The known mixed halide-phosphine (or -arsine) TBP complexes of nickel(II) are blue, green, or purple. The corresponding SPY complexes are red, brown, or purple, and if the number and kind of ligands are the same in the two geometries, as in those discussed here, the lowest energy ligand-field band occurs at lower energy in the case of the TBP. When we go to the mixed cyanide-arsine, however, the result is that the lowest energy absorption maximum is found in the SPY spectrum. The lowest energy band in the SPY complex is of relatively low intensity (for $[Ni(diars)_2CN]^+$, ϵ is 420 in 2-methyl-TBP-methanol at 300°K). If we compare the most intense ligand-field bands for the two compounds, we find that for both cyanides and halides, the *intense* absorption at lower energy is found in the TBP.

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Structural Characterization of the Dinuclear Metal Carbonyl Anions $[M_2(CO)_{10}]^{2-}$ (M = Cr, Mo) and $[Cr_2(CO)_{10}H]^-$. The Marked Stereochemical Effect of a Linearly Protonated Metal–Metal Bond

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Abstract: Single-crystal X-ray structural determinations of the metal carbonyl anions $[Cr_2(CO)_{10}H]^-$, $[Cr_2(CO)_{10}]^{2-}$, and $[Mo_2(CO)_{10}]^{2-}$ not only have unambiguously established their architectures but also have made possible for the first time a direct stereochemical comparison of two closely related transition metal complexes *with* and *without* a hydrogen atom as a bridging ligand. The $[Cr_2(CO)_{10}]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$ anions possess the D_{4d}-$\bar{8}2m$ $Mn_2(CO)_{10}$-type structure. The different metal–metal bond length changes observed between the isoelectronic $[Cr_2(CO)_{10}]^{2-}$–$Mn_2(CO)_{10}$ pair (Δ(M–M) = 0.05 Å) and the isoelectronic $[Mo_2(CO)_{10}]^{2-}$–$Tc_2(CO)_{10}$ pair (Δ(M–M) = 0.09 Å) as well as the significant difference in metal–metal bond length changes between the former pair and the isoelectronic $[Fe_2(CO)_8]^{2-}$–$Co_2(CO)_8$ (nonbridged isomer) pair of D_{3h}-$\bar{6}2m$ geometry are analyzed. The prototype $[Cr_2(CO)_{10}H]^-$ structure, which is an unprecedented example of a *linear* three-center two-electron X–H–X system, may be formally derived from the protonation of the Cr–Cr electron-pair bond in the $[Cr_2(CO)_{10}]^{2-}$ anion. This linear protonation of a metal–metal bond produces a conformational change of the two sets of equatorial carbonyl ligands from the staggered D_{4d} arrangement in the $[Cr_2(CO)_{10}]^{2-}$ anion to an exactly eclipsed arrangement (crystallographically required by symmetry) in the $[Cr_2(CO)_{10}H]^-$ anion which approximately possesses a D_{4h}-4/m2/m2/m geometry. The conformation in the $[Cr_2(CO)_{10}H]^-$ anion is ascribed to the two halves of the hydrogen-bridged anion being sufficiently far apart that the attractive part of van der Waals forces dominates to give an eclipsed orientation of the equatorial carbonyl groups. The marked shortening by 0.44 Å between the two chromium atoms in the $[Cr_2(CO)_{10}H]^-$ anion (3.41 ± 0.01 Å) due to deprotonation to give the resulting $[Cr_2(CO)_{10}]^{2-}$ anion (2.97 ± 0.01 Å) apparently causes a sufficient increase in the repulsive part of van der Waals forces to give the staggered conformation. The three-center electron-pair bonding representation of the Cr–H–Cr framework of the $[Cr_2(CO)_{10}H]^-$ anion is discussed with regard to the possibility of either a symmetric double-minimum potential well or a single-minimum potential well. It is accented that in a linear M–H–M system, which represents a maximum separation of the two metal atoms, as well as in other known "bent" M–H–M systems, where the contact distance between the two metal atoms decreases toward that of a deprotonated electron-pair metal–metal bond, there is extensive metal–metal bonding character due to the large direct overlap of the metal orbitals with each other as well as with the hydrogen 1s orbital. The X-ray analysis of the $[Cr_2(CO)_{10}H]^-$ anion was carried out on the tetraethylammonium salt, while both dianions were structurally characterized as bis(triphenylphosphine)iminium salts, $\{[(C_2H_5)_3P]_2N\}_2[M_2(CO)_{10}]\cdot CH_2Cl_2$ (M = Cr, Mo). The $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$ salt crystallizes with one formula species in a triclinic unit cell of dimensions a = 6.82 ± 0.01 Å, b = 10.13 ± 0.01 Å, c = 8.91 ± 0.01 Å, α = 102.0 ± 0.2°, β = 101.6 ± 0.2°, γ = 86.3 ± 0.2°; the crystal-disordered model utilized in the least-squares refinements assumes an average unit cell of centrosymmetric $P\bar{1}$ symmetry with the one $[Cr_2(CO)_{10}H]^-$ anion located on an average center of symmetry and the one cation randomly oriented in one of two centrosymmetrically related positions. The isomorphous $\{[(C_6H_5)P]_2\}_2[M_2(CO)_{10}]\cdot CH_2Cl_2$ (M = Cr, Mo) salts crystallize in the monoclinic system with symmetry C2/c and with a = 13.125 ± 0.009 Å, b = 25.973 ± 0.016 Å, c = 22.491 ± 0.015 Å, β = 94.11 ± 0.02°, ρ_{obsd} = 1.32 g/cm³ *vs.* ρ_{calcd} = 1.35 g/cm³ (z = 4) for the chromium comopund; and with a = 13.362 ± 0.008 Å, b = 26.243 ± 0.016 Å, c = 22.256 ± 0.015 Å, β = 94.21 ± 0.02°, ρ_{obsd} = 1.36 g/cm³ *vs.* ρ_{calcd} = 1.40 g/cm³ (z = 4) for the molybdenum compound.

In recent years there has been considerable interest concerning the stereochemistry and bond properties of systems involving a transition metal to hydrogen bond. Our previous work on several polynuclear tran-

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(2) This paper is based in part on a dissertation submitted by L. B. Handy to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, Aug 1968.

sition metal hydrido carbonyl complexes established[3-5] the existence of *bent* three-center electron-pair metal-hydrogen-metal bonds, which in each case account for the compounds' diamagnetism without the additional involvement of a separate electron-pair metal-metal bond. Another especially intriguing system appeared to be the series of chromium group carbonyl anions initially synthesized by Behrens and coworkers.[6-8] In particular, the two anions $[Cr_2(CO)_{10}H]^-$ and $[Cr_2(CO)_{10}]^{2-}$ appeared to differ only in the presence or absence of the hydrogen atom. These anions were first prepared[6-8] with liquid ammonia as a solvent system, but recent studies[9-13] showed that they could be isolated from $Cr(CO)_6$ by the use of other solvents (*e.g.*, tetrahydrofuran, diglyme, or hexamethylphosphoramide) with a borohydride, an alkali metal amalgam, or NaBipy (Bipy = 2,2′-bipyridine)[12] employed as a reducing agent. A comprehensive investigation of the course of this reduction has been reported recently by Kaska.[13] An X-ray crystal structural analysis of $[Cr_2(CO)_{10}H]^-$, undertaken early in this investigation and outlined in a previous communication,[10] together with infrared and nmr spectral studies carried out independently by Hayter[11] and by Anders and Graham[9] established the chromium-hydrogen-chromium framework of the $[Cr_2(CO)_{10}H]^-$ anion as an unprecedented example of a *linear* electron-deficient X-H-X system.

After the X-ray characterization of this homobimetallic hydrido carbonyl anion, $[Cr_2(CO)_{10}H]^-$, our next objective was to determine the structure of the related nonprotonated dianion, $[Cr_2(CO)_{10}]^{2-}$. This dichromium anion and the corresponding ones of the congeners molybdenum and tungsten are of particular stereochemical interest, since the infrared spectrum of each of these $[M_2(CO)_{10}]^{2-}$ anions was found by Hayter[11] to exhibit a carbonyl stretching band below 1800 cm^{-1}, and therefore it was initially presumed[11,14,15] that this low frequency implied the existence of bridging carbonyl groups which, if present, would require a very substantial change in geometry from the D_{4h} architecture observed for the $[Cr_2(CO)_{10}H]^-$ anion. This possible stereochemistry is in contradistinction to that of the heterodinuclear metal anions $[(OC)_5M\text{-}M'(CO)_5]^-$ (M = Mn, Re; M′ = Cr, Mo, W) prepared by Anders and Graham,[15] who proposed the $Mn_2(CO)_{10}$-type structure for these isoelectronic anions on the basis of their infrared spectra.

Crystals of the tetraethylammonium salts of both the $[Cr_2(CO)_{10}]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$ anions were generously supplied by Dr. Roy G. Hayter (Shell Development Co.), but these compounds unfortunately proved too X-ray sensitive even in argon-filled capillaries to allow collection of intensity data. The tetraphenylarsonium salt of the $[Cr_2(CO)_{10}]^{2-}$ anion was prepared by one of us (L. B. H.), but an attempted three-dimensional photographic X-ray determination was unsuccessful, owing presumably to crystal disordering of the $[Cr_2(CO)_{10}]^{2-}$ anions in the lattice. In order to stabilize the reactive dianions, particularly toward oxygen and water, the chromium, molybdenum, and tungsten species were prepared (by J. K. R.) and crystallized as salts of the bis(triphenylphosphine)iminium cation (abbreviated PPN).[16] Crystals of these compounds could be exposed to air for several hours and suffered only moderate decomposition upon prolonged exposure (2 weeks) to X-ray irradiation.

The X-ray studies of both the $[Cr_2(CO)_{10}]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$ anions have unambiguously established their configurations as the D_{4d}-$\bar{8}2m$ $Mn_2(CO)_{10}$-type structure, and thereby have made possible, from a comparison of molecular parameters with those of their corresponding neutral counterparts, $Mn_2(CO)_{10}$[17] and $Tc_2(CO)_{10}$,[18] an evaluation of the change in metal-metal bond length with increased localized negative charge on the metal atom.[19-21] More importantly, these studies presented here have allowed a detailed stereochemical appraisal of the observed conformational change in the molecular $[M_2(CO)_{10}]^{2-}$ species due to protonation of the metal-metal bond. The large changes in molecular parameters found for this resulting *linear* M-H-M system are assessed in connection with known molecular parameters in other *bent* M-H-M systems in order to determine structural interrelationships.

Experimental Procedure

Preparation and X-Ray Data Collection of $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$. The $[Cr_2(CO)_{10}H]^-$ anion was prepared (by L. B. H.) by the reduction of $Cr(CO)_6$ with $(C_2H_5)_4NBH_4$ in THF solution as previously reported.[10,11] Well-formed single crystals of $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$ were obtained from slowly cooled ethanol solutions.

A needle-like crystal of length 0.35 mm and uniform thickness 0.18 mm was mounted about the needle axis in a thin-walled Lindemann glass capillary. The capillary was then evacuated and filled

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(19) Hayter[11] originally found five infrared carbonyl stretching bands for the $Na_2[Cr_2(CO)_{10}]$ salt dissolved in THF. It was first pointed out by Edgell and coworkers[20] for the $[Co(CO)_4]^-$ anion and shown independently by Lindner, Behrens, and Birkle,[12] by Kaska,[13] and by Edgell and Paauwe[21] for the $[Cr_2(CO)_{10}]^{2-}$ anion that solvent effects as well as the cations may markedly affect the frequencies and shapes of the carbonyl bands; the five infrared carbonyl bands in THF for $Na_2[Cr_2(CO)_{10}]$ were demonstrated[12,13,21] to be due to incomplete dissociation of the solvated cations and anions (*viz.*, contact ion pairs), which causes a breakdown in the molecular symmetry, thereby giving rise to the observed complex spectral pattern. The above three groups[12,13,21] independently showed in more polar solvents (where dissociation is essentially complete) the existence of only three fundamental carbonyl stretching frequencies (at 1912, 1883, and 1786 cm^{-1} for $Na_2[Cr_2(CO)_{10}]$ dissolved in DMSO)[21] in accord with the selection rules for the D_{4d} molecular geometry of the $[Cr_2(CO)_{10}]^{2-}$ anion reported here. The relatively low carbonyl frequencies found for this anion are therefore a consequence of a low carbon-oxygen bond order resulting from extensive dissipation of the electron charge from the filled d_π orbitals of the chromium atoms into the empty π^* orbitals of the carbonyl groups.
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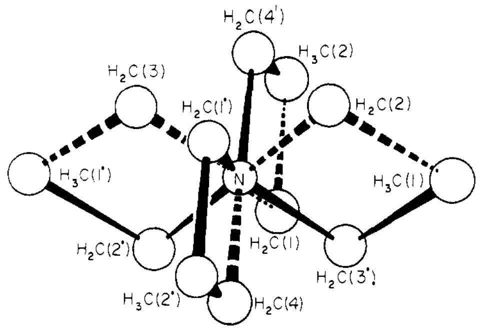

Figure 1. The disordered tetraethylammonium cation in crystalline $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$. On the basis of an analysis of the Fourier peak positions of the nonhydrogen atoms, a rigid-body model employed in the final least-squares refinement assumes a random distribution of the cation in one of two centrosymmetrically related orientations in the crystal, with an ordering of the methyl carbon atoms (due to presumed superimposed positioning) and disordering of the tetrahedrally disposed methylene carbon atoms. The disordered cation ideally conforms to D_{4h} symmetry with the methyl carbon atoms located on the horizontal mirror plane. The drawing shows for one orientation the nitrogen and carbon atoms linked by solid lines and for the other orientation the atoms linked by dashed lines.

with argon to prevent decomposition. Preliminary X-ray photographs of this crystal revealed only triclinic C_i-$\bar{1}$ Laue symmetry. Multiple-film equi-inclination Weissenberg photographs of reciprocal layers $0kl$–$7kl$ were taken with Zr-filtered Mo Kα radiation. For all nonzero levels two sets of photographs, each covering approximately 220°, were taken at spindle settings 180° apart. In this way only Weissenberg spot extension corrections[22] needed to be applied as only the top half of the film was used for intensity measurements.

