Molecular Structures of $[(C_6H_5)_2PCoC_5H_5]_2$ and $[(C_6H_5)_2PNiC_5H_5]_2$. An Assessment of the Influence of a Metal–Metal Bond on the Molecular Geometry of an Organometallic Ligand-Bridged Complex[1]

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Abstract: Structural determinations of the corresponding diamagnetic complexes $[XCoC_5H_5]_2$ and $[XNiC_5H_5]_2$ (where X = $(C_6H_5)_2P$) have provided the first known demonstration of the effect of an electron spin-coupling interaction on the molecular geometry of a binuclear organo-(transition metal) complex containing bridging groups. A separate metal–metal single-bond interaction, of bond strength no doubt equivalent to that found in dimeric organo-(transition metal) complexes linked only by metal–metal bonds, is required for the cobalt dimer in order to explain the radical difference between the molecular geometries of the cobalt and nickel structures. Both molecular compounds crystallize in the monoclinic system with two dimeric molecules in a centrosymmetric unit cell. For $[(C_6H_5)_2PCoC_5H_5]_2$ the unit cell has the symmetry P2/b (C_{2h}^4, No. 13) and dimensions a = 8.64, b = 15.72, c = 10.31 A, γ = 90° 50′, while for $[(C_6H_5)_2PNiC_5H_5]_2$ the unit cell has the symmetry $P2_1/n$ (C_{2h}^5, No. 14) and dimensions a = 9.46, b = 10.83, c = 16.78 A, γ = 122° 28′ (c axis unique in both cases). The diamagnetism of $[(C_6H_5)_2PCoC_5H_5]_2$ is achieved by the formation of a *bent* metal–metal bond in which the metal–metal distance has decreased from a nonbonding value of 3.36 A in $[(C_6H_5)_2PNiC_5H_5]_2$ to a bonding value of 2.56 A in $[(C_6H_5)_2PCoC_5H_5]_2$. The stereochemical consequence of this metal–metal bond (which occupies a regular coordination site about each cobalt atom) is a symmetrical bending deformation of the $(PM)_2$ framework along the P···P′ line from a planar $(PNi)_2$ system of dihedral angle 180° in $[(C_6H_5)_2PNiC_5H_5]_2$ to a nonplanar $(PCo)_2$ system of dihedral angle 105° in $[(C_6H_5)_2PCoC_5H_5]_2$. The degree of angular distortion is such as to decrease the bridging M–P–M′ angle by 30° from a normal unstrained value of 102.4° in the nickel complex to a sharply acute angle of 72.5° in the cobalt analog. The detailed molecular features of these two compounds are compared to those of $[C_2H_5SFe(CO)_3]_2$ and other related complexes. The close resemblance of the molecular configurations of the electronically equivalent complexes $[XCoC_5H_5]_2$ (X = $(C_6H_5)_2P$) and $[XFe(CO)_3]$ (X = C_2H_5S) is clearly illustrated by the essential invariance of the $(XM)_2$ bridging system on replacement of the three carbonyl groups by the cyclopentadienyl ring which occupies three coordination sites. The observation of a possible cyclopentadienyl ring distortion in $[(C_6H_5)_2PNiC_5H_5]_2$ and its theoretical implications are discussed. Qualitative inferences are drawn from the structural features concerning differences in the bond energy of a π-C_5H_5–Co *vs.* a π-C_5H_5–Ni interaction and in the π-bonding character of a doubly bridged M–(SR)–M′ *vs.* M–(PR_2)–M′ system for the first-row group VIII transition metals.

Since 1957 when several polynuclear metal carbonyl complexes first were reported from X-ray diffraction studies[4,5] to be held together only by metal–metal bonds, increasing attention has been focused around the large number of transition metal compounds for which metal–metal bonds have been detected. Although a wide variety of structural types with metal–metal interactions are now known,[6] little direct structural data are available concerning the degree of dependence of the molecular configuration on the metal–metal bond (except for those complexes stabilized by only metal–metal interactions).

The recent preparation and characterization by Hayter[7,8] of $[(C_6H_5)_2PCoC_5H_5]_2$ and $[(C_6H_5)_2PNiC_5H_5]_2$ offered the first real opportunity to examine the actual influence of a metal–metal interaction on the molecular geometry of an organometallic complex containing ligand-bridged groups in addition to the metal–metal interaction. These above two dimeric transition metal complexes, both of which possess bridging diphenylphosphine ligands, differ from each other only by the necessity of an electron spin-coupling interaction in $[(C_6H_5)_2PCoC_5H_5]_2$ as opposed to none being required in the nickel analog in order for each of the metal atoms to achieve a closed-shell electronic ground-state configuration in conformity with the diamagnetism of both compounds.

For dinuclear metal complexes with bridging ligand groups, it has been pointed out[6a,9] that the observed diamagnetism may not necessarily be attributable to the formation of a distinct metal–metal bond *per se* but instead may be the result of either a super-exchange mechanism which operates through the bridging ligand groups or a high spin–orbit metal coupling constant. The spin–orbit coupling constants of cobalt and nickel are not sufficiently large to quench an electron spin moment. Because of the presence of two bridging diphenylphosphine groups in $[(C_6H_5)_2PCoC_5H_5]_2$, it

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(3) Alfred P. Sloan Research Fellow, 1963–1965.

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

(5) L. F. Dahl, E. Ishishi and R. E. Rundle, *ibid.*, **26**, 1750 (1957); L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

(6) *Cf.* (a) J. Lewis in "Plenary Lectures of VIIIth International Conference on Coordination Chemistry," Butterworths, London, 1965, pp 11–36; (b) J. Lewis and R. S. Nyholm, *Sci. Progr.*, **52**, 557 (1964).

(7) R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

(8) R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, **26**, 1977 (1964).

(9) (a) *Cf.* B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964), and references contained therein; (b) W. E. Hatfield and J. S. Paschal, *J. Am. Chem. Soc.*, **86**, 3888 (1964); W. E. Hatfield, Y. Mato, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).

is not indisputable that a separate metal–metal bond is the prime factor in determining its molecular structure without a direct comparison of its configuration with that of the corresponding nickel analog.

A stereochemical consequence of the fact that these two complexes are representative members of the general type $[XMC_5H_5]_2$ (where M = Co or Ni and where X represents a bridging three-electron donor such as halogen, RS, R_2P, R_2As, or one-half of a bidentate group such as S_2, $S_2C_2R_2$, or $RPCH_2CH_2PR$) is that any of these related dimeric cobalt and nickel cyclopentadienyl complexes which contain metal-linked bridging atoms with a tetrahedral-like arrangement of four electron pairs undoubtedly are isostructural to a first approximation with the corresponding diphenylphosphine-cobalt or -nickel cyclopentadienyl complex. Of these possible dimeric analogs, the compounds $[RSCoC_5H_5]_2$ (R = CH_3),[10] $[RSNiC_5H_5]_2$ (R = CH_3, C_2H_5, and C_6H_5),[11] $[R_2PNiC_5H_5]_2$ (R = CH_3),[7] and $[R_2AsNiC_5H_5]_2$ (R = CH_3)[7] have also been isolated;[12] the selection of the diphenylphosphine derivatives for crystallographic studies primarily was due to their relative stability as well as availability.

An added incentive for this structural investigation was the opportunity to make a detailed comparison of the molecular features of an $[XCoC_5H_5]_2$ complex with that of the closely similar complex $[XFe(CO)_3]_2$ (where X = C_2H_5S) whose molecular geometry, established from an X-ray study, had been attributed to a *bent* metal–metal bond.[13] Since the $Fe(CO)_3$ group is electronically equivalent with the CoC_5H_5 group, it was of particular significance to ascertain the degree of alteration of the $(XM)_2$ skeleton on replacement of the three carbonyl groups with the cyclopentadienyl group.

Experimental Section

Samples of $[(C_6H_5)_2PCoC_5H_5]_2$ and $[(C_6H_5)_2PNiC_5H_5]_2$ were generously supplied to us by Dr. R. G. Hayter of Mellon Institute (now at Shell Development Company, Emeryville, Calif.).

For the cobalt compound, the black crystal utilized was a brick-shaped fragment cut from a plate-like crystal to the approximate dimensions 0.5 × 0.5 × 0.4 mm and aligned inside a thin-walled Lindemann glass capillary with the 0.4-mm axis as the rotation axis. Multiple-film equiinclination Weissenberg data, obtained for ten reciprocal layers (0*kl* through 9*kl*), resulted in 1119 independent reflections. Timed-exposure precession photographs were taken from the *hk*0 and *hk*1 levels and merged with the Weissenberg data by least squares[14] to give a total of 1180 reflections on a common scale; the weighted disagreement factor for the least-squares merging was 3.7%.

For gathering intensity data on the nickel compound, a dark brown crystal of dimensions 0.4 × 0.4 × 0.5 mm was mounted inside a thin-walled glass capillary about a rotation axis which corresponded to one of the 0.4 mm directions. Nine layers of multiple-film equiinclination Weissenberg data, 0*kl* through 8*kl*, were collected from which a total of 1229 independent diffraction maxima were obtained.

