The Crystal and Molecular Structures of [N,N-Bis(2-diphenylphosphinoethyl)ethylamine]-tricarbonylchromium[1]

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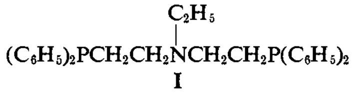
Abstract: The crystal and molecular structure of [N,N-bis(2-diphenylphosphinoethyl)ethylamine]tricarbonylchromium, $[(C_6H_5)_2PCH_2CH_2N(CH_2CH_3)CH_2CH_2P(C_6H_5)_2]Cr(CO)_3$, have been determined by single-crystal X-ray diffraction techniques. The crystals belong to the monoclinic system, space group $B2_1/c$ with the dimensions $a = 14.884$, $b = 18.826$, $c = 21.274$ Å; $\beta = 94.05$. The calculated density assuming $Z = 8$ is 1.353 g/cc; the observed density is 1.35 g/cc. The final value of the conventional R factor is 7.5 % for 2547 independent nonzero reflections measured at 21° with a manually operated General Electric counter diffractometer. The least-squares refinement employed anisotropic temperature factors for all nonhydrogen atoms. The structure is a distorted octahedron, with the N and the two P atoms in mutually *cis* positions. The Cr–C(carbonyl) distances *trans* to phosphorus atoms (1.83 and 1.82) are almost as short as the Cr–C(carbonyl) distance (1.80 Å) *trans* to a nitrogen atom. Also, the Cr–N distance is anomalously long (2.31 Å). It appears that there are severe strains in this molecule as a result of the formation of fused chelate rings, with perhaps additional strain resulting from nonbonded repulsions. Because of the strains and distortions involved, it is unwise to base discussions of Cr–C multiple bonding or correlations of such bonding with structural and spectroscopic parameters on data obtained from this or similarly strained molecules.

Despite the fact that a great deal of attention has been devoted to the preparation, vibrational spectra, and ligand-replacement kinetics of mononuclear complexes containing both carbon monoxide molecules and group V (N, P, As, Sb) atoms as ligands, relatively few accurate structural studies have so far been reported on such molecules. Because of the value of structural parameters in providing a basis for the discussion of bonding in such compounds, several X-ray crystallographic studies have recently been undertaken in these laboratories. Previous reports have dealt with $(dien)Mo(CO)_3$[3] and $(dien)Cr(CO)_3$[4] (dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$) and with $(diphos)Cr(CO)_4$[5] (diphos = $[(C_6H_5)_2PCH_2-]_2$).

In the present report we describe the structure of a compound containing the $Cr(CO)_3$ group and a tridentate ligand in which there are both P and N donor atoms. The ligand, N,N-bis(2-diphenylphosphinoethyl)ethylamine (I) will usually be represented by the



$$(C_6H_5)_2PCH_2CH_2\overset{\overset{\large C_2H_5}{|}}{N}CH_2CH_2P(C_6H_5)_2$$

I

abbreviation PNP. The compound studied, (PNP)Cr-$(CO)_3$, was reported by Dobson, Taylor, and Walsh,[6] who proposed on the basis of its infrared spectrum that it has a *cis* configuration.

Procedure

The sample of $(PNP)Cr(CO)_3$ was kindly supplied by Professor G. R. Dobson of the University of South Dakota, Vermillion, S. D. Yellow single crystals suitable for X-ray work were obtained by crystallization from xylene and were mounted in thin-walled Lindeman glass capillaries. Single crystals examined by Weissenberg and precession photography were found to be monoclinic. The systematic absences $h0l$ for $l = 2n + 1$, $0k0$ for $k = 2n + 1$, and hkl for $h + l = 2n + 1$ observed on the $h0l$, $0kl$, $1kl$, and $2kl$ levels uniquely identify the space group as $B2_1/c$ with the general (eightfold) positions $x, y, z;\ -x, -y, -z;\ x, {}^1/_2 - y, {}^1/_2 + z;\ -x, {}^1/_2 + y, {}^1/_2 - z;\ {}^1/_2 + x, y, {}^1/_2 + z;\ {}^1/_2 - x, -y, {}^1/_2 - z;\ {}^1/_2 + x, {}^1/_2 - y, z;\ {}^1/_2 - x, {}^1/_2 + y, -z$. The unit-cell dimensions at 20.5° are: $a = 14.884 \pm 0.006$ Å, $b = 18.826 \pm 0.008$ Å, $c = 21.274 \pm 0.003$ Å, and $\beta = 94.05 \pm 0.05°$. The angle β was measured from the precession photographs. The quoted values for a, b, and c were derived[7] by plotting values obtained for various 2θ settings on a manually operated General Electric single-crystal orienter against the function ${}^1/_2[(\cos^2\theta)/(\sin\theta) + (\cos^2\theta)/\theta]$ and linearly extrapolating these plots to $\theta = 90.0°$. Copper radiation (λ ($K\alpha_1$) = 1.5405 Å; λ ($K\alpha_2$) = 1.5443 Å) was used. The uncertainty intervals quoted are estimates of precision. The standard setting ($P2_1/c$ with $a = 13.405$ Å, $b = 18.826$ Å, $c = 21.274$ Å, $\beta = 146.38°$), uses 101 planes of $B2_1/c$ to define the a direction. It was not chosen due to the large β angle.