Timed sets of precession photographs were obtained from a second needle-like crystal of length 0.25 mm and uniform thickness 0.09 mm. This crystal was grown from an acetone–water mixture and was also sealed in a Lindemann capillary under argon. Sets of 12 films were obtained for each of reciprocal levels $h0l$, $h2l$, $hk0$, and $hk1$. Cell parameters were determined from $h0l$ and $hk0$ precession photographs on each of which was superimposed the $hk0$ diffraction pattern of a sodium chloride crystal.

All intensity data from the Weissenberg and precession films were judged by visual comparison with a timed set of standard intensities prepared from the same crystal and by the same camera method utilized to collect the intensity data. The data for each reciprocal level were averaged, and analytical corrections were made for Lorentz–polarization effects as well as for Weissenberg spot extension.[22] Standard deviations for each reflection were assigned as follows:[23] if $I_0 \geq \sqrt{10}I_{min}$, $\sigma(F_o) = 0.05|F_o|$; if $I_0 < \sqrt{10}I_{min}$, $\sigma(F_o) = 0.05|F_o|(\sqrt{10}I_{min}/I_0)^2$. The linear absorption coefficient (μ) for Mo Kα radiation is 10.4 cm^{-1}; since μr_{max} for both crystals was less than 0.2, no absorption corrections were applied. The maximum intensity variation on a given reciprocal layer due to absorption was estimated to be less than 6%. The Weissenberg and precession data were merged[24] to one relative scale factor *via* least squares to give 830 independent observations. The weighted reliability index for this merge was 4.6%, based on 303 duplicate and 43 triplicate reflections. This low value for the reliability index suggests that no serious systematic errors are present in the data.

Normal atomic scattering factors for all atoms were taken from the Hartree–Fock–Slater calculations of Hanson, *et al.*[25] The real and imaginary anomalous contributions to the chromium scattering factor were taken from the tabulation by Templeton.[26]

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Crystal Data of $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$. Crystals of $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$ are triclinic with primitive cell parameters of $a = 6.82 \pm 0.01$ Å, $b = 10.13 \pm 0.01$ Å, $c = 8.91 \pm 0.01$ Å, $\alpha = 102.0 \pm 0.2°$, $\beta = 101.6 \pm 0.2°$, $\gamma = 86.3 \pm 0.2°$; the unit cell volume equals 590 Å^3. The observed density of 1.49 g/cm^3, measured by flotation in 1-bromonaphthalene, is in satisfactory agreement with the calculated value of 1.45 g/cm^3 for one formula species per unit cell.

The presence of one tetraethylammonium cation per cell suggested that P1 rather than P$\bar{1}$ is the probable space group. Subsequent refinement of the structure disclosed a disorder of this cation consistent with P$\bar{1}$. This centrosymmetric space group necessitates that the average unit cell contain the one $[Cr_2(CO)_{10}H]^-$ anion located on an average center of symmetry, arbitrarily designated at $^1/_2,^1/_2,^1/_2$ to fix the origin of the cell, and the one $[(C_2H_5)_4N]^+$ cation then positioned on the average center of symmetry at 0,0,0. For the anion the solution of the structure involved the location of one chromium, five carbon, and five oxygen atoms, with the hydrogen atom (if nondisordered) residing on the center of symmetry. The cation was assumed from the structural analysis to be randomly oriented in one of two centrosymmetrically related positions such as to require in general the determination of 4 half-weighted methylene carbon atoms, 4 half-weighted methyl carbon atoms, and 20 half-weighted hydrogen atoms; final least-squares refinements were based on an assumed superimposed positioning of pairs of half-weighted methyl carbon atoms to give 2 independent whole-weighted methyl carbon atoms. For this particular disorder observed, the crystallographically independent unit contains 1 chromium, 5 oxygen, 7 whole-weighted carbon, 4 half-weighted carbon, and 20 half-weighted hydrogen atoms, all of which occupy the twofold set of general positions (i) at $\pm(x,y,z)$, together with 1 nitrogen atom, which occupies the onefold special position (a) at 0,0,0 and 1 hydrogen atom which (if nondisordered) occupies the onefold special position (h) at $^1/_2,^1/_2,^1/_2$.[27]

Solution of the Structure of $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$. A three-dimensional Patterson function established the relative positions of the two chromium atoms in the unit cell. A three-dimensional Fourier map based on space group P$\bar{1}$ and phased on the one independent chromium revealed the positions of the four equatorial carbonyl groups and the nitrogen atom at the cell origin. A second Fourier map phased on the above partial structure showed the axial carbonyl group but not the cation carbon atoms. No images of the carbonyl groups were observed, so the carbonyl groups also conformed to space group P$\bar{1}$. Several cycles of full-matrix isotropic least-squares refinement resulted in an unweighted discrepancy factor of $R_1 = 10.7\%$ and a weighted discrepancy factor of $R_2 = 13.8\%$.[28] A difference map then indicated that the methylene carbon atoms of the tetraethylammonium cation were disordered by inversion through the origin, while the methyl carbon atoms were related by the center of symmetry without any obvious disorder (Figure 1). Further isotropic refinement based on this model resulted in $R_1 = 9.1\%$ and $R_2 = 8.9\%$. Discrepancy factors based on each of the possible ordered acentric models with P1 symmetry were only slightly higher, with $R_2 = 9.1\%$ and 9.5%. All attempts at refinement of an ordered structure based on P$\bar{1}$ symmetry were unsuccessful, however, owing to extremely high correlation between the previously centrosymmetrically related atoms. Four cycles of refinement were carried out for each acentric model. Correlations remained high, and the attempted refinements resulted in discrepancy factors greater than 12%. For the disordered centric model, the isotropic temperature factors for the disordered methylene carbon atoms were all within the range of 6–8 Å^2, while those for the presumably ordered methyl carbon atoms were slightly higher at 9 and 11 Å^2. Both ordered acentric orientations failed to display similar consistency of thermal parameters; the isotropic temperature factors ranged from −1 to 20 Å^2. Packing considerations also did not reveal any advantage for either possible ordered orientation of the cation. For each orientation there is one nonbonding (methylene carbon)–(carbonyl oxygen) distance of only 3.0 Å, which might indicate weak hydrogen bonding. Hence, it is concluded that the disordered centric model is preferable.

An examination of the atomic parameters obtained from the isotropic least-squares refinement based on the disordered centric

(27) Reference 26, Vol. I, p 75.

(28) 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. The discrepancy factors, R_1 and R_2 are defined as follows: $R_1 = 100 \cdot [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$; $R_2 = 100[\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|]^{1/2}$.

model showed that the thermal parameters for the carbonyl groups were quite high, from 7 to 9 $Å^2$ for the carbon atoms and from 10 to 12 $Å^2$ for the oxygen atoms. A difference Fourier map phased on this ordered–disordered centric model showed residual electron density characteristic of anisotropic thermal motion for the chromium, carbon, and oxygen atoms of the anion. Hence, further refinement was carried out with anisotropic temperature factors for these atoms. Final discrepancy factors were $R_1 = 7.4$ and $R_2 = 7.0\%$. A difference Fourier map calculated at this point revealed no residual electron density greater than 0.6 or less than −0.7 e/$Å^3$. No indication of the hydrogen positions was obtained. In particular, no maximum of this residual density was located within a 2-Å diameter sphere centered between the chromium atoms.

Examination of the positional parameters of the tetraethylammonium ion suggested that some constraint should be applied, since carbon–carbon distances were as large as 1.74 Å. The disordered cation appeared to conform very nearly to D_{4h} symmetry with the methyl carbon atoms located on the idealized horizontal mirror plane and the methylene carbon atoms positioned above and below this plane. A rigid-body model[29,30] with C–N bonds of length 1.50 Å and C–C bonds of length 1.54 Å was therefore prepared. The H_2C–N–CH_2 angles were assumed to be tetrahedral, which results in N–CH_2–CH_3 angles of 113°. The origin of the rigid body was taken to be the nitrogen atom at the crystallographic origin and so could not be varied. This cation model was refined with individual atomic isotropic thermal parameters for the rigid body atoms, while anisotropic thermal parameters were again employed for the anion. The final discrepancy factors were $R_1 = 7.7$ and $R_2 = 7.9\%$. This geometrical constraint on the cation had no significant effect on the structure of the anion, since none of the calculated interatomic distances and angles in the anion changed by more than one estimated standard deviation; in particular, the important chromium–chromium distance changed by only 0.001 Å, or one-ninth of the standard deviation of this distance.

Preparation and X-Ray Data Collection of $[PPN]_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$ and $[PPN]_2[Mo_2(CO)_{10}]\cdot CH_2Cl_2$. Both compounds were prepared (by J. K. R.) according to the Hayter procedure.[11] The bis(triphenylphosphine)iminium cation (PPN)[16] was employed as the counterion in the crystallizations. Well-formed single crystals were obtained by recrystallization from methylene chloride–ethyl acetate solutions. Prismatic crystals of approximate dimensions 0.4 × 0.2 × 0.2 mm were cemented to a glass fiber, with an obvious twofold crystal axis oriented along the fiber axis. Preliminary oscillation and Weissenberg photographs confirmed that both crystals were monoclinic with the unique axis b as the oscillation axis. Each crystal in turn (the Mo compound first) was then transferred to a General Electric four-circle automatic diffractometer and centered by optical and X-ray techniques.[31] The orientation of the crystal was then defined by the manual centering of 50 reflections with known indices for the molybdenum compound, and 16 reflections for the chromium compound. Lattice parameters and the orientation of all reflections with $2\theta \leq 40°$ were derived from these manually centered reflections with a local version of the Argonne National Laboratory orientation and angle setting program.[32]

Intensity data were collected by the θ–2θ scan technique at a takeoff angle of 2°. Symmetric scans of 2° in 2θ at a rate of 4°/min were employed for all reflections. Stationary crystal–stationary counter background counts of 15 sec were taken at both extremes of each scan range. A counter aperture of 2-mm diameter was located 31 mm from the crystal. Zirconium-filtered Mo Kα radiation was used with a scintillation detector followed by a pulse-height analyzer which accepted approximately 90% of the Mo Kα pulse distribution.

For the molybdenum compound, intensity data were collected for one asymmetric unit, octants hkl and $hk\bar{l}$. A set of four standard reflections was measured every 100 reflections as a check on crystal and instrument stability.

For the chromium compound, intensity data were collected for two equivalent forms, octants hkl, $hk\bar{l}$ and $\bar{h}k\bar{l}$, $\bar{h}kl$. A set of five standard reflections was measured every 100 reflections, and a linear decrease in intensity of 19% was observed for the total period of data collection. The derived structure factors were corrected for this linear decay.

Structure factors were calculated from the intensity data by means of the data reduction program DATRED,[33] in which the intensities were corrected for background and Lorentz-polarization corrections, and $\sigma(I)$'s for each reflection were calculated as previously outlined.[33,34] Reflections were considered unobserved if $I \leq 3\sigma(I)$ for the molybdenum compound and $I \leq 2\sigma(I)$ for the chromium compound. Unobserved data were not employed in any subsequent analysis. The two equivalent forms for the chromium compound were merged by a least-squares procedure[35] to give a single set of data on one scale. A total of 822 common reflections gave a weighted discrepancy factor of 5.0%. A total of 1256 independent observed reflections resulted from this procedure. For the molybdenum compound, only data for which $2\theta \leq 30°$ were processed, since the data from 30° to 40° were largely unobserved or weak. For $2\theta \leq 30°$, a total of 1090 independent observed reflections were processed. No absorption corrections were applied since μr_{max} for both compounds was less than 0.15; the maximum possible variation in the intensities caused by neglect of absorption corrections was estimated to be 11%. The atomic scattering factors used for all atoms were those based on the Hartree–Fock–Slater calculations as compiled by Hanson, *et al.*[25] Crystal data for $[PPN]_2[M_2(CO)_{10}]\cdot CH_2Cl_2$ (M = Cr, Mo) are given in Table I.