All intensity data for both compounds were taken with Zr-filtered Mo Kα radiation. The intensities for both compounds were estimated visually by comparison with a calibrated set of intensities taken with the same crystals. Corrections for Lorentz-polarization effects and spot extension[15] were applied to all photographic data, but absorption corrections were neglected because of the small absorption coefficients of $\mu R_{\max} = 0.13$ and 0.17 for the cobalt and nickel compounds, respectively. The standard deviations of the individual structure amplitudes were estimated as follows. If $I(hkl)_0 < \sqrt{10}I_{\min}$, $\sigma(F(hkl)_0) = [|F(hkl)_0|/20][\sqrt{10}I_{\min}/I(hkl)_0]^2$; if $I(hkl)_0 \geq \sqrt{10}I_{\min}$, $\sigma(F(hkl)_0 = |F(hkl)_0|/20$.

For each compound lattice constants were determined for two principal zones from precession photographs which were calibrated by the superposition of a zero-level NaCl exposure on the same film. The γ angles[16] for the two monoclinic compounds were determined from *hk*0 precession photographs.

Crystal Data

$[(C_6H_5)_2PCoC_5H_5]_2$. The monoclinic crystals of the cobalt compound (mol wt, 618.4) have lattice parameters $a = 8.64 \pm 0.02$, $b = 15.72 \pm 0.03$, $c = 10.31 \pm 0.02$ A, $\gamma = 90° 50' \pm 10'$; volume of unit cell = 1401 A^3. The flotation-measured density of 1.49 g cm^{-3} compares favorably with the calculated density of 1.47 g cm^{-3} for two dimeric molecules per unit cell. The total number of electrons per unit cell $F(000) = 636$. The linear absorption coefficient for Mo Kα radiation (λ 0.7107 A) is 12.9 cm^{-1}. The only systematic absences are $\{hk0\}$ for k odd, which indicate the probable space group to be either Pb (C_s^2, No. 7) or P2/b (C_{2h}^4, No. 13).[16] The latter space group demands that a dimeric molecule possesses either a twofold axis or a center of symmetry which would relate one-half of the dimer to the other. The correct selection of this centrosymmetric group with each of the two dimeric molecules in the unit cell centered about one of two twofold axes (located at 0, $^1/_4$ and 0, $^3/_4$) was indicated from the distribution of the cobalt and phosphorus vectors on the Patterson map and subsequently was verified by the satisfactory refinement of the structure. All atoms occupy the general fourfold set of positions: $\pm(x, y, z;\ x, {}^1/_2 + y, \bar{z})$.[16]

$[(C_6H_5)_2PNiC_5H_5]_2$. X-Ray photographs showed that this compound (mol wt, 618.0) has monoclinic Laue symmetry (2/m) with lattice cell parameters $a = 9.46 \pm 0.02$, $b = 10.83 \pm 0.02$, $c = 16.78 \pm 0.03$ A, $\gamma = 122° 28' \pm 10'$; volume of unit cell = 1450 A^3. The experimental density of 1.42 g cm^{-3} agrees exactly with that calculated on the basis of two dimeric molecules per unit cell; $F(000) = 640$. The linear absorption coefficient for Mo Kα radiation is 14.6 cm^{-1}. The observed systematic absences, $\{hk0\}$ for $h + k$ odd and $\{00l\}$ for l odd, define $P2_1/n$ (C_{2h}^5, No. 14)[16] as the probable space group which later was confirmed by the resulting structural analysis. The

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[10] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

[11] W. K. Schropp, *J. Inorg. Nucl. Chem.*, **24**, 1688 (1962).

[12] Although only monomeric complexes of formula $(CF_3)_2C_2S_2Co$-C_5H_5 and $(CF_3)_2C_2S_2NiC_5H_5$ have been prepared from bis(trifluoromethyl)dithietene (R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963)), King has also shown (R. B. King, *ibid.*, **85**, 1584 (1963)) that this reagent as well as a number of other 1,2-dithiol derivatives react with iron pentacarbonyl or triiron dodecacarbonyl to give ligand-bridged dimeric complexes in which each of the two sulfur atoms is doubly bridged to the two iron tricarbonyl groups. The molecular geometries of these dimeric complexes no doubt are similar to those of $[C_2H_5SFe(CO)_3]_2$[13] and the analogous complex $[(C_6H_5)_2PCoC_5H_5]_2$ reported in this paper.

[13] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 2, 328 (1963).

[14] P. W. Sutton and M. D. Glick, "A Crystallographic Data Correlation Program for the CDC 1604 Computer," University of Wisconsin, 1964.

[15] D. C. Phillips, *Acta Cryst.*, 7, 746 (1954).

[16] The lattice constant settings and space group symmetry for both compounds are based on the choice of the *c* axis (rather than the *b* axis) as the unique crystallographic symmetry axis, which was required for our original use of the Scheringer rigid-body least-squares program [C. Scheringer, *Acta Cryst.*, **16**, 546 (1963)] in the monoclinic crystal system.

crystallographically independent unit consists of one-half of a dimeric molecule with all atoms occupying the general fourfold set of positions: $\pm(x, y, z;\ ^1/_2 - x,\ ^1/_2 - y,\ ^1/_2 + z)$.[16] The two halves of each dimeric molecule are related to each other by a crystallographic center of symmetry.

Determination of the Structures

Analysis of $[(C_6H_5)_2PCoC_5H_5]_2$. The structural determination of the nonhydrogen atoms in the cobalt complex necessitated the location of one cobalt, one phosphorus, and seventeen carbon atoms. Initial coordinates for the cobalt and phosphorus atoms, obtained from an interpretation of a three-dimensional Patterson function, were refined by successive Fourier syntheses from which all the carbon atoms were found. A least-squares rigid-body refinement[17] then was initiated with the Scheringer program[17a] in which each of the two independent phenyl rings was fixed to its well-known geometry. Refinement was first carried out with one over-all isotropic thermal parameter for each phenyl ring and individual isotropic thermal parameters for the other nonrigid atoms together with the one scale factor. Convergence was reached after three cycles, during which the unweighted R_1 value was lowered from 19.0 to 14.8%. At this point a more flexible rigid-body refinement program[17d] became available which permitted the assignment of a more realistic rigid-body thermal model involving the use of individual atomic isotropic temperature factors. After three cycles the unweighted R_1 was reduced to 11.7%, while the weighted $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100$ stood at 14.5%. A three-dimensional Fourier difference map based on the final isotropic thermal parameters showed no residual electron density greater than 1.3 electrons/A^3 or less than -1.2 electrons/A^3 except for some density anisotropically distributed around the cobalt and phosphorus positions. Accordingly, a rigid-body least-squares refinement with anisotropic thermal coefficients for the cobalt and phosphorus atoms and isotropic thermal parameters for the other nonrigid-body cyclopentadienyl and rigid-body phenyl carbon atoms was continued until no parameter changed by more than one-half of its standard deviation. This mixed anisotropic–isotropic refinement resulted in reliability values of $R_1 = 10.0\%$ and $R_2 = 12.99\%$; a Fourier difference map showed the absence of any residual electron density peak greater or less than 1.2 electrons/A^3 except for a peak at the cobalt position which had decreased to 2.4 electrons/A^3. All atomic coordinates for this anisotropic heavy atom refinement differed by less than 1.5σ from their corresponding values for the completely isotropic refinement.[18]

Although the cyclopentadienyl C–C bond lengths obtained from the anisotropic–isotropic refinement (Table IV) do not vary significantly from their mean value, it was decided to ascertain their equivalence by the restriction of the cyclopentadienyl ring to a regular pentagon of bond length 1.41 A. The resultant reliability factors for this mixed anisotropic–isotropic refinement with individual atomic isotropic thermal parameters for all rigid-group atoms was $R_1 = 10.0\%$ and $R_2 = 13.08\%$. Based on the inherent assumption of no systematic error in the crystallographic data, the Hamilton statistical R-factor ratio test[19] was applied to indicate the statistical significance between the imposed rigid-body cyclopentadienyl model with equivalent C–C distances and the model with no constraints on the molecular parameters. The determined weighted R-factor ratio of 1.007 for $[R_2(D_{5h})/R_2(\text{no constraints})]$ implies an improvement for the nonrigid cyclopentadienyl model which is significant only at the 7.5% level. This means that our rigid-body restriction of the cyclopentadienyl ring to one of D_{5h} symmetry is a valid model (although statistically only barely acceptable), which is in agreement with the bond length differences obtained from the nonrigid-body refinement not being statistically significant in terms of their estimated standard deviations.

Analysis of $[(C_6H_5)_2PNiC_5H_5]_2$. The nickel and phosphorus atoms were located from a diagnosis of the Patterson function and the carbon atoms then established from successive Fourier syntheses. Least-squares refinement with the phenyl rings constrained as rigid groups and with individual isotropic thermal parameters for all atoms together with a separate scale factor for each reciprocal layer yielded values of $R_1 = 16.7\%$ and $R_2 = 17.5\%$; all parameter shifts in the last cycle were less than 0.4σ. Since a Fourier difference synthesis revealed no anomalies other than some residual electron density in the areas of the nickel and phosphorus atoms attributable to anisotropic thermal motion, least-squares refinement was pursued in which an anisotropic thermal model was employed only for these two crystallographically independent atoms. The resultant discrepancy values were $R_1 = 13.7\%$ and $R_2 = 15.02\%$; all atomic coordinates from this mixed anisotropic–isotropic refinement differed by less than σ from the corresponding values for the isotropic refinement except for those of three cyclopentadienyl carbon atoms which shifted no more than 3σ. A Fourier difference synthesis based on the output parameters of this refinement revealed no residual density greater than 2.2 electrons/A^3 or less than -3.1 electrons/A^3.[18]

In an attempt to evaluate the significance of the indicated deformation of the cyclopentadienyl ring from D_{5h} symmetry in $[(C_6H_5)_2PNiC_5H_5]_2$, an analogous rigid-body least-squares refinement[17d] was performed with the ring again constrained to a regular pentagonal configuration of length 1.41 A. On reiteration until convergence was attained, the R_1 and R_2 values in-

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[17] For a general description together with applications of rigid body least-squares refinement, see (a) C. Scheringer, *Acta Cryst.*, 16, 546 (1963); (b) S. J. LaPlaca and J. A. Ibers, *ibid.*, 18, 511 (1965), and references contained therein; (c) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, 88, 4847 (1966), and references contained therein; (d) "DBCGHW, A Fortran Crystallographic Least-Squares Rigid-Body Program for the CDC 1604 and 3600 Computers," University of Wisconsin, 1965.

