described in terms of a qualitative molecular orbital model which successfully relates their molecular geometries, including the absence of direct cobalt–cobalt bonding in $Co_4(CO)_{12}Sb_4$, in accord with an observed average nonbonding Co···Co internuclear distance of 4.115 (4) Å. The $Co_4(CO)_{12}Sb_4$ compound crystallizes in the tetragonal system with cell dimensions $a$ = 14.561 (3), $c$ = 10.507 (4) Å, and with centrosymmetric space group symmetry $I4_1/amd$. Each of the four molecules per cell possesses crystallographic site symmetry $D_{2d}$-$\bar{4}2m$. The application of the symbolic-addition method in space group $I4_1/amd$ to determine this crystal structure is briefly outlined. Full-matrix least-squares refinement of the structure yielded $R_1$ = 5.0% and $R_2$ = 5.2% for the 282 independent reflections with $|F_o| > 4\sigma(F_o)$.

The synthesis and study of transition-metal complexes containing metal–metal bonds has shown a meteoric rise in the last few years.[3–7] Prior to about 10 years ago, metal–metal bonding was primarily a curiosity, and the deliberate synthesis of a compound containing a metal–metal bond was virtually unknown.

The recent preparation and characterization of $Co_2(CO)_6As_2$ in our laboratory led to the postulation of the existence of an As–As multiple bond of $\pi$ order near

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[1] Previous paper in this series: A. S. Foust, M. S. Foster, and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 5633 (1969).

[2] This paper is based in part on a dissertation submitted by A. S. F. to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, Jan 1970.

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