Table I. Crystal Data for $[PPN]_2[M_2(CO)_{10}]\cdot CH_2Cl_2$ (M = Cr, Mo)

	$[PPN]_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$	$[PPN]_2[Mo_2(CO)_{10}]\cdot CH_2Cl_2$
a, Å	13.125 (9)	13.362 (8)
b, Å	25.793 (16)	26.243 (16)
c, Å	22.491 (15)	22.256 (15)
β, deg	94.11 (2)	94.21 (2)
V, $Å^3$	7594.4	7783.3
ρ_{obsd}, g/cm^3	1.32	1.36
ρ_{calcd}, g/cm^3	1.35 (z = 4)	1.40 (z = 4)
μ, cm^{-1}	4.3	4.9

Systematic absences of $\{hkl\}$ for $h + k$ odd and $\{h0l\}$ for l odd established the probable space groups as either C2/c-C_{2h}^6 or Cc-C_s^4. Subsequent solution and refinement of the structures verified the centrosymmetric choice, C2/c. The four formula species occupy the cell in the following way: the two metal atoms, the axial carbonyl carbon and oxygen atoms, and the methylene chloride carbon atom occupy the fourfold set of special positions (e) on twofold axes: (0,0,0; $^1/_2$,$^1/_2$, 0) ± (0,y,$^1/_4$); all other atoms occupy the eightfold set of general positions (f): (0,0,0; $^1/_2$,$^1/_2$,0) ± (x, y,z; $\bar{x}$,y,$^1/_2 - z$).[36] Thus, the solution of the structure required the location of 2 metal (Mo or Cr), 2 phosphorus, 1 chlorine, 6 oxygen, 1 nitrogen, and 43 carbon atoms. The 30 phenyl hydrogen atoms were included in the least-squares refinements after the location of the carbon atoms of the 6 phenyl groups enabled each C_6H_5 group to be treated as a rigid body.

Solution of the Structures of $[PPN]_2[M_2(CO)_{10}]\cdot CH_2Cl_2$ (M = Cr, Mo). A three-dimensional Patterson synthesis based on the molybdenum data revealed the positions of the two independent molybdenum atoms on the crystallographic twofold axis. Successive Fourier syntheses established reasonable positions for all remaining atoms except for those of the solvated methylene chloride molecule. Several cycles of full-matrix least-squares re-

(29) The rigid body rotation angles, ϕ, θ, and ρ, as used in the local least-squares program, are defined in the following manner: an orthonormal basis set of vectors, (x,y,z), is defined such that a is along x and b is in the x,y plane. Another orthonormal set, (x',y', z'), is defined relative to the actual crystallographic positions of the atoms which comprise the rigid body. The set (x,y,z) is then brought into coincidence with (x',y',z') by the following rotations: ϕ about z, θ about the resulting x, and ρ about final y.

(30) The orthonormal set (x',y',z') for the disordered tetraethylammonium ion has x' along ($H_2C(1)$–N), y' along ($H_2C(2)$–N), and z' along (x' cross y'). The origin is at the nitrogen atom position.

(31) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1966.

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

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

(34) 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).

(35) J. F. Blount, "INTAV3A, A Crystallographic Data Correlation Program," University of Wisconsin, 1967.

(36) Reference 26, Vol. I, p 101.

Table II. Final Parameters of $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$, Idealized Cation Model[a]

Atom	x	y	z	B
Cr	0.4742 (3)	0.3801 (3)	0.6025 (3)	
O(1)	0.425 (2)	0.166 (2)	0.763 (2)	
O(2)	0.336 (3)	0.595 (2)	0.864 (2)	
O(3)	0.905 (2)	0.403 (2)	0.772 (1)	
O(4)	0.608 (2)	0.167 (2)	0.347 (2)	
O(5)	0.041 (2)	0.339 (1)	0.429 (2)	
C(1)	0.443 (2)	0.245 (2)	0.701 (2)	
C(2)	0.391 (3)	0.512 (2)	0.766 (3)	
C(3)	0.740 (3)	0.401 (2)	0.704 (2)	
C(4)	0.556 (2)	0.257 (3)	0.444 (2)	
C(5)	0.202 (3)	0.364 (2)	0.492 (2)	
N	0	0	0	5.9 (4)
$H_3C(1)$	−0.076	0.011	−0.285	8.6 (5)
$H_3C(2)$	−0.164	−0.225	−0.063	10.9 (6)
$H_2C(1)$	0.032	−0.150	−0.042	6.7 (7)
$H_2C(2)$	−0.150	0.045	−0.128	6.6 (7)
$H_2C(3)$	0.076	−0.035	−0.151	6.5 (7)
$H_2C(4)$	−0.193	−0.070	−0.020	7.1 (7)

Rigid-Body Parameters[b]

Group	x	y	z	ϕ	θ	ρ
$[(C_2H_5)_4N]$	0	0	0	−28.1 (4)	−167.6 (3)	−96.5 (4)

Anisotropic Thermal Parameters ($\times 10^3$)[c]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	13.1 (4)	4.8 (2)	9.0 (3)	0.3 (2)	3.5 (2)	1.4 (2)
O(1)	85 (6)	41 (4)	40 (4)	1 (4)	26 (4)	28 (4)
O(2)	90 (7)	26 (3)	31 (4)	1 (4)	13 (4)	−6 (3)
O(3)	37 (4)	32 (3)	33 (3)	−2 (2)	2 (3)	14 (3)
O(4)	53 (4)	25 (3)	32 (3)	1 (3)	7 (3)	0 (3)
O(5)	27 (3)	28 (3)	42 (3)	−4 (2)	4 (3)	−3 (3)
C(1)	44 (6)	26 (4)	18 (4)	4 (4)	8 (4)	7 (4)
C(2)	40 (6)	30 (5)	39 (6)	−19 (5)	−21 (5)	22 (5)
C(3)	28 (4)	25 (3)	29 (4)	−3 (3)	9 (3)	10 (3)
C(4)	40 (5)	23 (4)	22 (4)	−6 (4)	6 (4)	2 (4)
C(5)	30 (4)	19 (3)	32 (4)	3 (3)	9 (4)	2 (3)

[a] Estimated standard deviation of the last significant figure is given in parentheses. [b] See ref 29, 30. [c] Anisotropic thermal parameters are of the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

finement, with the phenyl groups treated as rigid bodies,[29,37] failed to reduce the value of R_1 below 19%. Three of the phenyl groups failed to refine in a satisfactory manner, with group isotropic temperature factors of about 12 Å^2 compared to values of 4–5 Å^2 for the other three groups. The structural determination was temporarily abandoned at this point, while the structure of the isomorphous and presumably isostructural chromium compound was determined.

Owing to the unexplained difficulty encountered in the molybdenum refinement, no assumptions were made concerning the chromium structure. A three-dimensional Patterson synthesis proved nearly identical with that of the molybdenum analog and provided initial coordinates of the two chromium and two phosphorus atoms. Successive Fourier syntheses again revealed all the remaining atoms except those of the methylene chloride molecule of solvation. Refinement was somewhat more satisfactory than that for the molybdenum compound, but appeared to converge at R_1 = 15 and R_2 = 16%. An electron-density difference map calculated at this point revealed a peak, nearly as intense as a typical phenyl carbon atom, near the twofold axis. Close examination of the Fourier difference map along the twofold axis revealed a very weak peak on the axis within bonding distance of the first pegk. Since the crystals were grown from a methylene chloride–ethyl acetate mixture, methylene chloride solvation was suspected, and samples of both the chromium and molybdenum compounds were recrystallized by the same procedure as for the crystals used for the X-ray structure determination. Subsequent chemical analyses[38] showed the presence of one molecule of CH_2Cl_2 per formula species. The peaks observed on the difference map, however, indicated that only about half of a methylene chloride statistically occupied the position on the twofold axis. In order to estimate the occupancy factors of the methylene chloride atoms, the chlorine and carbon temperature factors were fixed at 6 and 8 Å^2, respectively, and their scattering factor multipliers were varied. Both multipliers converged rapidly to a value of approximately 0.5, although the exact value would certainly change if different arbitrary temperature factors were employed. A final Fourier difference synthesis failed to reveal any significant features with no peaks greater than 0.54 or less than −0.51 e/Å^3. In particular, no other positive electron density interpretable as solvent could be found near the axial carbonyl group attached to Cr(2), either in the final Fourier difference synthesis or in a similar Fourier synthesis in which the contribution from this carbonyl group was not included. The very high temperature factors for this axial group, the relatively high standard deviations, the moderately high discrepancy factors, and the elemental analysis all indicate the presence of additional methylene chloride of solvation, but these molecules presumably must be quite randomly disordered, as no further evidence of their atomic coordinates could be found. The final discrepancy factors for the isotropic least-squares refinement are R_1 = 14.3 and R_2 = 10.0%.

Comparison of the corresponding final parameters from the refinement of $[PPN]_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$ with those of the partial refinement of $[PPN]_2[Mo_2(CO)_{10}]\cdot CH_2Cl_2$ showed essential agreement, but the three phenyl groups which had previously failed to refine were displaced by nearly 0.2 Å in the Mo compound. The values of all parameters were then taken from the refinement of $[PPN]_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$ and used as a starting set for the Mo analog. Iso-

(37) All phenyl group refinements were based on the following model. Each ring has D_{6h} symmetry with a C–C bond length of 1.392 Å. The hydrogen atoms are located on the lines defined by diagonally opposite carbons with a C–H bond length 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.

(38) Analyses were carried out at the Rohm and Haas Co., Redstone Research Laboratories, Huntsville, Ala. *Anal.* Calcd for $\{[(C_6H_5)_3P]_2N\}_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$: C, 64.5; H, 4.1; N, 1.8; Cl, 4.6. Found: C, 64.1; H, 4.2; N, 1.9; Cl, 5.0. Calcd for $\{[(C_6H_5)_3P]_2N\}_2[Mo_2(CO)_{10}]\cdot CH_2Cl_2$: Cl, 4.3. Found: Cl, 4.6.

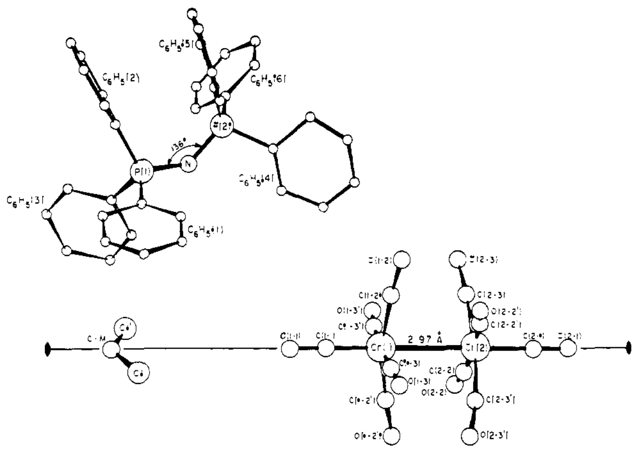

Figure 2. View of the $[\{(C_6H_5)_3P\}_2N]^+$ cation and the $[Cr_2(CO)_{10}]^{2-}$ anion as found in the structure of $[PPN]_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$. The solvated methylene chloride molecule (half-weighted) lying on the same crystallographic twofold axis which passes through the $[Cr_2(CO)_{10}]^{2-}$ anion is also shown.

tropic least-squares refinement then proceeded without further complications to give final discrepancy factors of $R_1 = 9.8$ and $R_2 = 11.5\%$. A final Fourier difference synthesis again failed to to reveal any additional solvent with no peaks greater than 0.66 or less than -0.51 e/Å^3.

Because of the large number of parameters required to carry out the isotropic thermal least-squares refinements of $[PPN]_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$ and $[PPN]_2[Mo_2(CO)_{10}]\cdot CH_2Cl_2$, the resulting computing time per least-squares cycle was already sufficiently long, and therefore expensive, that it could not be justified by us to continue with anisotropic thermal refinement in these particular cases from the standpoint that the scientific value of obtaining more refined structures with somewhat better molecular parameters (involving mainly the nonmetal atoms) was not worth the financial cost. The relatively large estimated standard deviations of both the positional parameters of the carbonyl atoms and the bond lengths and angles involving these atoms are attributed not only to the effect of the methylene chloride of solvation (of which only half of one molecule could be crystallographically resolved) on the refinement of the entire crystal structure but also in part to the isotropic thermal model not being adequate to compensate for the presumed high anisotropic thermal motion of the carbonyl atoms in the $[Cr_2(CO)_{10}]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$ anions; large anisotropic thermal motion of the carbonyl atoms was previously detected in the structural determinations[17,18] of the $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ homologs. Both the crystallographically resolved and unresolved methylene chloride molecules of solvation as well as presumed large anisotropic thermal character probably account for the very high isotropic temperature factors (Table II) of the axial carbonyl atoms, C(2-1) and O(2-1), since the packing appears somewhat congested in the regions of the unit cell near these and their symmetry-related atoms.

All Patterson and Fourier calculations were carried out with the Blount program.[39] Least-squares refinements were carried out with a local modification of the Busing–Martin–Levy ORFLS program.[40] Interatomic distances and angles and their estimated standard deviations (which include the effect of estimated errors in lattice parameters) were calculated with the Busing–Martin–Levy ORFFE program[41] from the full inverse matrix. The atomic parameters from the output of the last least-squares cycle[42] are given in Table II for $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$, while Table III gives selected bond lengths and angles. Atomic and rigid-body parameters from the output of the last least-squares cycles[42] are presented in Tables IV and V for $[PPN]_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$ and $[PPN]_2[Mo_2(CO)_{10}]\cdot CH_2Cl_2$; bond lengths and angles are recorded in Table IV.