[18] Calculated and observed structure factors for both $[(C_6H_5)_2PCoC_5H_5]_2$ and $[(C_6H_5)_2PNiC_5H_5]_2$ are deposited as Document No. 9157 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief: Photoduplication Service, Library of Congress.

[19] W. C. Hamilton, "Statistics in Physical Science," The Ronald Press Co., New York, N. Y., 1964, p 159; W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

creased to 13.9 and 15.25%, respectively. Application of the Hamilton R-factor ratio test[19] yielded a ratio of 1.015 for $[R_2(D_{5h})/R_2(\text{no constraints})]$ which indicates an improvement (based on the assumed presence of only random error in the data) that is significant at the 0.5% level. Hence, in $[(C_6H_5)_2PNiC_5H_5]_2$ this statistical test suggests that the D_{5h} rigid-body constraint is not a good model.

Throughout the structural determinations the atomic scattering factors were taken from the "International Tables";[20] both real and imaginary dispersion corrections[21] of the scattering factors were made in the least-squares refinements. Unobserved data were generated out to the edge of the observed reciprocal lattice sphere at $\sin \theta/\lambda < 0.7$ for both the cobalt and nickel compounds. Comparison of the calculated and observed structure factors for these unobserved reflections corroborated the structural analyses of these two compounds; none of the F_c values for the unobserved but accessible reflections exceeded $1.5F_{o(\min)}$.

As expected for photographic data, an analysis of the interaction constants from the correlation matrices of the least-squares refinements shows substantial interaction between the thermal coefficients and scale factors. Since it also is well known that thermal parameters are unusually sensitive to systematic errors, no physical meaning should be attached to these parameters in terms of root-mean-square atomic displacements. However, the very low positional-thermal and positional-(scale factor) interaction constants together with the small changes of the positional parameters (and resulting molecular distances and bond angles) of both compounds produced by the application of the different isotropic and anisotropic thermal models indicated that the reported molecular parameters and estimated standard deviations calculated from a full inverse matrix are reasonably realistic.

The final atomic parameters of $[(C_6H_5)_2PCoC_5H_5]_2$ and $[(C_6H_5)_2PNiC_5H_5]_2$ obtained from the mixed anisotropic–isotropic least-squares refinements are given in Tables I and II, respectively. Table III gives the final group parameters associated with these rigid-body refinements. Tables IV and V give the distances and bond angles, respectively, which were calculated with the Busing–Martin–Levy function and error program[22] with errors obtained from the full inverse matrix (which included the uncertainties in the lattice parameters). The "best" molecular planes formed by sets of specified atoms and the perpendicular distances of these and other atoms from these planes were calculated for both molecular compounds by a least-squares method with the Smith program;[23] the results are given in Table VI. All Patterson and Fourier syntheses were computed with the Blount program.[24]

Table I. Individual Atomic Parameters of $[(C_6H_5)_2PCoC_5H_5]_2$ with Standard Deviations from (a) Anisotropic–Isotropic Least-Squares Refinement with No Constraint for the Cyclopentadienyl Ring and (b) Anisotropic–Isotropic Least-Squares Refinement with Rigid-Body Constraint for the Cyclopentadienyl Ring

Atom		$x\ (10^4\sigma_x)$	$y\ (10^4\sigma_y)$	$z\ (10^4\sigma_z)$	$B\ (10^2\sigma_B)$
Co	(a)	−0.1143 (2)	0.6975 (1)	−0.2441 (2)	...[a]
	(b)	−0.1143 (2)	0.6975 (1)	−0.2441 (2)	...[a]
P	(a)	0.1064 (5)	0.6803 (3)	−0.1491 (5)	...[a]
	(b)	0.1063 (5)	0.6803 (3)	−0.1490 (5)	...[a]
C(1)	(a)	−0.1952 (27)	0.6623 (13)	−0.4254 (23)	5.30 (47)
	(b)	−0.1901 (20)	0.6631 (10)	−0.4273 (14)	5.41 (47)
C(2)	(a)	−0.3064 (29)	0.7016 (14)	−0.3616 (27)	6.64 (60)
	(b)	−0.3123	0.6998	−0.3573	6.98 (60)
C(3)	(a)	−0.3379 (25)	0.6506 (13)	−0.2472 (27)	6.02 (48)
	(b)	−0.3359	0.6514	−0.2437	6.06 (48)
C(4)	(a)	−0.2275 (24)	0.5846 (12)	−0.2425 (24)	5.62 (44)
	(b)	−0.2293	0.5852	−0.2433	5.66 (44)
C(5)	(a)	−0.1417 (30)	0.5927 (14)	−0.3572 (27)	6.62 (59)
	(b)	−0.1386	0.5921	−0.3567	6.52 (58)
C(6)	(a)	0.2304 (11)	0.5935 (6)	−0.2006 (11)	2.93 (33)
	(b)	0.2305 (11)	0.5934 (6)	−0.2008 (11)	2.94 (33)
C(7)	(a)	0.2456	0.5850	−0.3345	4.10 (42)
	(b)	0.2457	0.5848	−0.3346	4.09 (42)
C(8)	(a)	0.3312	0.5186	−0.3857	3.72 (40)
	(b)	0.3314	0.5183	−0.3857	3.74 (40)
C(9)	(a)	0.4016	0.4608	−0.3030	4.33 (43)
	(b)	0.4018	0.4606	−0.3028	4.27 (42)
C(10)	(a)	0.3864	0.4693	−0.1692	4.53 (45)
	(b)	0.3865	0.4693	−0.1690	4.44 (44)
C(11)	(a)	0.3008	0.5357	−0.1180	4.37 (44)
	(b)	0.3009	0.5357	−0.1180	4.38 (44)
C(12)	(a)	0.1258 (16)	0.6733 (8)	0.0301 (9)	3.57 (37)
	(b)	0.1259 (16)	0.6733 (8)	0.0298 (9)	3.48 (36)
C(13)	(a)	0.0136	0.6298	0.1020	5.09 (48)
	(b)	0.0136	0.6298	0.1017	5.09 (48)
C(14)	(a)	0.0292	0.6227	0.2360	6.30 (51)
	(b)	0.0291	0.6227	0.2357	6.35 (51)
C(15)	(a)	0.1570	0.6592	0.2981	6.62 (58)
	(b)	0.1569	0.6591	0.2978	6.70 (59)
C(16)	(a)	0.2691	0.7027	0.2261	6.20 (52)
	(b)	0.2692	0.7026	0.2259	6.13 (52)
C(17)	(a)	0.2536	0.7098	0.0922	6.05 (54)
	(b)	0.2537	0.7096	0.0919	6.25 (55)

[a] For the Co and P atoms, anisotropic temperature factors of the form $\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$ were used; the resulting thermal coefficients (with standard deviation of the last significant figure given in parentheses) are as follows for refinements a and b.

		10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
Co	(a)	65 (2)	25 (1)	49 (2)	−7 (1)	−4 (3)	1 (2)
	(b)	65 (2)	25 (1)	49 (2)	−7 (1)	−4 (3)	1 (2)
P	(a)	83 (6)	35 (2)	77 (6)	−10 (3)	2 (5)	3 (3)
	(b)	84 (6)	35 (2)	78 (6)	−11 (3)	2 (5)	3 (3)

Discussion

The crystal structures of both $[(C_6H_5)_2PCoC_5H_5]_2$ and $[(C_6H_5)_2PNiC_5H_5]_2$ consist of discrete dimeric molecules in which each of the two metal atoms in a given molecular unit is coordinated to a π-cyclopentadienyl ring and two bridging phosphorus atoms which are equally shared between the two metal atoms. The additional magnetic requirement of an electron spin-coupling interaction in $[(C_6H_5)_2PCoC_5H_5]_2$ is substantiated by a decrease in the metal–metal distance from a nonbonding value of 3.36 A in $[(C_6H_5)_2PNiC_5H_5]_2$ to a bonding value of 2.56 A in $[(C_6H_5)_2PCoC_5H_5]_2$ which results in a drastic conformational difference between the cobalt and nickel structures (Figures 1 and 2). The stereochemical consequence of this formation

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(20) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(21) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955); ref 20, p 215.

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

(23) D. L. Smith, Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962. The dihedral angles given in this manuscript are defined as the angles directly between pairs of planes rather than as angles between normals to the planes.