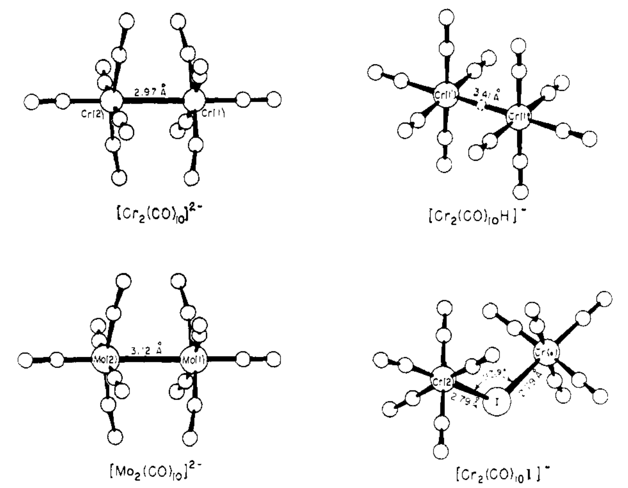

Figure 3. Comparison of the geometries of the $[Cr_2(CO)_{10}]^{2-}$, $[Mo_2(CO)_{10}]^{2-}$, $[Cr_2(CO)_{10}H]^-$, and $[Cr_2(CO)_{10}I]^-$ anions. The $[Cr_2(CO)_{10}]^{2-}$ anion is isoelectronic and isostructural with $Mn_2(CO)_{10}$, while the isosteric $[Mo_2(CO)_{10}]^{2-}$ anion is isoelectronic with $Tc_2(CO)_{10}$. The $[Cr_2(CO)_{10}H]^-$ anion, containing the unprecedented example of a *linear* three-center two-electron metal–hydrogen–metal bond, may be considered to arise from the protonation of the electron-pair Cr–Cr bond in the $[Cr_2(CO)_{10}]^{2-}$ anion. This protonation not only increased the Cr–Cr bonding distance by 0.44 Å but also results in a conformational change of the equatorial carbonyl groups from the D_{4d}-$\bar{8}$2m "staggered" arrangement in the $[Cr_2(CO)_{10}]^{2-}$ anion to an "eclipsed" D_{4h}-4/m2/m2/m structure in the $[Cr_2(CO)_{10}H]^-$ anion. In contrast, the monohalogen-bridged $[Cr_2(CO)_{10}I]^-$ anion has a dinstinctly nonlinear Cr–I–Cr framework whose linkage may be appropriately formulated from a localized valence-bond representation as two electron-pair Cr–I σ bonds.

Results and Discussion

The $[Cr_2(CO)_{10}]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$ Anions. (a) **Comparison of the $[Cr_2(CO)_{10}]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$ Anions with Their Respective Isoelectronic Neutral Molecules $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$.** Crystals of $[PPN]_2[M_2(CO)_{10}]\cdot CH_2Cl_2$ (M = Cr, Mo) are essentially isomorphous and isostructural, as is evident from a comparison of lattice and atomic parameters for the two compounds. The dimeric $[M_2(CO)_{10}]^{2-}$ anion, located on a crystallographic twofold axis coincident with the metal–metal bond, approximately possesses D_{4d}-$\bar{8}$2m symmetry with nearly octahedral coordination about each metal atom such that the two sets of four equatorial carbonyl groups are in a staggered conformation (Figure 2). This configuration of the $[Cr_2(CO)_{10}]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$ anion is contrasted in Figure 3 with the D_{4h}-4/m2/m2/m configuration of the $[Cr_2(CO)_{10}H]^-$ anion and with the configuration of the $[Cr_2(CO)_{10}I]^-$ anion.[43] Thus, the $[Cr_2(CO)_{10}]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$ anions have virtually the same configuration as their respective isoelectronic neutral analogs $Mn_2(CO)_{10}$[17] and $Tc_2(CO)_{10}$.[18]

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

(40) 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.

(41) 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.

(42) 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.

(43) L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7327 (1970).

Table III. Intramolecular Distances (Å) and Angles (deg) for $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$

A. Bond Lengths	
Cr–Cr′	3.406 (9)
Chromium to Equatorial Carbonyl Carbon	
Cr–C(2)	1.91 (3)
Cr–C(3)	1.87 (2)
Cr–C(4)	1.83 (2)
Cr–C(5)	1.92 (2)
	1.88 (av)
Chromium to Equatorial Carbonyl Oxygen	
Cr···O(2)	3.09 (2)
Cr···O(3)	3.02 (2)
Cr···O(4)	3.03 (2)
Cr···O(5)	3.06 (2)
	3.05 (av)
Chromium to Axial Carbonyl Carbon	
Cr–C(1)	1.82 (2)
Chromium to Axial Carbonyl Oxygen	
Cr···O(1)	2.90 (2)
Carbonyl Carbon to Oxygen	
C(1)–O(1)	1.09 (2)
C(2)–O(2)	1.18 (3)
C(3)–O(3)	1.16 (2)
C(4)–O(4)	1.21 (2)
C(5)–O(5)	1.15 (2)
	1.16 (av)
B. Bond Angles	
Cr′–Cr–Carbonyl C_{eq}	
Cr′–Cr–C(2)	91.8 (6)
Cr′–Cr–C(3)	89.7 (6)
Cr′–Cr–C(4)	86.7 (7)
Cr′–Cr–C(5)	87.8 (6)
	89.0 (av)
Cr′–Cr–Carbonyl O_{eq}	
Cr′–Cr···O(2)	91.4 (4)
Cr′–Cr···O(3)	92.0 (4)
Cr′–Cr···O(4)	89.1 (3)
Cr′–Cr···O(5)	90.5 (4)
	90.8 (av)
Cr′–Cr–Carbonyl C_{ax}	
Cr′–Cr–C(1)	176.8 (6)
Cr′–Cr–Carbonyl O_{ax}	
Cr′–Cr···O(1)	177.2 (4)
C_{eq}–Cr–C_{eq}	
C(2)–Cr–C(3)	90.3 (8)
C(3)–Cr–C(4)	89.4 (8)
C(4)–Cr–C(5)	90.1 (8)
C(5)–Cr–C(2)	90.2 (8)
	90.0 (av)
C_{eq}–Cr–C_{ax}	
C(2)–Cr–C(1)	91.0 (8)
C(3)–Cr–C(1)	90.0 (8)
C(4)–Cr–C(1)	90.6 (9)
C(5)–Cr–C(1)	90.6 (8)
	91.0 (av)
Cr–C–O	
Cr–C(1)–O(1)	179 (2)
Cr–C(2)–O(2)	178 (2)
Cr–C(3)–O(3)	174 (2)
Cr–C(4)–O(4)	174 (2)
Cr–C(5)–O(5)	172 (2)
	175 (av)
C. Nonbonding Distances	
within the $Cr(CO)_5$ Fragment	
C(1)···C(2)	2.65 (3)
C(1)···C(3)	2.66 (4)
C(1)···C(4)	2.65 (3)
C(1)···C(5)	2.59 (3)
C(2)···C(3)	2.71 (4)
C(3)···C(4)	2.68 (3)
C(4)···C(5)	2.60 (3)
C(5)···C(1)	2.66 (3)
between $Cr(CO)_5$ Fragments	
C(2)···C(4′)	3.32 (3)
C(3)···C(5′)	3.36 (3)
O(2)···O(4′)	3.54 (2)
O(3)···O(5′)	3.43 (3)
within the Constrained $[(C_2H_5)_4N]^+$ Cation	
$H_3C(1)\cdots H_3C(2)$	3.55
$H_3C(1)\cdots H_2C(4)$	2.93
$H_2C(1)\cdots H_2C(2)$	2.45

Although the crystalline $[PPN]_2[M_2(CO)_{10}]\cdot CH_2Cl_2$ structure is ionic, the packing depicted in Figure 4 is largely determined by the bulky $[PPN]^+$ cations. Accordingly, there are no interionic anion···anion distances less than 5.0 Å, while the shortest interionic carbon···carbon distances of the cations are in the range 3.5–3.8 Å. The interionic (cation carbon)···(anion oxygen) distances are all greater than 3.2 Å.

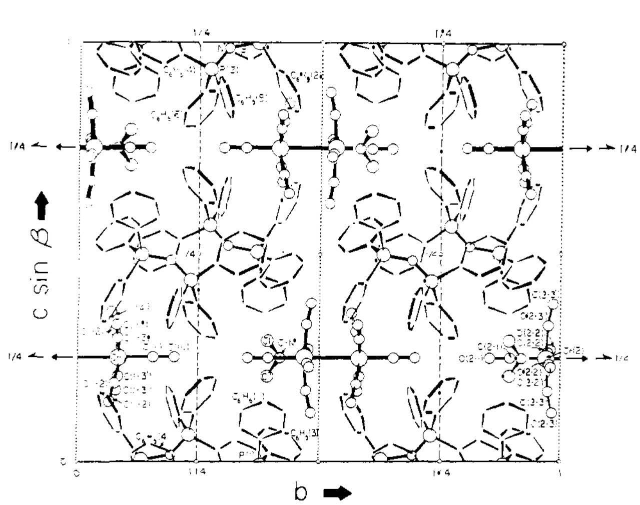

Figure 4. [100] projection of the monoclinic unit cell of $[PPN]_2[M_2(CO)_{10}]\cdot CH_2Cl_2$ (M = Cr, Mo), showing the orientations of the four formula species per cell related to one another by the space group symmetry C2/c.

The Cr–Cr distance of 2.97 ± 0.01 Å in the $[Cr_2(CO)_{10}]^{2-}$ anion is 0.05 Å greater than the Mn–Mn distance of 2.923 ± 0.003 Å in $Mn_2(CO)_{10}$,[17] while the Mo–Mo distance of 3.123 ± 0.007 Å in the $[Mo_2(CO)_{10}]^{2-}$ anion is 0.09 Å greater than the Tc–Tc distance of 3.036 ± 0.006 Å in $Tc_2(CO)_{10}$.[18] The equatorial carbonyl groups in both dianions are bent away from the axial carbonyl groups. The average C_{ax}–M–C_{eq} angles are 93 and 94° in the chromium and molybdenum compounds, respectively. This same distortion from exact octahedral coordination is observed not only in $Mn_2(CO)_{10}$[17] and $Tc_2(CO)_{10}$,[18] but also in both the solid[44,45] and gas-phase[46] structures of $Mn(CO)_5H$,

(44) S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, 3, 1491 (1964).
(45) S. J. La Placa, W. C. Hamilton, J. A. Ibers, and A. Davison, *ibid.*, 8, 1928 (1969).
(46) A. G. Robiette, G. M. Sheldrick, and R. N. F. Simpson, *Chem. Commun.*, 506 (1968).

Table IV. Final Parameters for $[PPN]_2[Cr_2(CO)_{10}]\cdot CH_2Cl_2$[a]

Atom	x	y	z	B
Cr(1)	0	0.0836 (3)	0.25	4.3 (2)
Cr(2)	0	−0.0317 (4)	0.25	5.4 (2)
C(1–1)	0	0.153 (2)	0.25	8 (2)
O(1–1)	0	0.197 (1)	0.25	7 (1)
C(2–1)	0	−0.105 (4)	0.25	12 (3)
O(2–1)	0	−0.148 (2)	0.25	18 (2)
C(1–2)	0.077 (2)	0.076 (1)	0.187 (2)	6.1 (9)
O(1–2)	0.122 (2)	0.0659 (8)	0.143 (1)	6.8 (7)
C(1–3)	0.124 (3)	0.082 (1)	0.296 (2)	7 (1)
O(1–3)	0.195 (2)	0.079 (1)	0.329 (1)	9.6 (8)
C(2–2)	−0.146 (3)	−0.028 (1)	0.264 (1)	7 (1)
O(2–2)	−0.225 (2)	−0.023 (1)	0.270 (1)	8.9 (8)
C(2–3)	−0.037 (2)	−0.028 (1)	0.171 (2)	6.8 (9)
O(2–3)	−0.161 (2)	−0.018 (1)	0.118 (1)	8.6 (7)
C–M	0	0.417 (3)	0.25	8[b]
Cl	0.076 (1)	0.393 (1)	0.292 (1)	6[b]
P(1)	−0.0349 (6)	0.3695 (4)	−0.0030 (4)	2.8 (2)
P(2)	−0.0252 (6)	0.2700 (3)	−0.0643 (4)	3.1 (2)
N	−0.053 (1)	0.3095 (8)	−0.0160 (9)	2.3 (5)
$C_6H_5(1)$				
PC(1–1)	0.063	0.378	0.055	2.3 (7)
PC(1–2)	0.112	0.335	0.080	4.3 (8)
PC(1–3)	0.188	0.340	0.126	6.2 (9)
PC(1–4)	0.216	0.390	0.147	5.0 (8)
PC(1–5)	0.168	0.433	0.121	7 (1)
PC(1–6)	0.091	0.428	0.075	6.2 (9)
PH(1–2)	0.090	0.297	0.065	10[c]
PH(1–3)	0.226	0.307	0.146	10
PH(1–4)	0.275	0.394	0.182	10
PH(1–5)	0.189	0.472	0.137	10
PH(1–6)	0.054	0.461	0.056	10
$C_6H_5(2)$				
PC(2–1)	0.002	0.405	−0.066	4.1 (8)
PC(2–2)	0.101	0.423	−0.070	6.1 (9)
PC(2–3)	0.126	0.450	−0.121	7 (1)
PC(2–4)	0.053	0.457	−0.168	6.4 (9)
PC(2–5)	−0.046	0.439	−0.164	8 (1)
PC(2–6)	−0.071	0.413	−0.113	4.0 (7)
PH(2–2)	0.158	0.418	−0.034	10[c]
PH(2–3)	0.203	0.464	−0.124	10
PH(2–4)	0.072	0.478	−0.207	10
PH(2–5)	−0.103	0.445	−0.200	10
PH(2–6)	−0.148	0.398	−0.110	10
$C_6H_5(3)$				
PC(3–1)	−0.148	0.399	0.020	3.3 (7)
PC(3–2)	−0.198	0.372	0.063	8 (1)
PC(3–3)	−0.284	0.393	0.086	8 (1)
PC(3–4)	−0.320	0.441	0.066	5.2 (9)
PC(3–5)	−0.270	0.468	0.024	9 (1)
PC(3–6)	−0.184	0.447	0.001	8 (1)
PH(3–2)	−0.170	0.334	0.078	10[c]
PH(3–3)	−0.324	0.372	0.119	10
PH(3–4)	−0.388	0.457	0.084	10
PH(3–5)	−0.298	0.506	0.009	10
PH(3–6)	−0.144	0.468	−0.032	10
$C_6H_5(4)$				
PC(4–1)	0.002	0.210	−0.029	4.3 (8)
PC(4–2)	0.063	0.173	−0.055	4.3 (8)
PC(4–3)	0.076	0.124	−0.030	5.9 (9)
PC(4–4)	0.027	0.111	0.021	6 (1)
PC(4–5)	−0.034	0.148	0.046	6.4 (9)
PC(4–6)	−0.047	0.197	0.021	4.2 (8)
PH(4–2)	0.102	0.183	−0.095	10[c]
PH(4–3)	0.124	0.096	−0.050	10
PH(4–4)	0.037	0.076	0.041	10
PH(4–5)	−0.073	0.138	0.086	10
PH(4–6)	−0.095	0.225	0.042	10
$C_6H_5(5)$				
PC(5–1)	0.084	0.287	−0.104	3.2 (7)
PC(5–2)	0.078	0.302	−0.164	5.0 (9)
PC(5–3)	0.165	0.317	−0.191	8 (1)
PC(5–4)	0.259	0.317	−0.158	8 (1)
PC(5–5)	0.266	0.303	−0.099	6 (1)
PC(5–6)	0.178	0.288	−0.072	5.9 (9)
PH(5–2)	0.005	0.301	−0.189	10[c]
PH(5–3)	0.160	0.328	−0.237	10
PH(5–4)	0.366	0.329	−0.179	10
PH(5–5)	0.339	0.304	−0.073	10
PH(5–6)	0.184	0.277	−0.025	10
$C_6H_5(6)$				
PC(6–1)	−0.130	0.257	−0.119	4.6 (8)
PC(6–2)	−0.124	0.221	−0.164	6.0 (9)
PC(6–3)	−0.207	0.213	−0.205	5.8 (9)
PC(6–4)	−0.296	0.242	−0.202	5.5 (9)
PC(6–5)	−0.301	0.279	−0.157	7 (1)
PC(6–6)	−0.218	0.287	−0.116	5.4 (9)[b]
PH(6–2)	−0.055	0.198	−0.167	10[c]
PH(6–3)	−0.203	0.184	−0.240	10
PH(6–4)	−0.360	0.236	−0.233	10
PH(6–5)	−0.370	0.301	−0.154	10
PH(6–6)	−0.222	0.315	−0.081	10

Rigid-Body Parameters[d]

Group	x	y	z	ϕ	θ	ρ
$C_6H_5(1)$	0.1396 (9)	0.3841 (6)	0.1008 (5)	−173.8 (7)	−177.4 (8)	132.5 (5)
$C_6H_5(2)$	0.028 (1)	0.4311 (4)	−0.1169 (6)	−82.7 (7)	−156.5 (8)	−116.3 (7)
$C_6H_5(3)$	−0.234 (1)	0.4200 (6)	0.0433 (6)	−8 (1)	144.9 (7)	−27.1 (9)
$C_6H_5(4)$	0.0145 (9)	0.1605 (6)	−0.0042 (6)	69 (1)	−134.5 (7)	−35.3 (9)
$C_6H_5(5)$	0.172 (1)	0.3023 (4)	−0.1312 (7)	−107 (1)	−120.6 (8)	59 (1)
$C_6H_5(6)$	−0.213 (1)	0.2496 (5)	−0.1604 (6)	−142.4 (8)	153.4 (8)	−47.8 (7)

[a] Estimated standard deviation of last significant figure is given in parentheses. [b] Temperature factors were fixed and the scale factors for the scattering factors were varied. The final scale factors are: 0.56 (5) for CM (corrected for the special position) and 0.49 (1) for Cl. [c] The isotropic thermal parameters for the hydrogen atoms of the phenyl groups were held constant throughout the refinement. [d] See ref 29, 30, and 37.

in the structure of each $MnFe(CO)_9$ segment of $Mn_2Fe(CO)_{14}$,[47,48] and in the structures of the $ReMn(CO)_9$ segment of $Re_2Mn(CO)_{14}H$[47,49] and of the $Re_2(CO)_9$ segment of $Re_3(CO)_{14}H$.[47,50]

(47) The $Mn_2Fe(CO)_{14}$ molecule[48] may be constructed in "tinkertoy" fashion by the *trans*-octahedral addition of two $Mn(CO)_5$ ligands to a planar $Fe(CO)_4$ fragment to give a molecule of D_{4h} symmetry, in which the four equatorial carbonyl groups attached to each octahedrally coordinated manganese atom are staggered relative to the four equatorial carbonyl groups of the central iron atom. On the other hand, the Fellmann–Kaesz trimetallic hydrido complexes $Re_2Mn(CO)_{14}H$[49] and $Re_3(CO)_{14}H$[50] have a nonlinear trinuclear metal framework which may be visualized in terms of each of the three metal atoms being in an octahedral-like environment, with the central $Re(CO)_4$ fragment *cis*-disubstituted with a $M(CO)_5$ group (M = Mn or Re) and a $HRe(CO)_5$ fragment.

(48) P. A. Agron, R. D. Ellison, and H. A. Levy, *Acta Crystallogr.*, **23**, 1079 (1967); E. H. Schubert and R. K. Sheline, *Z. Naturforsch. B*, **20**, 1306 (1965).

(49) H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Amer. Chem. Soc.*, **89**, 2775 (1967); M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).

Table V. Final Parameters for $[PPN]_2[Mo_2(CO)_{10}]\cdot CH_2Cl_2$[a]

Atom	x	y	z	B
Mo(1)	0	0.0875 (2)	0.25	4.4 (1)
Mo(2)	0	−0.0315 (3)	0.25	5.5 (1)
C(1–1)	0	0.158 (3)	0.25	10 (2)
O(1–1)	0	0.203 (2)	0.25	9 (1)
C(2–1)	0	−0.106 (3)	0.25	12 (3)
O(2–1)	0	−0.151 (3)	0.25	16 (2)
C(1–2)	0.077 (3)	0.080 (1)	0.187 (2)	7 (1)
O(1–2)	0.125 (2)	0.0701 (8)	0.143 (1)	5.5 (6)
C(1–3)	0.128 (3)	0.082 (1)	0.298 (2)	7 (1)
O(1–3)	0.196 (2)	0.079 (1)	0.336 (1)	9.3 (8)
C(2–2)	−0.144 (3)	−0.027 (1)	0.265 (1)	5.0 (8)
O(2–2)	−0.230 (2)	−0.021 (1)	0.272 (1)	7.3 (6)
C(2–3)	−0.038 (3)	−0.026 (2)	0.168 (2)	9 (1)
O(2–3)	−0.060 (2)	−0.018 (1)	0.144 (1)	8.1 (7)
C–M	0	0.416 (4)	0.25	8[b]
Cl	0.078 (2)	0.396 (1)	0.291 (1)	6[b]
P(1)	−0.0311 (6)	0.3691 (4)	−0.0017 (4)	3.3 (2)
P(2)	−0.0214 (6)	0.2718 (4)	−0.0648 (4)	3.8 (2)
N	−0.049 (2)	0.3108 (9)	−0.016 (1)	3.7 (6)
$C_6H_5(1)$				
PC(1–1)	0.066	0.377	0.059	4.0 (8)
PC(1–2)	0.115	0.334	0.085	5.0 (9)
PC(1–3)	0.193	0.341	0.129	6 (1)
PC(1–4)	0.222	0.390	0.148	7 (1)
PC(1–5)	0.173	0.432	0.122	6 (1)
PC(1–6)	0.095	0.426	0.078	7 (1)
PH(1–2)	0.093	0.297	0.070	10[c]
PH(1–3)	0.231	0.308	0.149	10
PH(1–4)	0.282	0.395	0.182	10
PH(1–5)	0.195	0.470	0.137	10
PH(1–6)	0.057	0.458	0.058	10
$C_6H_5(2)$				
PC(2–1)	0.004	0.404	−0.066	4.0 (8)
PC(2–2)	0.100	0.422	−0.073	5.0 (9)
PC(2–3)	0.121	0.448	−0.125	7 (1)
PC(2–4)	0.046	0.458	−0.169	6 (1)
PC(2–5)	−0.051	0.440	−0.163	7 (1)
PC(2–6)	−0.072	0.414	−0.111	6 (1)
PH(2–2)	0.160	0.414	−0.038	10[c]
PH(2–3)	0.197	0.462	−0.130	10
PH(2–4)	0.062	0.479	−0.209	10
PH(2–5)	−0.110	0.448	−0.197	10
PH(2–6)	−0.147	0.400	−0.106	10

Atom	x	y	z	B
$C_6H_5(3)$				
PC(3–1)	−0.144	0.396	0.024	4.1 (9)
PC(3–2)	−0.197	0.367	0.063	7 (1)
PC(3–3)	−0.282	0.386	0.087	11 (1)
PC(3–4)	−0.314	0.435	0.072	7 (1)
PC(3–5)	−0.262	0.464	0.033	10 (1)
PC(3–6)	−0.177	0.445	0.009	8 (1)
PH(3–2)	−0.172	0.328	0.075	10[c]
PH(3–3)	−0.323	0.363	0.117	10
PH(3–4)	−0.380	0.450	0.091	10
PH(3–5)	−0.287	0.503	0.021	10
PH(3–6)	−0.136	0.468	−0.021	10
$C_6H_5(4)$				
PC(4–1)	0.003	0.211	−0.029	3.7 (8)
PC(4–2)	0.062	0.175	−0.056	6 (1)
PC(4–3)	0.074	0.127	−0.032	6 (1)
PC(4–4)	0.026	0.114	0.019	7 (1)
PC(4–5)	−0.033	0.149	0.046	7 (1)
PC(4–6)	−0.044	0.198	0.022	5.1 (9)
PH(4–2)	0.100	0.186	−0.096	10[c]
PH(4–3)	0.120	0.099	−0.054	10
PH(4–4)	0.035	0.076	0.037	10
PH(4–5)	−0.070	0.139	0.086	10
PH(4–6)	−0.090	0.226	0.043	10
$C_6H_5(5)$				
PC(5–1)	0.086	0.288	−0.106	3.7 (8)
PC(5–2)	0.076	0.305	−0.166	6 (1)
PC(5–3)	0.160	0.321	−0.194	8 (1)
PC(5–4)	0.254	0.320	−0.162	7 (1)
PC(5–5)	0.264	0.303	−0.103	7 (1)
PC(5–6)	0.179	0.288	−0.075	7 (1)
PH(5–2)	0.003	0.306	−0.190	10[c]
PH(5–3)	0.153	0.334	−0.240	10
PH(5–4)	0.320	0.332	−0.184	10
PH(5–5)	0.337	0.303	−0.079	10
PH(5–6)	0.187	0.275	−0.029	10
$C_6H_5(6)$				
PC(6–1)	−0.126	0.260	−0.121	4.3 (9)
PC(6–2)	−0.121	0.224	−0.165	5.3 (9)
PC(6–3)	−0.204	0.215	−0.206	6 (1)
PC(6–4)	−0.291	0.242	−0.202	6 (1)
PC(6–5)	−0.296	0.279	−0.157	6 (1)
PC(6–6)	−0.214	0.288	−0.117	6 (1)
PH(6–2)	−0.053	0.202	−0.169	10[c]
PH(6–3)	−0.199	0.186	−0.240	10
PH(6–4)	−0.355	0.235	−0.233	10
PH(6–5)	−0.364	0.301	−0.154	10
PH(6–6)	−0.218	0.317	−0.082	10

Rigid-Body Parameters[d]

Group	x	y	z	ϕ	θ	ρ
$C_6H_5(1)$	0.144 (1)	0.3832 (7)	0.1034 (6)	−173.9 (8)	−176.3 (8)	134.8 (8)
$C_6H_5(2)$	0.025 (1)	0.4310 (5)	−0.1178 (7)	−84.7 (9)	−159.5 (8)	−118.7 (8)
$C_6H_5(3)$	−0.229 (1)	0.4155 (7)	0.0480 (7)	−10 (1)	150.1 (9)	−26 (1)
$C_6H_5(4)$	0.015 (1)	0.1623 (7)	−0.0052 (8)	69 (1)	−133.7 (8)	−34 (1)
$C_6H_5(5)$	0.170 (1)	0.3042 (5)	−0.1344 (8)	−110 (2)	−123.2 (9)	55 (2)
$C_6H_5(6)$	−0.208 (1)	0.2514 (6)	−0.1612 (7)	−142.2 (9)	153.3 (8)	−46.1 (9)

[a] Estimated standard deviation of last significant figure is given in parentheses. [b] Temperature factors were fixed and the scale factors for the scattering factors were varied. The final scale factors are: 0.44 (6) for CM (corrected for the special position) and 0.44 (2) for Cl. [c] The isotropic thermal parameters for the hydrogen atoms of the phenyl groups were held constant throughout the refinement. [d] See ref 29, 30, and 37.