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

Table II. Individual Atomic Parameters of $[(C_6H_5)_2PNiC_5H_5]_2$ with Standard Deviations from (a) Anisotropic–Isotropic Least-Squares Refinement with No Constraint for the Cyclopentadienyl Ring and (b) Anisotropic–Isotropic Least-Squares Refinement with Rigid-Body Constraint for the Cyclopentadienyl Ring

Atom		x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B ($10^2\sigma_B$)
Ni	(a)	0.5319 (4)	0.6097 (3)	−0.4223 (1)	. . .[a]
	(b)	0.5318 (4)	0.6096 (3)	−0.4223 (1)	. . .[a]
P	(a)	0.3738 (7)	0.3855 (5)	−0.4600 (3)	. . .[a]
	(b)	0.3737 (7)	0.3856 (5)	−0.4600 (3)	. . .[a]
C(1)	(a)	0.4975 (34)	0.6145 (25)	−0.3017 (14)	3.80 (54)
	(b)	0.4884 (21)	0.6139 (16)	−0.3007 (10)	3.93 (56)
C(2)	(a)	0.4128 (40)	0.6792 (30)	−0.3466 (15)	5.03 (64)
	(b)	0.4111	0.6732	−0.3444	5.01 (64)
C(3)	(a)	0.5406 (33)	0.8016 (24)	−0.3836 (14)	3.54 (52)
	(b)	0.5379	0.7990	−0.3844	3.48 (51)
C(4)	(a)	0.6800 (34)	0.8098 (25)	−0.3665 (13)	3.64 (54)
	(b)	0.6923	0.8175	−0.3655	4.03 (57)
C(5)	(a)	0.6592 (32)	0.7051 (25)	−0.3122 (13)	3.21 (48)
	(b)	0.6626	0.7033	−0.3138	3.19 (48)
C(6)	(a)	0.3788 (17)	0.2502 (12)	−0.3951 (6)	1.01 (35)
	(b)	0.3795 (17)	0.2504 (12)	−0.3952 (6)	0.95 (35)
C(7)	(a)	0.5083	0.2967	−0.3402	1.92 (41)
	(b)	0.5086	0.2970	−0.3401	1.92 (41)
C(8)	(a)	0.5159	0.1949	−0.2929	3.11 (48)
	(b)	0.5160	0.1951	−0.2927	3.10 (49)
C(9)	(a)	0.3940	0.0464	−0.3004	3.79 (53)
	(b)	0.3944	0.0466	−0.3004	3.79 (54)
C(10)	(a)	0.2644	−0.0001	−0.3552	6.18 (75)
	(b)	0.2653	0.0000	−0.3554	6.05 (75)
C(11)	(a)	0.2568	0.1017	−0.4025	2.52 (46)
	(b)	0.2578	0.1019	−0.4028	2.48 (46)
C(12)	(a)	0.1545 (16)	0.3313 (16)	−0.4582 (9)	1.93 (39)
	(b)	0.1546 (16)	0.3316 (16)	−0.4582 (9)	1.84 (39)
C(13)	(a)	0.0594	0.2750	−0.3890	3.80 (53)
	(b)	0.0594	0.2753	−0.3890	3.71 (53)
C(14)	(a)	−0.1051	0.2404	−0.3875	5.60 (69)
	(b)	−0.1051	0.2407	−0.3875	5.69 (70)
C(15)	(a)	−0.1745	0.2622	−0.4550	5.88 (71)
	(b)	−0.1745	0.2624	−0.4551	5.88 (72)
C(16)	(a)	−0.0794	0.3185	−0.5242	5.24 (66)
	(b)	−0.0793	0.3187	−0.5242	5.18 (66)
C(17)	(a)	0.0851	0.3531	−0.5258	4.47 (60)
	(b)	0.0852	0.3533	−0.5258	4.50 (61)

[a] For the Ni and P atoms anisotropic temperature factors of the form $\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$ were used; the resulting thermal coefficients (with standard deviations of the last significant figures given in parentheses) are as follows for refinements a and b.

		10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
Ni	(a)	70 (14)	57 (3)	7 (1)	36 (3)	−6 (2)	−4 (2)
	(b)	68 (14)	56 (3)	7 (1)	35 (3)	−7 (2)	−4 (2)
P	(a)	66 (18)	53 (7)	8 (2)	36 (7)	−0 (3)	−2 (3)
	(b)	66 (18)	57 (7)	8 (2)	39 (7)	0 (4)	−2 (3)

of a distinct metal–metal bond in the cobalt complex is a folding of the two halves of the molecule along the P···P′ line such that the normal unstrained bridging M–P–M′ angle of 102.4° in the planar $(PNi)_2$ bridging system of $[(C_6H_5)_2PNiC_5H_5]_2$ is reduced by 30° to a sharply acute value of 72.5° in the resulting nonplanar $(PCo)_2$ bridging system of $[(C_6H_5)_2PCoC_5H_5]_2$. The extent of the bending deformation of the $(PM)_2$ framework due to the metal–metal bond is reflected in the dihedral angle[23] between the two planes each formed by the two phosphorus atoms and one of the two metal atoms being decreased from 180° in the nickel molecule to 105° in the cobalt molecule. It is noteworthy that the observed metal–phosphorus bridging bond lengths are invariant to this immense structural alteration.

Based on the assumption of cylindrical symmetry for each cyclopentadienyl ring, the idealized molecular geometry of D_{2h} symmetry for the $[PNiC_5H_5]_2$ fragment (without the phenyl rings) is reduced to that of C_{2v} symmetry for the corresponding $[PCoC_5H_5]_2$ fragment; in the $[(C_6H_5)_2PNiC_5H_5]_2$ molecule a center of symmetry is crystallographically demanded, while the molecular twofold axis in $[(C_6H_5)_2PCoC_5H_5]_2$ is rigorously required by the space group symmetry. This X-ray study thus provides the first direct experimental evidence concerning the significant influence of a distinct metal–metal interaction in determining the molecular configuration of a *ligand-bridged organometallic* complex.

These structural features also clearly exemplify that the bond strengths of single electron-pair metal–metal interactions in other ligand-bridged organo-(transition metal) complexes (such as found from X-ray investigations of $[(C_2H_5SFe(CO)_3]_2$,[13] $[SFe(CO)_3]_2$,[25]

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(25) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965); C. H. Wei and L. F. Dahl, *ibid.*, **4**, 493 (1965).

Table III. Final Group Parameters from Least-Squares Rigid-Body Refinements (a) and (b) of $[(C_6H_5)_2PCoC_5H_5]_2$ and $[(C_6H_5)_2PNiC_5H_5]_2$[a,b]

Group		ϕ, deg	θ, deg	ρ, deg
		$[(C_6H_5)_2PCoC_5H_5]_2$		
C_6H_5 ring 1	(a)	−144.1 (4)	−22.3 (4)	91.4 (5)
(C_6–C_{11})	(b)	−144.1 (4)	−22.2 (4)	91.4 (5)
C_6H_5 ring 2	(a)	−58.5 (4)	−2.4 (5)	−83.1 (5)
(C_{12}–C_{17})	(b)	−58.6 (4)	−2.4 (5)	−83.2 (4)
C_5H_5 ring 3 (C_1–C_5)	(b)	−138.0 (7)	0.2 (6)	−60.8 (7)
		$[(C_6H_5)_2PNiC_5H_5]_2$		
C_6H_5 ring 1	(a)	−35.0 (5)	25.7 (5)	−39.3 (6)
(C_6–C_{11})	(b)	−34.8 (5)	25.9 (5)	−39.4 (6)
C_6H_5 ring 2	(a)	−163.5 (8)	72.0 (6)	−3.5 (6)
(C_{12}–C_{17})	(b)	−163.6 (18)	72.1 (6)	−3.4 (18)
C_5H_5 ring 3	(b)	−82.9 (7)	−167.0 (7)	−143.9 (7)

[a] The standard deviations of the last significant figures are enclosed in parentheses. [b] The internal orthogonal axial system (x', y', z') for the two phenyl rings and the cyclopentadienyl ring of $[(C_6H_5)_2PCoC_5H_5]_2$ and $[(C_6H_5)_2PNiC_5H_5]_2$ are defined as follows. The origin of each phenyl ring is at the carbon atom attached to the phosphorus atom (*viz.*, C(6) and C(12) for rings 1 and 2, respectively). For the cobalt molecule the $+x'$ and $+y'$ directions in phenyl ring 1 are the C(11)–C(7) and C(9)–C(6) vectors, respectively, while in ring 2 the $+x'$ and $+y'$ directions are the C(15)–C(12) and C(17)–C(13) vectors, respectively. For the nickel molecule the $+x'$ direction in both rings 1 and 2 is from the origin to the *para* ring carbon (*i.e.*, the C(9)–C(6) and C(15)–C(12) vectors), while the $+y'$ direction in ring 1 is the C(7)–C(11) vector and in ring 2 the C(13)–C(17) vector. The z' direction is the vector product of x' and y'. For the cyclopentadienyl ring in both molecules the origin is at C(1), and the $+x'$ direction is the vector from C(1) to the midpoint of C(4) and C(3). The $+y'$ direction in the cobalt molecule is the C(5)–C(2) vector and in the nickel molecule the C(2)–C(5) vector. The z' direction again is the vector product of x' and y'. The three angles, ϕ, θ, and ρ, refer to the orientation of the internal axial system with respect to an external orthogonal system by rotation about y', x', and z', respectively. In our program the orthogonal axes a_0, b_0, c_0 for a right-handed system are defined relative to the crystal axes as: $a_0 = a, b_0 = c_0 \times a_0, c_0 = a \times b$. For a left-handed system the following definitions used are $a_0 = a$, $b_0 = a_0 \times c_0$, $c_0 = b \times a$. The fractional coordinates for the origin of each ring at a given carbon atom are given in Tables I and II.