(b) Estimation of Chromium and Molybdenum Radii. One-half of the metal-metal single-bond distance which is 1.48 Å for the $[Cr_2(CO)_{10}]^{2-}$ anion and 1.56 Å for the $[Mo_2(CO)_{10}]^{2-}$ anion may be taken as the covalent metal radius. Although there are no previous direct evaluations of a covalent chromium radius in the sense of one-half of a Cr–Cr distance, from the Cr–N bond lengths in the compound *cis*-Cr(dien)$(CO)_3$ Cotton and Richardson[51] estimated a value of 1.48 Å, which is in excellent agreement with the value obtained in this work. However, a similar estimate of the molybdenum radius based on the isostructural compound *cis*-Mo(dien)$(CO)_3$[52] gives a value of 1.62 Å which

(50) R. P. White, Jr., T. E. Block, and L. F. Dahl, submitted for publication.

(51) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 1851 (1966).

(52) F. A. Cotton and R. M. Wing, *ibid.*, **4**, 314 (1965).

Table VI. Intramolecular Distances (Å) and Angles (deg) for $[PPN]_2[M_2(CO)_{10}] \cdot CH_2Cl_2$ (M = Cr, Mo)[a]

	M = Cr	M = Mo
A. Bond Lengths		
Metal–Metal		
M(1)–M(2)	2.97 (1)	3.123 (7)
Metal–Equatorial Carbon		
M(1)–C(1–2)	1.81 (4)	1.81 (4)
M(1)–C(1–3)	1.87 (4)	1.96 (4)
M(2)–C(2–2)	1.97 (4)	1.98 (3)
M(2)–C(2–3)	1.82 (4)	1.86 (4)
	1.87 (av)	1.90 (av)
Metal–Axial Carbon		
M(1)–C(1–1)	1.79 (6)	1.86 (7)
M(2)–C(2–1)	1.90 (9)	1.95 (9)
	1.84 (av)	1.90 (av)
Metal–Equatorial Oxygen		
M(1)···O(1–2)	3.01 (2)	3.04 (2)
M(1)···O(1–3)	3.02 (3)	3.13 (3)
M(2)···O(2–2)	3.03 (3)	3.16 (3)
M(2)···O(2–3)	3.04 (3)	3.09 (3)
	3.02 (av)	3.10 (av)
Metal–Axial Oxygen		
M(1)···O(1–1)	2.93 (4)	3.03 (5)
M(2)···O(2–1)	3.01 (6)	3.14 (7)
	2.97 (av)	3.08 (av)
Carbon–Oxygen		
C(1–1)–O(1–1)	1.14 (6)	1.17 (7)
C(1–2)–O(1–2)	1.21 (3)	1.24 (4)
C(1–3)–O(1–3)	1.15 (3)	1.18 (4)
C(2–1)–O(2–1)	1.11 (8)	1.19 (8)
C(2–2)–O(2–2)	1.06 (4)	1.18 (3)
C(2–3)–O(2–3)	1.23 (3)	1.23 (4)
	1.15 (av)	1.20 (av)
Phosphorus–Nitrogen		
P(1)–N	1.59 (2)	1.58 (2)
P(2)–N	1.55 (2)	1.56 (2)
	1.57 (av)	1.57 (av)
Phosphorus–Phenyl Carbon-1		
P(1)–PC(1–1)	1.78	1.82
P(1)–PC(2–1)	1.78	1.80
P(1)–PC(3–1)	1.77	1.80
P(2)–PC(4–1)	1.77	1.80
P(2)–PC(5–1)	1.80	1.81
P(2)–PC(6–1)	1.81	1.83
	1.78 (av)	1.81 (av)
Methylene Chloride		
CM–Cl	1.46 (3)	1.44 (4)
B. Bond Angles		
Metal–Metal–Equatorial Carbon		
M(2)–M(1)–C(1–2)	84 (1)	84 (1)
M(2)–M(1)–C(1–3)	89 (1)	86 (1)
M(1)–M(2)–C(2–2)	87 (1)	86 (1)
M(1)–M(2)–C(2–3)	87 (1)	86 (1)
	87 (av)	86 (av)
Equatorial Carbon–Metal–Equatorial Carbon		
C(1–2)–M(1)–C(1–3)	85 (1)	84 (2)
C(2–2)–M(2)–C(2–3)	88 (1)	88 (1)
	86 (av)	86 (av)
Metal–Carbon–Oxygen		
M(1)–C(1–2)–O(1–2)	173 (3)	173 (3)
M(1)–C(1–3)–O(1–3)	173 (3)	168 (4)
M(2)–C(2–2)–O(2–2)	175 (4)	176 (3)
M(2)–C(2–3)–O(2–3)	172 (3)	174 (4)
	173 (av)	173 (av)
Phosphorus–Nitrogen–Phosphorus		
P(1)–N–P(2)	137 (1)	137 (2)
Nitrogen–Phosphorus–Phenyl Carbon-1		
N–P(1)–PC(1–1)	111	110
N–P(1)–PC(2–1)	114	113
N–P(1)–PC(3–1)	111	109
N–P(2)–PC(4–1)	109	108
N–P(2)–PC(5–1)	115	116
N–P(2)–PC(6–1)	113	112
Phenyl Carbon-1–Phosphorus–Phenyl Carbon-1		
PC(1–1)–P(1)–PC(2–1)	107	109
PC(1–1)–P(1)–PC(3–1)	108	107
PC(2–1)–P(1)–PC(3–1)	107	109
PC(4–1)–P(2)–PC(5–1)	107	108
PC(4–1)–P(2)–PC(6–1)	105	105
PC(5–1)–P(2)–PC(6–1)	107	106
	107 (av)	107 (av)
Phosphorus–Phenyl Carbon-1–Phenyl Carbon-4		
P(1)–PC(1–1)–PC(1–4)	179	177
P(1)–PC(2–1)–PC(2–4)	177	177
P(1)–PC(3–1)–PC(3–4)	175	176
P(2)–PC(4–1)–PC(4–4)	175	174
P(2)–PC(5–1)–PC(5–4)	176	175
P(2)–PC(6–1)–PC(6–4)	177	177
	176 (av)	176 (av)
Chlorine–Carbon–Chlorine		
Cl–CM–Cl	129 (6)	137 (8)
C. Nonbonding Distances		
within the $M(CO)_5$ Fragment		
C(1–1)···C(1–2)	2.69 (5)	2.72 (7)
C(1–1)···C(1–3)	2.62 (5)	2.80 (7)
C(2–1)···C(2–2)	2.79 (7)	2.87 (7)
C(2–1)···C(2–3)	2.70 (7)	2.80 (8)
C(1–2)···C(1–3)	2.50 (4)	2.53 (5)
C(2–2)···C(2–3)	2.63 (5)	2.66 (5)
between $M(CO)_5$ Fragments		
C(1–2)···C(2–3)	3.06 (5)	3.20 (6)
C(1–2)···C(2–2′)	3.01 (5)	3.11 (5)
C(1–3)···C(2–2′)	3.17 (5)	3.20 (5)
C(1–3)···C(2–3′)	3.15 (5)	3.20 (6)
O(1–2)···O(2–3)	3.26 (3)	3.42 (3)
O(1–2)···O(2–2′)	3.24 (3)	3.30 (3)
O(1–3)···O(2–2′)	3.49 (4)	3.59 (4)
O(1–3)···O(2–3′)	3.32 (4)	3.36 (4)

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

is 0.06 Å larger than that derived from the $[Mo_2(CO)_{10}]^{2-}$ anion. This difference in derived molybdenum radius, which is difficult to explain in view of the agreement obtained for the chromium radius from the similarly related chromium compounds, deserves some comment. Numerous other estimates have been made of a molybdenum radius for a variety of formal oxidation states with values ranging from 1.44 to 1.64 Å.[53] The value of 1.61 Å obtained from the molybdenum–molybdenum distance in $[Mo(h^5\text{-}C_5H_5)(CO)_3]_2$[54] is in good agreement with the value derived from *cis*-Mo(dien)$(CO)_3$. Stevenson and Dahl[53] pointed out that this

(53) D. L. Stevenson and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 3721 (1967), and references therein.

(54) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

range of values for the molybdenum radius supports the premise that the type of substituents attached to the molybdenum atom, and in partiuclar their steric and charge acceptor properties, is a more important factor in determining the resulting bond lengths used to obtain the metal radius than the particular formal oxidation state assigned to the metal. Hence, unknown differences in nonbonding ligand-ligand interactions due to differing steric compression effects prevent a meaningful rationalization of the difference of 0.05 Å in the molybdenum radii obtained from one-half the Mo-Mo electron-pair bond lengths in the $[Mo_2(CO)_{10}]^{2-}$ anion and in $[Mo(h^5\text{-}C_5H_5)(CO)_3]_2$. For identical structures where steric effects can be neglected, it is qualitatively expected that ligands which reduce the negative charge localized on the metal will cause a contraction of the metal orbitals, thus reducing the internuclear separation for maximum overlap (more rigorously minimum molecular energy).

The metal-metal bond length changes in the two pairs of isoelectronic dinuclear metal complexes $[Fe_2(CO)_8]^{2-}$–$Co_2(CO)_8$ (nonbridged) and $[Cr_2(CO)_{10}]^{2-}$–$Mn_2(CO)_{10}$ together with the essential invariance of metal-metal bond lengths in phosphine-substituted $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ complexes provide a means of assessment of the influence of the stereochemistry of each type metal carbonyl species on the degree of electron delocalization from the metal atoms of different coordination. Although the Co-Co distance for the non-carbonyl-bridged $Co_2(CO)_8$ tautomer,[55–63] which is isostructural with the $[Fe_2(CO)_8]^{2-}$ anion, has not been directly determined, X-ray diffraction studies[60–62] of three nonbridged phosphine-substituted cobalt carbonyl homologs $Co_2(CO)_6R_2$ (where R represents $P(n\text{-}C_4H_9)_3$,[59–61] $P(OC_6H_5)_3$,[62] and $P(C_6H_5)_3$[62]) showed rather unexpectedly that the cobalt-cobalt bond lengths in these three molecular complexes are all experimentally equivalent (of range 2.66–2.67 Å) despite a significant variation of 0.1 Å being observed[62] in the Co-P bond lengths. A similar situation exists for the $Mn_2(CO)_{10}$ system, where X-ray investigations[64,65] showed that substitution of PF_3[64] and $P(C_2H_5)_3$[65] in place of the two axial carbonyl groups to give $Mn_2(CO)_8R_2$ molecules leaves the Mn-Mn distance virtually unchanged from that in $Mn_2(CO)_{10}$. This invariance of the metal-metal distance for different axial ligands strongly suggests that the Co-Co distance in the non-bridged $Co_2(CO)_8$ tautomer is within 0.01 Å of 2.66 Å. The iron-iron distance for the isoelectronic $[Fe_2(CO)_8]^{2-}$ anion of 2.75 Å[56] gives a difference of 0.09 Å in the metal-metal bond length for these isostructural species. For the corresponding $[Cr_2(CO)_{10}]^{2-}$–$Mn_2(CO)_{10}$ pair, the increase in metal-metal bond length from the manganese to the chromium homolog is only 0.05 Å, as already noted. When the basic assumption that for each of these pairs of isosteric dinuclear metal complexes the predominant factor responsible for the metal-metal bond length increase in the anion is the increased negative charge localized on each metal atom (by which, owing to increased orbital expansion, there is equilibration of the metal-metal bond at a greater distance), it follows that a somewhat higher increased negative charge is anticipated on each iron atom relative to that localized on each cobalt atom in the isosteric $[Fe_2(CO)_8]^{2-}$–$Co_2(CO)_8$ (nonbridged) pair, and furthermore this charge increase is greater than the increase in charge localized on each chromium atom relative to that found on each manganese atom in the isosteric $[Cr_2(CO)_{10}]^{2-}$–$Mn_2(CO)_{10}$ pair.

The insensitivity of the metal-metal bond lengths in both $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ (nonbridged) to axial substitution by different phosphine ligands has been attributed[62] to energetics involving a compensating ability of the π_{CO} and π^*_{CO} orbitals to maintain a relatively constant negative charge localized on the metal atoms. In the case of the $[Cr_2(CO)_{10}]^{2-}$ and $[Fe_2(CO)_8]^{2-}$ anions, where the negative charge increase on each metal atom is much more pronounced than that due to the charge donor-acceptor differences of the various phosphine-substituted ligands, it is presumed that the π^*_{CO} orbitals energetically participate to such an extent in the M-CO back-bonding that electronic energy differences are assumed not to dominate. Hence, an octahedral-like coordination of *five* carbonyl ligands and the other metal atom about each chromium atom should give rise to a lower negative charge localized on a metal atom than the trigonal-bipyramidal-like coordination of *four* carbonyl groups and the other axially directed metal atoms about each iron atom. The expected directional shifts of the infrared carbonyl bands to lower frequencies (indicative of increased population in the π^*_{CO} orbitals) in the doubly negative charged anions from those in the corresponding neutral metal carbonyl monomers are roughly the same for both types of metal coordination.[66–69]

(55) Each metal atom in the $[Fe_2(CO)_8]^{2-}$ anion[56] and in the non-carbonyl-bridged isomer of $Co_2(CO)_8$ (*i.e.*, the nonbridged form exists only in solution in equilibrium with the carbonyl-bridged form)[57] as well as in mono- and disubstituted cobalt carbonyl phosphine complexes (with one or both axial carbonyl groups replaced by a phosphine ligand)[58] has a localized trigonal-bipyramidal environment with the two halves of the dimeric molecule linked along their trigonal axes by a direct metal-metal bond such that the two sets of three equatorial carbonyl groups are arranged in a staggered conformation with each other. X-Ray analyses[56,59–62] have shown the geometries of the $[Fe_2(CO)_8]^{2-}$ anion and of the common $Co_2(CO)_6P_2$ fragment in each of the disubstituted cobalt carbonyl complexes to conform approximately to D_{3d}-$\bar{3}2/m$ symmetry. The Co-Co distance in the carbonyl-bridged isomer (*i.e.*, the low-temperature solution and solid-state form of $Co_2(CO)_8$) was found from an X-ray study[63] to be 2.524 ± 0.002 Å.