$[C_2H_5SFe(NO)_2]_2$,[26] $Co_2(CO)_8$,[27] $Co_2(CO)_9C_2H_2$,[28] $Co_2(CO)_6(C_6H_5C_2C_6H_5)$,[29] $Co_2(CO)_6(C_4F_6C_2)$,[30] $[C_5H_5Fe(CO)_2]_2$,[31] and $[C_5H_5FeS]_4$[32]) are *not* at all those characteristic of weak spin-pairing interactions but instead are of a large magnitude comparable with regular bond energies of covalent metal–ligand single bonds (*e.g.*, M–H) as well as of electron-pair metal–metal bonds in organometallic complexes stabilized by only metal–metal interactions.

The suggestion by Hayter and Williams[8] that the geometry of $[(C_6H_5)_2PCoC_5H_5]_2$ is formally analogous to that of $[C_2H_5SFe(CO)_3]_2$ with the cyclopentadienyl ring accordingly occupying three coordination positions was verified. The close resemblance of the molecular geometries of these two electronically equivalent complexes is readily apparent both from Figure 1 and from a comparison given in Table VII of the corresponding molecular parameters of these two complexes with those of $[SFe(CO)_3]_2$[25] and $[C_2H_5SFe(NO)_2]_2$.[26] The similar distortion of the bridging $(PCo)_2$ system and the $(SFe)_2$ systems in $[C_2H_5SFe(CO)_3]_2$ and $[SFe(CO)_3]_2$ is manifested by equivalent metal–metal bond lengths of 2.56 A in $[(C_6H_5)_2PCoC_5H_5]_2$, 2.54 A in $[C_2H_5SFe(CO)_3]_2$, and 2.55 A in $[SFe(CO)_3]_2$. The symmetrically acute Co–P–Co′ bridging angle of 72.5° is similar to the bridging Fe–S–Fe′ angle of 68.3° (av) in $[C_2H_5SFe(CO)_3]_2$ and 69.9° (av) in $[SFe(CO)_3]_2$. A so-called "bent" metal–metal bond[33] was proposed[37]

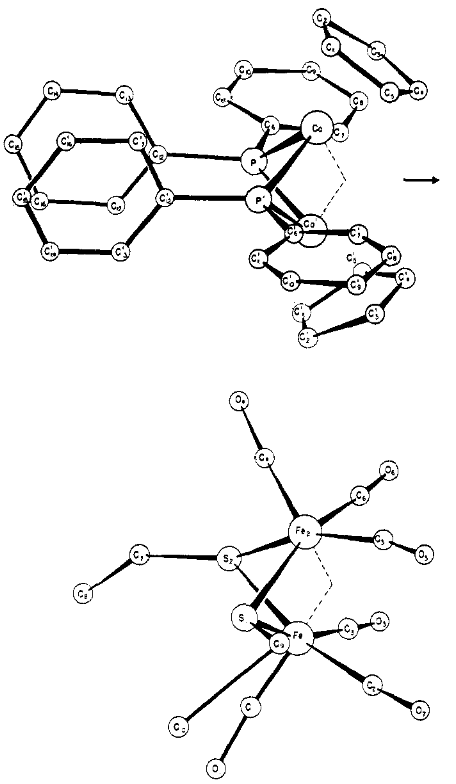

Figure 1. The molecular configurations of $[(C_6H_5)_2PCoC_5H_5]_2$ and $[C_2H_5SFe(CO)_3]_2$.

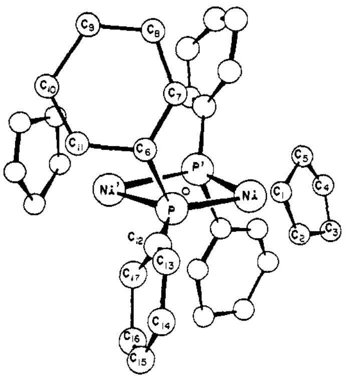

Figure 2. The molecular configuration of $[(C_6H_5)_2PNiC_5H_5]_2$.

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(26) J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, **11**, 599 (1958).

(27) G. G. Sumner, H. P. Klug, and L. E. Alexander, *ibid.*, **17**, 732 (1964).

(28) O. S. Mills and G. Robinson, *Proc. Chem. Soc.* 156 (1959).

(29) W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959).

(30) N. A. Bailey, M. R. Churchill, R. Hunt, R. Mason, and G. Wilkinson, *Proc. Chem. Soc.* 401 (1964).

(31) O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

(32) C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *Inorg. Chem.*, **5**, 900 (1966); R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *ibid.*, **5**, 892 (1966).

(33) A "bent" bond is represented by two σ-like orbitals which do not point directly toward each other. Although the concept of "bent" metal–metal bonds in transition metal complexes is without unambigu-

Table IV. Intramolecular Distances (A) of $[(C_6H_5)_2PCoC_5H_5]_2$ and $[(C_6H_5)_2PNiC_5H_5]_2$[a]

	$[(C_6H_5)_2PCoC_5H_5]_2$		$[(C_6H_5)_2PNiC_5H_5]_2$	
	Refinement a	Refinement b	Refinement a	Refinement b
Co(Ni)–Co′(Ni′)	2.56 (1.3)	2.56 (1.3)	3.36 (0.8)	3.35 (0.9)
Co(Ni)–P	2.16 (0.6)	2.16 (0.6)	2.15 (0.7)	2.15 (0.8)
Co(Ni)–P′	2.16 (0.5)	2.16 (0.5)	2.16 (0.8)	2.16 (0.8)
P–P′	2.88 (2)	2.88 (2)	2.70 (1)	2.70 (1)
Co(Ni)–C(1)	2.07 (2)	2.07	2.06 (2)	2.09
Co(Ni)–C(2)	2.06 (2)	2.04	2.09 (4)	2.08
Co(Ni)–C(3)	2.06 (2)	2.04	2.14 (2)	2.12
Co(Ni)–C(4)	2.01 (2)	2.01	2.07 (2)	2.15
Co(Ni)–C(5)	2.03 (2)	2.03	2.14 (2)	2.13
P–C(6)	1.83 (2)	1.83 (2)	1.85 (2)	1.85 (2)
P–C(12)	1.86 (2)	1.85 (2)	1.83 (2)	1.83 (2)
C(1)–C(2)	1.32 (3)	(1.41)	1.52 (4)	(1.41)
C(2)–C(3)	1.45 (3)	(1.41)	1.37 (3)	(1.41)
C(3)–C(4)	1.42 (3)	(1.41)	1.30 (3)	(1.41)
C(4)–C(5)	1.40 (3)	(1.41)	1.38 (3)	(1.41)
C(5)–C(1)	1.38 (3)	(1.41)	1.31 (3)	(1.41)

[a] With standard deviations of the last significant figures enclosed in parentheses. The positions of the primed atoms in $[(C_6H_5)_2PCoC_5H_5]_2$ are related to the positions of the unprimed ones by $\bar{x}$, $^3/_2 - y$, z; the corresponding primed atoms in $[(C_6H_5)_2PNiC_5H_5]_2$ are related to the unprimed ones by $1 - x$, $1 - y$, $-1 - z$.

Table V. Bond Angles (degrees) of $[(C_6H_5)_2PCoC_5H_5]_2$ and $[(C_6H_5)_2PNiC_5H_5]_2$[a]

	$[(C_6H_5)_2PCoC_5H_5]_2$		$[(C_6H_5)_2PNiC_5H_5]_2$	
Angle	Refinement a	Refinement b	Refinement a	Refinement b
Co(Ni)–P–Co′(Ni′)	72.5 (5)	72.5 (5)	102.4 (2)	102.3 (2)
P–Co(Ni)–P′	83.7 (5)	83.7 (5)	77.6 (2)	77.7 (2)
C(6)–P–C (12)	101.0 (4)	101.0 (4)	104.1 (6)	104.4 (6)
C(6)–P–Co(Ni)	119.3 (4)	119.3 (4)	115.0 (5)	115.0 (5)
C(6)–P–Co′(Ni′)	121.5 (3)	121.4 (3)	111.9 (5)	111.7 (5)
C(12)–P–Co(Ni)	122.5 (3)	122.6 (3)	109.8 (5)	109.8 (5)
C(12)–P–Co′(Ni′)	120.2 (3)	120.2 (3)	114.0 (5)	114.0 (5)
C(1)–C(2)–C(3)	106.1 (22)	(108°)	105.1 (26)	(108°)
C(2)–C(3)–C(4)	108.0 (21)	(108°)	107.5 (24)	(108°)
C(3)–C(4)–C(5)	105.4 (20)	(108°)	113.3 (23)	(108°)
C(4)–C(5)–C(1)	108.5 (21)	(108°)	107.2 (23)	(108°)
C(5)–C(1)–C(2)	111.7 (25)	(108°)	106.4 (22)	(108°)

[a] With standard deviations of the last significant figures enclosed in parentheses. The positions of the primed atoms in $[(C_6H_5)_2PCoC_5H_5]$ are related to the positions of the unprimed ones by $\bar{x}$, $^3/_2 - y$, z; the corresponding primed atoms in $[(C_6H_5)_2PNiC_5H_5]_2$ are related to the unprimed ones by $1 - x$, $1 - y$, $-1 - z$.

to be responsible for the molecular configurations of both $[C_2H_5SFe(CO)_3]_2$ and $[SFe(CO)_3]_2$. The structural similarity of $[(C_6H_5)_2PCoC_5H_5]_2$ and these two iron tricarbonyl dimers not only confirms the significance of a *separate* iron–iron bond in each of these homologous structures but also provides a rational basis for the adoption of an analogous "bent" bonding description in $[(C_6H_5)_2PCoC_5H_5]_2$.

In $[(C_6H_5)_2PCoC_5H_5]_2$ the π-cyclopentadienyl ring is symmetrically bonded to the cobalt atom. There is no evidence for any ring distortion. In the least-squares refinement involving no constraint for the cyclopentadienyl ring, the C–C bonds are equivalent within their standard deviations. Also, the refinement involving the constrained ring of D_{5h} symmetry appears to be a statistically acceptable model relative to the refinement with the unconstrained-ring model. For both refinements the perpendicular distance of the cobalt from the "best" plane of cyclopentadienyl carbon atoms is 1.66 A, which compares well with the corresponding perpendicular distances found in $C_5H_5Co\{(CH_3C_2CH_3)_2CO\}$ (1.67 A),[38] $C_5H_5Co\{(CH_3C_2CH_3)_2(CO)_2\}\cdot 2H_2O$ (1.65 A),[39] and $C_5H_5Co\{(CF_3C_2CF_3)_2(CO)\}$ (1.68 A).[40]

However, in $[(C_6H_5)_2PNiC_5H_5]_2$ there is an indication from the molecular parameters as well as from the application of the Hamilton *R*-factor ratio test (discussed previously) that the independent π-cyclopentadienyl

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ous experimental or theoretical justification,[34,35] its use in a formal representation of metal valency allows a general basis for the classification of geometries of seemingly different organometallic complexes into a relatively few standard structural types.

(34) For semiempirical molecular orbital calculations based on bent metal–metal bonding, see, for example, those of D. A. Brown, *J. Chem. Phys.*, **33**, 1037 (1960), for $Co_2(CO)_6(C_6H_5C_2C_6H_5)$.

(35) The similar localized environments of the metal atoms in the $HMn_2(CO)_6B_2$ fragment of $HMn_3(CO)_{10}(BH_3)_2$[36] and the $Fe_2(CO)_6S_2$ molecule[25] with the hydrogen in the former compound substituted in place of the presumed bent metal–metal bond in the thioiron carbonyl dimer to give a symmetrical, bent three-center electron-pair bond has been proposed[36] as indirect evidence for the existence of a bent metal–metal bond occupying a regular coordination site in $[SFe(CO)_3]_2$ and in the structurally related complexes $[C_2H_5SFe(CO)_3]_2$ and $[(C_6H_5)_2PCoC_5H_5]_2$.

(36) H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965).

(37) L. F. Dahl, C. Martell, and D. L. Wampler, *ibid.*, **83**, 1761 (1961).

(38) L. F. Dahl and D. L. Smith, *ibid.*, **83**, 752 (1961).

(39) V. A. Uchtman and L. F. Dahl, to be published.

(40) N. A. Bailey, M. Gerloch, and R. Mason, *Nature*, **201**, 72 (1964).

ring, situated perpendicularly to the $(PNi)_2$ system as shown by the calculated dihedral angle of 87.8°, is *not* completely cylindrical. This deviation from fivefold symmetry approximately conforms to a vertical mirror plane which comprises C(4), the midpoint of C(1)–C(2), and the Ni(II) atom. Moreover, this localized cyclopentadienyl mirror plane makes an approximate angle of only 15° with respect to the planar $(PNi)_2$ system; the lack of coincidence of these two planes to the extent that the independent cyclopentadienyl ring is not bisected by the $(PNi)_2$ plane can be explained in terms of intermolecular packing forces which no doubt can bias the relative orientation of the ring from that dictated by any intramolecular energy minimum. Hence, the indicated distortion of the cyclopentadienyl ring can be rationalized theoretically in terms of the nickel(II)–phosphorus bonding in which the two phosphorus ligands remove the cylindrical degeneracy of nickel(II) valence orbitals which in turn destroy the degeneracy of the nickel(II)-coordinated doubly degenerate cyclopentadienyl orbitals. These symmetry arguments predict a nonuniformity of electron density about the cyclopentadienyl ring, although the degree of nonuniformity and resulting molecular ring deformation cannot be estimated with any certainty.

This possibility of a cyclopentadienyl ring distortion and its theoretical explanation are not without precedent. The concept of a localized interaction involving metal–cyclopentadienyl bonding was first made by Dahl and Wei[41] for the same type of complex (*viz.*, one containing a metal atom coordinated to *only two* other monodentate ligands besides the π-cyclopentadienyl ring) in connection with their X-ray study of $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$. Bennett, *et al.*,[42] later cited further examples of possible localization of electron density in cyclopentadienyl rings coordinated to metal atoms.

For complexes containing a π-cyclopentadienyl ring and only two monodentate ligands coordinated to a transition metal atom, it is not at all surprising that the nmr solution spectra invariably show all five hydrogen atoms are equivalent or that any gaseous electron-diffraction study similarly would show fivefold ring symmetry. One simply would not expect to observe any possible ring distortion either in solution or the gaseous state (as well as in many solids at room temperature) due to dynamic librational effects. In their extensive investigation of the cyclopentadienyl ring motion in orthorhombic $[C_5H_5FeS]_4$, Schunn, Fritchie, and Prewitt[43] pointed out that the widely varying extent of thermal motion in cyclopentadienyl rings in different crystals and the known low barrier to ring rotation in the gaseous state show in general that thermal movement of cyclopentadienyl rings in the crystalline state is largely determined by intermolecular forces. Therefore, it is evident that ultimate proof of any physically meaningful distortion of the cyclopentadienyl ring in these complexes attributable to electronic interactions must be deferred until accurate structural measurements of several complexes at low temperatures are made.

Table VI. Equations of Best Molecular Planes and Distances (A) of Atoms from These Planes[a,b]

$[(C_6H_5)_2PCoC_5H_5]_2$ (Least-Squares Refinement b)					
(a) Plane through Co, P, and P′					
$0.463X + 0.395Y - 0.794Z - 5.796 = 0$					
Co′	1.55				
(b) Plane through Co, Co′, and P					
$0.363X - 0.429Y - 0.827Z + 3.044 = 0$					
C(6)	1.42	C(12)	−1.42	P′	−1.62
(c) Plane through Co, Co′, and the midpoint of P and P′					
$0.646X - 0.764Y + 9.116 = 0$					
P	1.44	C(6)	3.19	C(12)	1.64
P′	−1.44	C(7)	3.38	C(13)	1.54
C(1)	−0.01	C(8)	4.66	C(14)	1.71
C(2)	−1.13	C(9)	5.76	C(15)	1.98
C(3)	−0.68	C(10)	5.57	C(16)	2.08
C(4)	0.72	C(11)	4.28	C(17)	1.91
C(5)	1.14				
(d) Plane through P, P′, and the midpoint of Co and Co′					
$0.761X + 0.649Y - 7.522 = 0$					
Co	−1.28	C(5)	−2.50	C(11)	−0.17
Co′	1.28	C(6)	−0.05	C(12)	0.06
C(1)	−2.12	C(7)	−0.04	C(13)	−1.12
C(2)	−2.56	C(8)	−0.14	C(14)	−1.08
C(3)	−3.20	C(9)	−0.26	C(15)	0.12
C(4)	−3.16	C(10)	−0.27	C(16)	1.30
				C(17)	1.26
(e) Plane through cyclopentadienyl ring [C(1), C(2), C(3), C(4), and C(5)]					
$-0.648X - 0.586Y - 0.487Z + 2.796 = 0$					
Co	−1.66				
(f) Plane through phenyl ring 1 [C(6), C(7), C(8), C(9), C(10), and C(11)]					
$-0.815X - 0.579Y - 0.022Z + 6.869 = 0$					
P	0.09				
(g) Plane through phenyl ring 2 [C(12), C(13), C(14), C(15), C(16), and C(17)]					
$0.513X - 0.850Y - 0.119Z + 8.555 = 0$					
P	0.04				
$[(C_6H_5)_2PNiC_5H_5]_2$ (Least-Squares Refinement a)					
(a′) Plane through Ni, Ni′, P, and P′					
$-0.898X + 0.205Y - 0.389Z - 1.152 = 0$					
C(6)	−1.43	C(2)	1.01	C(4)	−0.20
C(12)	1.47	C(3)	1.03	C(5)	−1.12
C(1)	−0.46				
(b′) Plane through P, P′, C(6) and C(12)					
$0.156X - 0.589Y - 0.793Z + 0.562 = 0$					
P	0.00	C(4)	−3.46	C(11)	0.85
P′	0.00	C(5)	−3.55		
C(6)	0.00			C(13)	−0.71
C(12)	0.01	C(7)	−0.83	C(14)	−0.76
C(1)	−3.36	C(8)	−0.81	C(15)	−0.10
C(2)	−3.30	C(9)	0.04	C(16)	0.61
C(3)	−3.38	C(10)	0.87	C(17)	0.65
(c′) Plane through cyclopentadienyl ring [C(1), C(2), C(3), C(4), and C(5)]					
$0.255X - 0.560Y - 0.788Z + 3.084 = 0$					
C(1)	0.03	C(3)	−0.02	C(5)	−0.04
C(2)	−0.01	C(4)	0.04	Ni	1.74
(d′) Plane through phenyl ring 1 [C(6), C(7), C(8), C(9), C(10), and C(11)]					
$0.711X - 0.088Y - 0.697Z - 7.727 = 0$					
P	0.06				
(e′) Plane through phenyl ring 2 [C(12), C(13), C(14), C(15), C(16), and C(17)]					
$0.210X - 0.928Y - 0.308Z + 8.248 = 0$					
P	−0.08				

[a] The equations of the planes are given in an orthogonal Ångstrom coordinate system (X, Y, Z) which is related to the monoclinic fractional unit cell coordinate system (x, y, z) with the c axis unique[16] by the following transformation: $X = ax + by \cos \gamma$, $Y = by \sin \gamma$, and $Z = cz$. [b] The positions of the primed atoms in $[(C_6H_5)_2PCoC_5H_5]_2$ are related to the positions of the unprimed ones by $\bar{x}$, $^3/_2 - y$, z; corresponding primed atoms in $[(C_6H_5)_2PNiC_5H_5]_2$ are related to the unprimed ones by $1 - x$, $1 - y$, $-1 - z$.