(56) O. S. Mills, private communication to L. F. Dahl, 1961; the Fe-Fe bond length was originally given as 2.88 Å; subsequently, a refinement of the structure of the salt $[Fe(en)_3][Fe_2(CO)_8]$ (F. S. Stephens, *Acta Crystallogr., Sect. A*, 21, 154 (1966)) was found to result in an Fe-Fe bond length of 2.75 Å for the anion: F. S. Stephens and O. S. Mills, private communication to L. F. Dahl, 1970.

(57) (a) K. Noack, *Spectrochim. Acta*, 19, 1925 (1963); *Helv. Chim. Acta*, 47, 1555 (1964); (b) G. Bor and L. Marko, *Chem. Ind. (London)*, 912 (1963).

(58) *Cf.* A. R. Manning, *J. Chem. Soc. A*, 1135 (1968), and references contained therein.

(59) This compound displays two crystalline modifications. The one examined by Ibers[60] is cubic, while the one studied by Bryan and Manning[61] is monoclinic.

(60) J. A. Ibers, *J. Organometal. Chem.*, 14, 423 (1968).

(61) R. F. Bryan and A. R. Manning, *Chem. Commun.*, 1316 (1968).

(62) J. Molin-Case, A. S. Foust, Jr., and L. F. Dahl, submitted for publication.

(63) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, 17, 732 (1964).

(64) H. M. Powell, *et al.*, unpublished work cited in D. J. Parker and M. H. B. Stiddard, *J. Chem. Soc. A*, 695 (1966).

(65) M. J. Bennett and R. Mason, *ibid.*, *A*, 75 (1968).

(66) For the $[Fe_2(CO)_8]^{2-}$ anion, ir-active carbonyl stretching bands in DMF solution are observed[67] at 1916, 1866, and 1842 cm^{-1} compared to bands found[68,69] at 2034 and 2014 cm^{-1} in the gas phase for $Fe(CO)_5$. For the $[Cr_2(CO)_{10}]^{2-}$ anion bands are found[21] at 1912, 1883, and 1786 cm^{-1} in DMSO solution compared to the $Cr(CO)_6$ band determined[68] at 2000 cm^{-1} in the gas phase.

(67) W. F. Edgell, M. T. Yang, B. J. Bulkin, B. Bayer, and N. Koizumi, *J. Amer. Chem. Soc.*, 87, 3080 (1965).

(68) G. Bor, *Spectrochim. Acta*, 18, 817 (1962).

In an excellent recent review of metal carbonyl cluster systems, Chini[70] concluded from an examination of the infrared spectra of a large number of anionic clusters that in the negatively charged carbonyl metalates, $[Cr_2(CO)_{10}]^{2-}$ and $[Fe_2(CO)_8]^{2-}$, back-bonding is roughly independent of coordination number. Therefore, the number of carbonyl ligands per metal atom in these anions should become an important factor in accord with our arguments for a larger negative charge on each iron atom in $[Fe_2(CO)_8]^{2-}$ compared to that on each chromium atom in $[Cr_2(CO)_{10}]^{2-}$.

A quantitative estimate of the difference in charge localized on the metal atom due to the additional negative charge in the isoelectronic anionic species being largely dissipated onto the carbonyl ligands is found from the results of a series of MO calculations carried out by Caulton and Fenske[71] for the isoelectronic $[V(CO)_6]^-$, $Cr(CO)_6$, and $[Mn(CO)_6]^+$ species. Their assumption that a rough estimate of the charge on each of these three metal atoms is the difference in orbital population of the metal 3d orbitals gives a value of about 0.3 electron of additional charge localized on the metal atom in these octahedral carbonyl species for a decrease in nuclear charge of +1. A similar increase in negative charge localized on each metal atom may be reasonably expected for the $[Cr_2(CO)_{10}]^{2-}$ anion compared to $Mn_2(CO)_{10}$.

Evidence that the carbonyl groups are more strongly bonded to the metal atoms in $Mn_2(CO)_{10}$ than in $Tc_2(CO)_{10}$ is given by the much shorter Mn-CO bond lengths [Mn–C, 1.83 Å (av) *vs.* Tc–C, 1.98 Å (av)] in that only 0.06 Å of the difference of 0.15 Å in the metal–carbon bond length can be attributed to the larger single-bond covalent radius of technetium (based on the difference in the metal–metal bond lengths in $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ being 0.12 Å).[18] Although this result is consistent with the observed relative ease of cleavage of carbonyl groups being greater in $Tc_2(CO)_{10}$ than in $Mn_2(CO)_{10}$,[72] it is noteworthy that the close similarity of their corresponding infrared carbonyl stretching frequencies[72] does *not* reflect any increase in the π^*_{CO} orbital participation in accounting for the stronger metal-to-carbonyl bonds in $Mn_2(CO)_{10}$. These particular results as well as the greater metal–metal bond length alteration of 0.09 Å for the $[Mo_2(CO)_{10}]^{2-}$–$Tc_2(CO)_{10}$ pair relative to that of 0.05 Å for the isostructural $[Cr_2(CO)_{10}]^{2-}$–$Mn_2(CO)_{10}$ pair stress the fact that electron energy variations between first-row and second-row congeners in a given type of transition metal carbonyl cluster system can produce significant deviations in molecular parameters which are not necessarily detectable in an obvious way from infrared spectral data. Hence, the difference of 0.06 Å between the value of the Mo radius derived from *cis*-Mo(dien)$(CO)_3$ and that obtained from half of the Mo–Mo bond length in the $[Mo_2(CO)_{10}]^{2-}$ anion, as opposed to the nearly exact agreement in the values of the Cr radius derived from *cis*-Cr(dien)$(CO)_3$ and the $[Cr_2(CO)_{10}]^{2-}$ anion, does not then appear unusual and probably serves best to caution against the assumption that a single value for a single-bond covalent metal radius can be expected to be widely applicable.

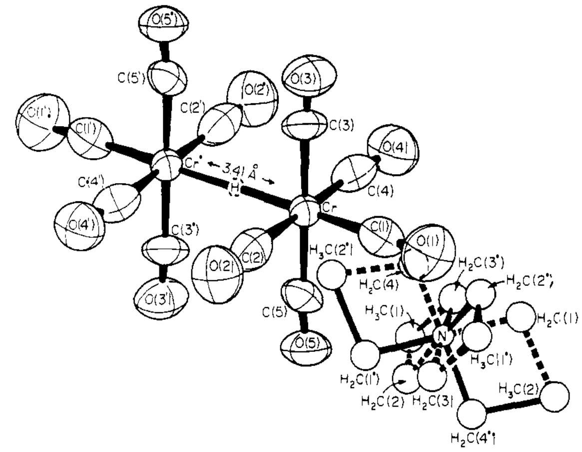

Figure 5. View of the anion and disordered cation as found in the crystal structure of $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$. The triclinic unit cell of average symmetry $P\bar{1}$ crystallographically demands that the one disordered cation and one anion per cell each possess a center of symmetry.

$[Cr_2(CO)_{10}H]^-$: A "Protonated" Metal-Metal Bond. (a) The Cr–H–Cr Framework. The effect of the addition of a proton to the $[Cr_2(CO)_{10}]^{2-}$ anion was investigated in the structural study of $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$. The infrared spectrum of this hydrido anion in both solution and solid state indicated a geometry of either D_{4h} or D_{4d} symmetry.[9–12,21] In the solid state this anion has idealized D_{4h} symmetry, with the two octahedrally coordinated $Cr(CO)_5$ groups related by a crystallographic center of symmetry (Figure 5). Although the hydrogen atom position was not directly revealed in this X-ray investigation, there is *no doubt* that it is located on the idealized molecular fourfold axis between and bonded to the chromium atoms. A typical transition-metal-bonded hydrogen proton nmr is observed for this ion, τ 29,[11] and nearly exact octahedral-like coordination of the carbonyl groups about each metal atom leaves the metal–metal axis as the only remaining coordination site.[73]

Although from bonding prejudices we favored[10] the notion that this collinear hydrogen atom was truly equidistant from the two symmetry-equivalent $Cr(CO)_5$ moieties (corresponding to it being in a symmetric single-minimum potential well), it was also pointed out[10] then that this bridging hydrogen atom lying on the crystallographic center of symmetry may be statistically symmetrical (or time averaged) owing to its being randomly distributed in one or two equivalent sites displaced from the center but still bonding at any instant to both metal atoms (corresponding to it being in a symmetric double-minimum potential well). The impossibility of being able to distinguish by only diffraction techniques in M–H–M systems (as in O–H–O and F–H–F systems) whether a crystallographically symmetric bridging hydrogen atom occupies either a single-minimum or double-minimum potential well was later elaborated in detail by Doedens, Robinson, and Ibers[74,75] in connection with their X-ray struc-

(69) W. F. Edgell, W. E. Wilson, and R. Summitt, *Spectrochim. Acta*, **19**, 863 (1963); W. F. Edgell and M. P. Dunkle, *J. Phys. Chem.*, **68**, 452 (1964).

(70) P. Chini, *Inorg. Chim. Acta Rev.*, **2**, 31 (1968).

(71) K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1273 (1968).

(72) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *ibid.*, **1**, 933 (1962).

(73) The equivalent association of the hydrogen atom with both tungsten atoms in the $[W_2(CO)_{10}H]^-$ anion was shown from the relative intensity bands of the triplet components of the high-field proton resonance peak.[9,11]

tural determination of $Mn_2(CO)_8[P(C_6H_5)_2]$, which located the position of the hydrogen atom on a crystallographic twofold axis and which thereby showed the molecule to possess the predicted geometry with a "bent" Mn-H-Mn linkage.

From an examination of proton nmr, O-H infrared frequencies, and neutron diffraction results for a series of hydrogen-bonded O-H-O systems, Blinc and Hadzi[76] concluded that short nmr relaxation times and two O-H stretching frequencies in the region 1800-3000 cm^{-1} are indicative of a double-minimum potential, while long relaxation times and the absence of the O-H stretching band above 1800 cm^{-1} indicate an approximately symmetric single minimum. No similar series is available for transition metal hydrides owing both to the absence of neutron diffraction studies of hydrogen-bridged systems and to the very low intensity often observed for M-H stretching modes. Edgell and Paauwe,[21] in a thorough investigation of the infrared and Raman spectra of $[Cr_2(CO)_{10}H]^-$ and $[Cr_2(CO)_{10}D]^-$, were unable to locate any bands assignable to the motion of the hydrogen atom. Therefore, the only evidence on which a distinction between single and double minima can be made is the nmr relaxation time. A relatively short relaxation time has been observed for the $[Cr_2(CO)_{10}H]^-$ anion,[11] which suggests a double-minimum potential, while long relaxation times are observed for both the $[Mo_2(CO)_{10}H]^-$ and $[W_2(CO)_{10}H]^-$ anions,[9,11] suggesting a single-minimum potential.[77]

(b) Comparison of $[Cr_2(CO)_{10}]^{2-}$ and $[Cr_2(CO)_{10}H]^-$. Although the related $[Cr_2(CO)_{10}]^{2-}$ and $[Cr_2(CO)_{10}H]^-$ anions are quite similar, the linear protonation of the Cr-Cr bond substantially influences the architecture of the dichromium decacarbonyl fragment. The chromium-chromium distance increases by 0.44 Å, which is entirely in accord with the empirically observed hydrogen radius of 0.2 Å used[10] to obtain a reasonably self-consistent set of metal-hydrogen bond lengths. The exactly eclipsed conformation (required by the crystallographic center of symmetry) observed in the $[Cr_2(CO)_{10}H]^-$ anion, in contradistinction to the staggered conformation found in the $[M_2(CO)_{10}]^{2-}$ anions (M = Cr, Mo) and in the isosteric $M_2(CO)_{10}$ (M = Mn, Tc, Re), may be attributed simply to intramolecular van der Waals interactions. In the $[Cr_2(CO)_{10}H]^-$ anion the two $Cr(CO)_5$ moieties are sufficiently far apart that from potential energy considerations the attractive part of van der Waals forces dominates to give an eclipsed arrangement.[78] Decreases in the nonbonding OC···CO distances between the two halves through the observed shortening in the metal-metal bond due to deprotonation then causes the repulsive part of van der Waals forces to become sufficiently great to give the resulting staggered conformation.