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Table VII. Comparison of Molecular Parameters of $[(C_6H_5)_2PNiC_5H_5]_2$ and $[(C_6H_5)_2PCoC_5H_5]_2$ with Those of Related Dimeric Complexes

Distance	$[(C_6H_5)_2PNiC_5H_5]_2$ Length, A	$[(C_6H_5)_2PCoC_5H_5]_2$ Length, A	$[C_2H_5SFe(CO)_3]_2$[13] Length, A	$[SFe(CO)_3]_2$[25] Length, A	$[C_2H_5SFe(NO)_2]_2$[26] Length, A
M–M[a]	3.36(1)	2.56(1)	2.54(1)	2.55(0.2)	2.72(0.3)
M–B	2.15(0.6)(av)	2.16(0.4)(av)	2.26(0.7)(av)	2.23(0.2)(av)	2.27(0.4)(av)
B–B[a]	2.70(1)	2.88(2)	2.93(1)	2.01(0.5)	3.63(0.4)
B–C[a]	1.84(1)(av)	1.84(1)(av)	1.81(3)(av)	. . .	1.84(2)
Angle	Degrees	Degrees	Degrees	Degrees	Degrees
M–B–M′	102.4(3)	72.5(5)	68.3(3)(av)	69.9(1)(av)	73.7(1)
B–M–B′	77.6(5)	83.7(5)	81.0(3)(av)	53.5(1)(av)	106.3(1)
M–B–C	112.7(3)(av)	120.9(2)(av)	113.5(7)(av)	. . .	106.6(5)(av)
C–B–C′	104.1(6)	101.0(4)	. . .	. . .	. . .
. . .[b]	180.0(–)	105.1(4)	95.2(5)	79.8(1)	180.0(–)

[a] Where M represents the metal atom, B the metal-linked bridging atom, and C the substituent carbon atom (if any) bonded to the bridging atom. [b] Dihedral angle between the plane formed by M, B, and B′ and the plane formed by M′, B, and B′.

The perpendicular distance of the nickel from the mean cyclopentadienyl carbon plane in $[(C_6H_5)_2PNiC_5H_5]_2$ is 1.74 A, which is consistent with the corresponding perpendicular distances determined in $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ (1.75 A) and $C_5H_5Ni\{(CH_3)_4C_4C_5H_5\}$ (1.76 A)[44] but is significantly longer by 0.1 A than the corresponding perpendicular cobalt–(cyclopentadienyl ring) distances in $[(C_6H_5)_2PCoC_5H_5]_2$ and the other monocyclopentadienylcobalt complexes cited previously. This difference in length may be ascribable to a generally smaller bond energy for a nickel–(cyclopentadienyl ring) interaction than that for a cobalt–(cyclopentadienyl ring) interaction.

Table IV shows the average doubly bridged Co–P$(C_6H_5)_2$ and Ni–P$(C_6H_5)_2$ bond lengths of 2.16 A in $[(C_6H_5)_2PCoC_5H_5]_2$ and 2.15 A in $[(C_6H_5)_2PNiC_5H_5]_2$ to be closely similar to each other and not unlike the terminal Co–P distances in $(C_3H_4CO_2C_6H_5)Co(CO)_2\{P(C_6H_5)_3\}$ (2.18 A)[45] and $Co\{P(C_6H_5)_2H\}_3Br_2$ (2.20 A)$_{46}$ but significantly shorter than the doubly bridged Fe–S distances in $[C_2H_5SFe(CO)_3]_2$ (2.26 A),[13] $[SFe(CO)_3]_2$ (2.23 A),[25] and $[C_2H_5SFe(NO)_2]_2$ (2.27 A),[26] and the doubly bridged Co–S distances in $Co_3(CO)_4(SC_2H_5)_5$ (2.26 A),[47] $Co_5(CO)_{10}(SC_2H_5)_5$ (2.24 A),[47] and $SCo_6(CO)_{11}(SC_2H_5)_4$ (2.21 A).[47] The corresponding sums of Pauling's covalent radii for Fe (1.16 A), Co (1.16 A), Ni (1.15 A), P (1.10 A), and S (1.04 A) give 2.26 A for the Co–P bond, 2.25 A for the Ni–P bond, 2.20 A for the Fe–S bond, and 2.20 A for the Co–S bond. Hence, even despite the fact that the estimated covalent radius of phosphorus is 0.06 A greater than that of sulfur, the doubly bridged metal–P$(C_6H_5)_2$ distances are significantly shorter than the doubly bridged metal–SC_2H_5 distances. These bond-length comparisons indicate substantially greater π bonding for a bridging $P(C_6H_5)_2$ group than a bridging SC_2H_5 group.

The average P–C_6H_5 distance of 1.84 A for both compounds is in good agreement with the corresponding distances found in $Co\{P(C_6H_5)_2H\}_3Br_2$ (1.83 A),[46] $IrClCO(SO_2)\{P(C_6H_5)_3\}_2$ (1.84 A),[48] $HRhCO\{P(C_6H_5)_3\}_3$ (1.83 A),[49] $IrO_2ClCO\{P(C_6H_5)_3\}_2$ (1.81 A),[50] $RuCl_2\{P(C_6H_5)_3\}_3$ (1.85 A),[51] $PtHCl\{P(C_6H_5)_2C_2H_5\}_2$ (1.85 A),[52] $[Cr(acac)_2\{OP(C_6H_5)_2O\}]_2$ (1.80 A),[53] $RhCOCl\{P(C_6H_5)_3\}_2$ (1.82 A),[54] and $(C_3H_4CO_2C_6H_5)Co(CO)_2\{P(C_6H_5)_3\}$ (1.83 A).[45]

Figure 1 shows that the arrangement of the two phenyl carbon atoms attached to each phosphorus atom in $[(C_6H_5)_2PCoC_5H_5]_2$ is similar to that of the two *anti*-methylene carbon atoms bonded to the two sulfur atoms in $[C_2H_5SFe(CO)_3]_2$. Therefore, the tetrahedral-like orientation of the four bonding electron pairs about each phosphorus atom in $[(C_6H_5)_2PCoC_5H_5]_2$ is not unlike the orientation to a first approximation of the three bonding pairs and one localized lone pair about each sulfur atom in $[C_2H_5SFe(CO)_3]_2$.

Calculations of the intra- and intermolecular contact distances indicate that the magnitudes of twisting of the phenyl rings in the cobalt molecule are fixed primarily by nonbonding intramolecular interactions. The almost symmetrical orientation of the phenyl rings such that the total molecular configuration roughly approximates C_{2v} symmetry (as found within experimental error for the $[PCoC_5H_5]_2$ fragment) is indicated for the least-squares plane calculations in Table VI (c and d). The dihedral angle between the two nearly perpendicular phenyl rings is 94.3°; the dihedral angles formed between the idealized vertical mirror plane defined by P, P′, and the midpoint of Co–Co′ and phenyl rings 1 and 2 are 5.3 and 80.8°, respectively.

Because of the P···P′ distance of 2.88 A, the symmetry-related phenyl rings 2 and 2′, which are required by the crystallographic twofold molecular axis to be parallel with each other, experience a mutual repulsion as evidenced by: (1) an increase in the separation of these phenyl rings (Figure 1) from 3.27 A for the phosphorus attached carbon atoms (C(12) and C(12′)), to 3.45 A for the *ortho* carbon atoms (C(13) and C(17′)), to 3.80 A for the *meta* carbon atoms (C(14) and C(16′)), to 3.97 A for the *para* carbon atoms (C(15) and C(15′)); and (2) a clockwise rotation of 9° for

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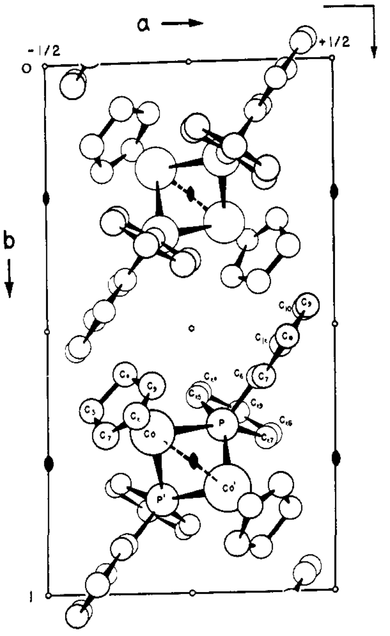

Figure 3. [001] projection of the unit cell of $[(C_6H_5)_2PCoC_5H_5]_2$.

each of these phenyl rings about its $P-C_6H_5$ axis from the orientation perpendicular to the idealized vertical mirror plane defined above (*viz.*, the one passing through P, P′, and the midpoint of Co–Co′) in order to decrease inter-ring π-orbital overlap. The known methyl–methyl and methylene–methylene van der Waals contact distance of 4.0 A,[55] as contrasted to a considerably shorter aromatic interaction distance of 3.4 A,[55] indicates that unless a pronounced deformation occurs in the $[PCoC_5H_5]_2$ moiety such as to cause a significant increase by 0.5 A in the separation of the C(12) and C(12′) carbon atoms, cyclic μ-dialkylphosphidocobalt cyclopentadienyl dimers should not be obtained. None is known to date, and attempts by Hayter and Williams[8] to prepare the methyl analog of $[(C_6H_5)_2PCoC_5H_5]_2$ by the corresponding reaction of tetramethylbiphosphine with $C_5H_5Co(CO)_2$ were unsuccessful; instead, a noncyclic dinuclear cobalt complex of formula $Co(CO)C_5H_5\{P_2(CH_3)_4\}Co(CO)C_5H_5$ was obtained.

However, the existence of the analogous electronically equivalent bis(μ-dialkylphosphido)bis(tricarbonyliron) complexes (with methyl and ethyl groups)[56,57] together with various related phosphine-substituted derivatives[58] does show that a sufficient nonrigidity of the $[XFe(CO)_3]_2$ skeleton exists such that bridging dialkylphosphido groups can formally replace bridging mercapto groups. In this regard, a detailed comparison of the nonbonding intramolecular distances of $[(C_6H_5)_2PCoC_5H_5]_2$ *vs.* those of $[C_2H_5SFe(CO)_3]_2$ shows that a drastic skeletal rearrangement of the $(XFe)_2$ system involving a considerably larger dihedral angle than the 95° found for $[C_2H_5SFe(CO)_3]_2$ is necessary in order to increase the closest *syn* methylene–methylene distance to a value greater than 3.6 A to render the complex energetically stable.

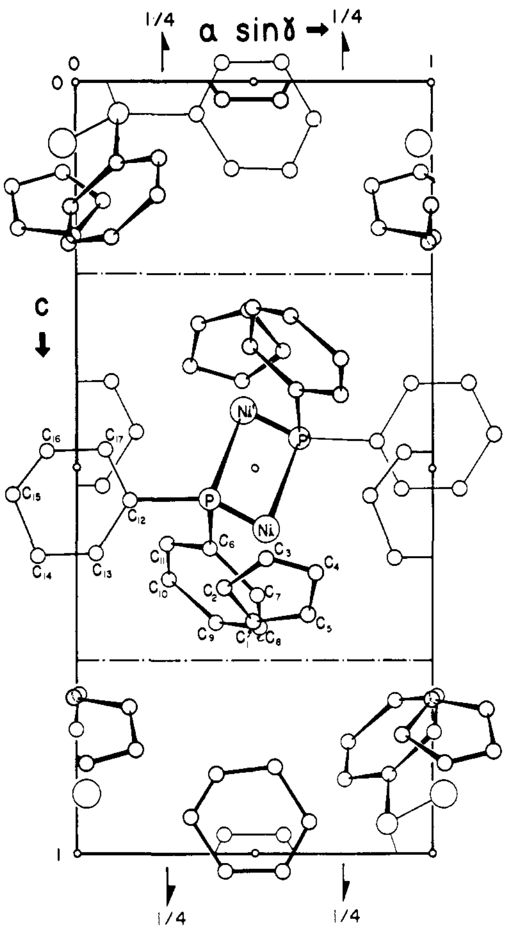

Figure 4. [010] projection of the unit cell of $[(C_6H_5)_2PNiC_5H_5]_2$.

For $[(C_6H_5)_2PNiC_5H_5]_2$ the two independent phenyl rings, which make a dihedral angle of 116.5° with each other, are situated well away from the other atoms in the molecule. The twistings of the phenyl rings 1 and 2 with respect to the planar $(PNi)_2$ system are such that the dihedral angles are 67.3 and 75.0°, respectively; the corresponding dihedral angles with respect to the mean plane comprised of the atoms P, P′, C(6), and C(12) (Table VI, b′) are 135.7° for phenyl ring 1 and 145.4° for phenyl ring 2.

Figure 3 shows the [001] unit cell projection of $[(C_6H_5)_2PCoC_5H_5]_2$, while Figure 4 gives the [010] unit cell projection of $[(C_6H_5)_2PNiC_5H_5]_2$. The smallest intermolecular HC···CH contact distances in both compounds are 3.5 A which indicate that these molecular crystals are held together by the usual van der Waals forces.

Other known diamagnetic pairs of ligand-bridged organometallic dimers of adjacent first-row transition metals, which differ from each other in configuration only by the necessity of a metal–metal interaction for one of the complexes (*viz.*, the number containing the two transition metal atoms of lower atomic number), include the dimeric systems $[XM(NO)_2]_2$ (M = Fe, Co) and $[XM(CO)_4]_2$ (M = Cr, Mn) where X again designates a three-electron donating bridging group such as halogen, SR, SeR, PR_2, etc. A direct stereochemical comparison of corresponding representative members of these two molecular classes is not available as yet, since structural studies have been reported only for

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$[C_2H_5SFe(NO)_2]_2$ (for which the observed Fe–Fe bonding distance of 2.72 A is compatible with the electron-spin pairing)[26] and for $[BrMn(CO)_4]_2$ (for which a molecular D_{2h} configuration with a nonbonding intramolecular $Mn\cdots Mn$ distance of 3.74 A was found).[59] However, the geometrical consequences of the metal–metal bonds in these two dimeric systems are apparent from stereochemical considerations. The dimeric cobalt nitrosyl complexes no doubt will retain a similar symmetrical configuration to the one ascertained in the known mercaptoiron nitrosyl dimer (in which the two NO groups and two S atoms form a tetrahedral-like environment about each iron atom) except for a longer nonbonding metal–metal distance of magnitude 3.3–3.4 A (together with normal bridging ligand angles of approximately 100°). Similarly, outside of the expected decrease in metal–metal distance to a single bond value of 3.0 A (as found in the related bridging complex $[C_5H_5CrS_2C_4F_6]_2$ for which a proposed chromium–chromium single bond is in agreement with the observed diamagnetism),[60] the $[XCr(CO)_4]_2$ species should remain invariant in its general shape relative to that of $[BrMn(CO)_4]_2$. Structural work is in progress to verify these deductions.

Acknowledgments. We are extremely grateful to Dr. Roy Hayter for furnishing us with samples of these two complexes and for his interest in this work. We also are pleased to acknowledge the Air Force Office of Air Research and Development Command for their financial support of this research. The use of the CDC 1604 and 3600 computers at the University of Wisconsin Computing Center was made possible by partial support of N.S.F. and W.A.R.F. through the University Research Committee.

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Aminopolycarboxylic Acid Ligand-Exchange Kinetics of Selected Alkaline Earth Ions[1]

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Abstract: The ligand-exchange kinetics of the strontium–ethylenediaminetetraacetic acid system and the calcium–N′-(2-hydroxyethyl)ethylenediamine-N,N,N′-triacetic acid system have been evaluated in aqueous solution using proton nmr line-broadening techniques. Exchange occurs by both first-order dissociation of the metal–ligand species and second-order processes involving free ligand and metal–ligand species. The pH dependence of the rate was used to evaluate the rate constants for the individual exchange steps. From comparison of the rate constants in these and other systems, mechanisms of the second-order exchange reactions are proposed, and the structure of the protonated metal–ligand species is concluded to be such that only one iminodiacetate segment of ethylenediaminetetraacetate is metal coordinated.

Despite the importance of the alkaline earth metal ions and the extensive thermodynamic data available on their complexes, only meager kinetic information on such complexes is available. This circumstance results from the rapid reaction rates involving these ions and eliminates the possibility of employing conventional techniques for rate studies. In an earlier paper, the ligand-exchange kinetics in the calcium–ethylenediaminetetraacetic acid (EDTA) system were studied using proton nuclear magnetic resonance (nmr) line-broadening techniques.[2] In the present paper we have studied the exchange kinetics of two related systems in an attempt to elucidate the mechanisms of aminopolycarboxylic acid ligand exchange with the alkaline earth ions. One of these systems is strontium and EDTA, which can be described by the same pH-dependent rate expression as calcium and EDTA, suggesting that exchange occurs by similiar mechanisms in both systems. The second system is calcium and N′-(2-hydroxyethyl)ethylenediamine-N,N,N′-triacetic acid (HEEDTA).[3] The latter ligand, while structurally related to EDTA, is capable of only pentadentate coordination to metal ions. Although the rates in the present investigation are generally greater than the corresponding rates found in the CaEDTA study, they are still within the time limits accessible to nmr line-broadening measurements. Advantage has been taken of the extensive pH range available with the alkaline earth ions to isolate the various pH-dependent rate processes. The lower pH limit is approximately 4 because of dissociation of the chelates, but there is no upper pH limit because metal–(hydroxy)–ligand species do not exist.

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[3] In this paper L^{3-} is used to designate the trianion of HEEDTA and HL^{2-} the monoprotonated anion; Y^{4-} represents the EDTA tetraanion and HY^{3-} the monoprotonated anion; M^{2+} represents either Ca^{2+} or Sr^{2+}.