Subsequent experimental support for this interpretation of the conformational change in the $[Cr_2(CO)_{10}H]^-$ and $[Cr_2(CO)_{10}]^{2-}$ anions being directly dependent on the metal-metal internuclear distance (and thereby based primarily on intramolecular nonbonding forces rather than a manifestation of crystal packing effects) was shown[50] from a comparison of the molecular geometries of $Re_2Mn(CO)_{14}H$[49] and $Re_3(CO)_{14}H$.[50] In both of these structurally related molecules the corresponding $(OC)_5M-Re(CO)_4$ bonded segments (M = Mn, Re) expectedly have a staggered arrangement of equatorial carbonyl groups. In the $(OC)_5Re-H-Re(CO)_4$ part of the $Re_2Mn(CO)_{14}H$ molecule, where the metal-metal separation of 3.392 ± 0.002 Å[49] is virtually identical with that in the $[Cr_2(CO)_{10}H]^-$ anion, the two sets of equatorial carbonyl ligands are eclipsed. However, this same $(OC)_5Re-H-Re(CO)_4$ fragment in the $Re_3(CO)_{14}H$ molecule possesses a staggered arrangement of equatorial carbonyl ligands due to increased van der Waals repulsions caused by an observed shortening of the metal-metal separation by 0.10 Å to a value of 3.295 ± 0.002 Å. A general correlation of smaller metal-metal separation with decreased metal-hydrogen-metal angle was found[50] to provide a satisfactory explanation for the observed large separation between the two rhenium atoms of range from 3.16 to 3.39 Å in the three-center electron-pair Re-H-Re systems present in four structurally determined rhenium carbonyl hydrido clusters (including the above two trinuclear metal complexes) recently synthesized by Kaesz and coworkers.[49,50,79-83] The largest internuclear separation of the metal atoms in a M-H-M systems occurs when the hydrogen atom is collinear with the two metal atoms (as is known to date only in the $[Cr_2(CO)_{10}H]^-$ anion).[84] When the M-H-M angle is decreased from 180°, the internuclear separation of the metal atoms approaches that of a normal electron-pair bond (as found for the Mn-H-Mn systems in $Mn_2(CO)_8(H)[P(C_6H_5)_2]$[74] and in $Mn_3(CO)_{10}$-

(74) R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **89**, 4323 (1967).

(75) For discussions with references of single- and double-well potentials pertaining to symmetrical hydrogen bonding see (a) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968; (b) R. E. Rundle, *J. Phys. Radium*, **25**, 487 (1964); (c) W. C. Hamilton, *Annu. Rev. Phys. Chem.*, **13**, 19 (1962).

(76) R. Blinc and D. Hadzi, *Spectrochim. Acta*, **16**, 853 (1960).

(77) The presumption by Rundle[75b] that single- and double-well distributions in O-H-O systems can be distinguished from each other (in that a hydrogen atom in a double-minimum well should exhibit a strong isotope effect with a significantly shorter O-H-O distance than O-D-O distance, in contrast to a hydrogen atom in a single-minimum well showing almost no isotope effect) suggests an operational test of the conclusions based on nmr relaxation times involving X-ray and/or neutron diffraction studies of the $[M_2(CO)_{10}H]^-$ and $[M_2(CO)_{10}D]^-$ anions (M = Cr, Mo, W) to see whether indeed a similar detectable variation in the M-M internuclear distances is observed only between two chromium analogs.

(78) An alternative but less preferred rationalization for the two sets of equatorial carbonyl ligands in the $[Cr_2(CO)_{10}H]^-$ anion being in an eclipsed orientation involves an electronic coupling of their π_{CO} and π^*_{CO} orbitals operating *via* reactions with the appropriate 3d orbitals of the two chromium atoms. Also, any possible directional influence of the empty 2p AO's of the bridging hydrogen atom due to configurational interaction with the appropriately filled chromium $3d\pi$ orbitals is completely ignored from energetic considerations.

(79) W. Fellmann and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, **2**, 63 (1966).

(80) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Amer. Chem. Soc.*, **90**, 7135 (1968).

(81) H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *ibid.*, **91**, 1021 (1969).

(82) J. M. Smith, K. Mehner, and H. D. Kaesz, *ibid.*, **89**, 1759 (1967).

(83) R. Bau, B. Fontal, H. D. Kaesz, and M. R. Churchill, *ibid.*, **89**, 6374 (1967).

(84) Based on the octahedral-like orientations of the carbonyl ligands about each metal atom, together with a Re-H(bridging) distance of approximately 1.70 Å, the resulting estimated Re-H-Re angle is 164° in $Re_2Mn(CO)_{14}H$ and 159° in $Re_3(CO)_{14}H$.[50] Prime justification for the use of an octahedral-like model (where the terminal carbonyl ligands are perpendicularly disposed about each metal atom and where the bridging hydrogen atoms are presumed to occupy the remaining octahedral-like coordination sites) to obtain estimated positions of the hydrogen atoms in these rhenium carbonyl hydride clusters is given by the X-ray structural studies of $Mn_2(CO)_8(H)[P(C_6H_5)_2]$[74] and $Mn_3(CO)_{10}(H)(BH_3)_2$,[4] in which the determined positions of the bridging hydrogen atoms about each manganese atom were found within experimental error to conform with their expected octahedral-like coordination sites.

$(H)(BH_3)_2$[4]). These metal–metal bonding distances in the M–H–M systems emphasize the large direct metal–metal bonding character present in the three-center electron-pair bond (*vide infra*).

The previously mentioned bending of equatorial carbonyl groups away from the axial groups, which has been observed in the $M_2(CO)_{10}$-type structure, is not as pronounced, if present at all, in the $[Cr_2(CO)_{10}H]^-$ anion. The average value of C_{ax}–Cr–C_{eq} is 91.0°, with individual estimated standard deviations of 0.8–0.9°. The same angles in the $[Cr_2(CO)_{10}]^{2-}$ anion average 93°. This marked difference in distortion of the equatorial carbonyl groups is further accented by the distances of the carbonyl carbon and oxygen atoms from the plane defined as containing the chromium atom and as being parallel to the "best" least-squares plane through the carbonyl carbon atoms. For the $[Cr_2(CO)_{10}H]^-$ anion, the carbon atoms are perpendicularly displaced by an average distance of +0.03 Å from this plane and the oxygen atoms by −0.04 Å. For the $[Cr_2(CO)_{10}]^{2-}$ anion the perpendicular displacements from a similarly defined plane average +0.12 Å for the carbon atoms and +0.29 Å for the oxygen atoms (*i.e.*, the positive direction is arbitrarily chosen away from the axial carbonyl group). Since the increased metal–metal distance increases the nonbonding O···O and C···C distances by 0.2 to 0.3 Å for the eclipsed conformation in the $[Cr_2(CO)_{10}H]^-$ anion relative to those for the staggered conformation in the $[Cr_2(CO)_{10}]^{2-}$ anion, it does not appear likely that repulsions between the eclipsed carbonyl groups in the two halves of the $[Cr_2(CO)_{10}H]^-$ anion are responsible for the smaller C_{ax}–Cr–C_{eq} angles, in accord with the above proposition that van der Waals attractive forces account for its D_{4h} stereochemistry.

Examination of the Cr–C and Cr···O distances in the $[Cr_2(CO)_{10}H]^-$ anion suggests that the axial Cr–C distance is significantly shorter than the equatorial Cr–C distances. Although the Cr–C distances themselves support this conclusion, it is observed throughout this work that the standard deviations of the M–C distances are probably underestimates of the actual uncertainty. The chemically equivalent M···O distances, however, are generally consistent within twice their estimated standard deviations. Thus the axial Cr···O distance of 2.90 ± 0.02 Å is substantially shorter than the average equatorial Cr···O distance of 3.05 Å (*i.e.*, the equatorial Cr···O values range from 3.02 to 3.09 Å with individual estimated standard deviations of 0.02 Å). The relatively poor probable accuracy of the carbon positions precludes any significant evaluation of the carbonyl C–O distances, but the known insensitivity of C–O bond length to bond order in the range of bond orders 2–3[52] makes it highly unlikely that the axial C–O distance is 0.15 Å shorter than the equatorial distances, as would be required if all M–C distances were to be the same. If anything, it is more likely that the axial C–O distance is slightly longer than the equatorial C–O distances. The shortening of axial M–C distances has been observed for several octahedrally coordinated metal carbonyls of the type $M(CO)_5X$, where X is a poorer charge acceptor than the carbonyl groups.[17,18,44,48–50] This same stereochemical effect may also be present for the previously discussed $[M_2(CO)_{10}]^{2-}$ anions (M = Cr, Mo), but the precision attained for those structures does not justify the assumption of a significant difference.

Bonding in the Anions. In a qualitative sense, the bonding in each of these anions is easy to visualize. The bonding of the $[M_2(CO)_{10}]^{2-}$ anions (M = Cr, Mo) and their isosteric neutral analogs, $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$, may be represented by a simple MO correlation diagram (not reproduced here) which, from purely topological arguments, can readily account for the diamagnetic character of the anions and their analogs and can adequately be used to rationalize the greater π^*_{CO} participation in the bonding which occurs in the anions, as evidenced by the observed infrared spectral data. The metal–metal interaction can be simply pictured as an electron-pair σ bond.

For the $[Cr_2(CO)_{10}H]^-$ anion, however, a simple two-center electron-pair bond picture is clearly no longer possible. The linkage of the linear Cr–H–Cr framework can be readily rationalized in terms of a three-center MO bonding scheme with the appropriate three linear combinations as follows

$$\text{antibonding}\quad \begin{array}{l} (\sigma_{Cr1} - aH_{1s} + b\sigma_{Cr2}) \\ (\sigma_{Cr1} - b\sigma_{Cr2})^{85} \end{array}$$

$$\text{bonding}\quad (\sigma_{Cr1} + aH_{1s} + b\sigma_{Cr2})$$

where σ_{Cr} may be considered an octahedral-like chromium orbital. These linear combinations are general in the sense that for $b \neq 1$ they represent the instantaneous description for asymmetric bonding of the hydrogen atom to the chromium atoms (for example, for a double-minimum potential well). The relative degree of antibonding character of the upper two levels cannot be easily estimated, since it depends on the extent of overlap of the metal orbitals with each other, but only the bonding combination is occupied in the electronic ground state.

It has been pointed out[3–5,10,86,87] that this three-center electron-pair concept can be successfully utilized to account for the closed-shell electronic configurations of the metal atoms in a number of transition metal complexes containing H–M–H′ systems,[3–5,10,49,50,74,80,81] M–H–B systems,[4,87–90] or other delocalized systems such as ones containing olefinic-like groups μ-bonded to two transition metal atoms.[86,87,91] The recent im-

(85) In our preliminary communication on the structure and bonding of the $[Cr_2(CO)_{10}H]^-$ anion, it was erroneously stated that this orbital combination was nonbonding (rather than antibonding), which of course implies no direct orbital interaction between the metal atoms. Orbital overlap calculations involving only the collinear Cr–H–Cr part of the $[Cr_2(CO)_{10}H]^-$ anion were carried out (by L. B. H.) at various Cr–Cr internuclear separations including those found in the $[Cr_2(CO)_{10}]^{2-}$ and $[Cr_2(CO)_{10}H]^-$ anions with the chromium 3d radial function employed being that used by Caulton and Fenske[71] in their MO calculations of the electronic structure of $Cr(CO)_6$. These calculations clearly demonstrated the dominance of the metal–metal interaction from orbital overlap considerations in the three-center Cr–H–Cr bond at the observed Cr–Cr internuclear distance.

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plication[74] that a three-center electron-pair description of a M-H-M linkage is consistent only when the hydrogen atom is symmetrically disposed between the two metal atoms in a single-minimum potential well (but not when the hydrogen atom is in a symmetric or asymmetric double-minimum potential well) is *not* valid. If the hydrogen atom is asymmetrically located (at a given instance) but still is simultaneously associated with both atoms (*i.e.*, corresponding to the double-minimum potential), or if the two metal atoms are different (*e.g.*, as in the Cr-H-W linkage in $[CrW(CO)_{10}H]^-$),[9,11] it automatically follows from simple quantum mechanical arguments (as outlined above for the $[Cr_2(CO)_{10}H]^-$ anion) that the three-center electron-pair bonding description is unchanged other than that the weighting coefficients for the metal orbitals in each of the three MO's (*viz.*, the one occupied with the two electrons and the two empty ones) are no longer equal. An alternative "windshield-wiper-like" bonding description, involving the superposition of a M-M σ bond and a "resonating" M-H σ bond, was advanced[74] for the bent Mn-H-Mn linkage in $Mn_2(CO)_8(H)[P(C_6H_5)_2]$ in order to account for the Mn-Mn distance of 2.937 ± 0.005 Å in this hydrogen-bridged complex being essentially the same as the Mn-Mn single-bond distance of 2.923 ± 0.003 Å in $Mn_2(CO)_{10}$. It must be emphasized that the mathematical equivalence between this latter bonding scheme and the three-center electron-pair model in rationalizing the bonding metal–metal distance merely necessitates that the three-center electron-pair representation in this case possess metal–metal bonding character due to direct overlap of the metal orbitals with each other as well as with the hydrogen 1s orbital. The existence of direct metal–metal bonding in a three-center electron-pair description of a M-H-M′ system may be considered as arising from the *protonation* of a direct electron-pair M-M′ bond. Besides it being conceptually more cumbersome, the main disadvantage of the windshield-wiper bonding scheme relative to the three-center electron-pair one is that it is restricted to systems such as M-H-M′ linkages, where direct metal-metal bonding occurs.

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