The density was measured by flotation in aqueous potassium iodide solution as 1.35 ± 0.01 g/cc. The density calculated from the formula weight of 605.579, the unit-cell volume of 5946.0 Å^3, and $Z = 8$ is 1.353 g/cc. With $Z = 8$ in the space group $B2_1/c$ there are no crystallographic symmetry elements imposed on the molecule.

Intensities were collected using a crystal which was approximately a rectangular parallelepiped with dimensions of 0.18 × 0.09 × 0.16 mm. The crystal was

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[1] Supported by the U. S. Atomic Energy Commission.

[2] National Institutes of Health Predoctoral Fellow, 1967–1969.

[3] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 4, 314 (1965).

[4] F. A. Cotton and D. C. Richardson, *ibid.*, 5, 1851 (1966).

[5] M. J. Bennett, F. A. Cotton, and M. D. LaPrade, submitted for publication.

[6] G. R. Dobson, R. C. Taylor, and T. D. Walsh, *Inorg. Chem.*, 6, 1929 (1967).

[7] A. Taylor and H. Sinclair, *Proc. Phys. Soc.* (London), 57, 126 (1945); J. B. Nelson and D. P. Riley, *ibid.*, 57, 160 (1945).

aligned with its a^* axis coincident with the ϕ axis of the goniometer. Cu Kα radiation filtered by nickel foil was used to measure 3885 independent reflections (index sets hkl and $h\bar{k}\bar{l}$) within the sphere $\theta \leq 56.2°$. Intensities were measured by a scintillation counter with the pulse-height discriminator set to accept 95% of the Cu Kα peak. The distances from the crystal to the source and from the crystal to the circular screening aperture (2°) were 14.6 cm and 17.9 cm, respectively. A moving-crystal–moving-counter scan technique was employed with a scan range of 1.33° to conform with the mosaic spread of the crystal and a take-off angle of 2°. The scan rate was 4°/min.

The integrated intensities (I) were obtained from the total counts (P) of a coupled 2θ–w scan[8] from $2\theta_{\text{calcd}} - 0.66°$ to $2\theta_{\text{calcd}} + 0.67°$ and stationary background measurements (B_1, B_2) of 10.0-sec duration at the limits of each scan. Assuming that the background varies linearly (or gives an equivalent integrated total) through the scan range, $I = P - B_1 - B_2$. Intensities were such that coincidence losses were negligible. Three reflections which were checked at 4-hr intervals exhibited a maximum variation of ±7%, which was random with time. Thus there was no evidence for significant crystal decomposition.

As the intensities were converted to values of $|F_o|^2$ and $|F_o|$ (on a relative scale) 1335 reflections including 52 systematically absent reflections (as shown in Table I) were rejected using two criteria: (1) $I \leq 0$; (2) $I/(P + B_1 + B_2)^{1/2} < 3$. Only the remaining 2550 were processed further and the corresponding $|F_o|$ and $|F_o|^2$ values used in solving and refining the structure. Three reflections (200, 202, and 012) were subsequently suspected of suffering seriously from extinction and were rejected.

Table I. Distribution of Observed Intensities[a]

Number measured: 3885
Number accepted: 2547
Number rejected, total: 1338
Number rejected for extinction: 3 (200, 202, 012)
Number rejected because $I/\Delta I < 3$ (including 152 systematically absent): 1335
Distribution of intensities

Range of $I/\Delta I$	No. of reflections
≤0	344
>0 but <1	304
≥1 but <2	326
≥2 but <3	361
≥3 but <4	207
≥4 but <6	412
≥6 but <10	587
≥10 but <20	703
≥20 but <50	478
≥50 but <100	118
≥100	45

[a] Standard deviation, ΔI, defined as $(P + B_1 + B_2)^{1/2}$, where I, the intensity, is equal to $P - B_1 - B_2$.

The Cr and P atoms were located in a three-dimensional Patterson map. A three-dimensional electron density difference synthesis, using structure factors with phases calculated from the chromium and phosphorus positions only, gave the coordinates of the other nonhydrogen atoms.

Since $\mu = 47.73$ cm^{-1} ($\mu r_{\max} = 0.45$) and since a 15% variation in intensity of the 400 reflection was observed in a ϕ scan at $X = 90°$, an absorption correction was considered necessary. The crystal was a rectangular parallelepiped with dimensions 0.18 × 0.09 × 0.16 mm with well-developed 010, 001, and 100 faces. Following the absorption correction the variation in intensity of the 400 reflection was 7%.

The structure was refined by full-matrix least-squares methods minimizing $\Sigma w(|F_o| - |F_c|)^2$. Scattering factors were those of Cromer and Waber[9a] except for hydrogen atoms for which those experimentally determined by Mason and Robertson were used.[9b] Anomalous dispersion corrections[9c] for chromium and phosphorus were included in the calculated structure factors.

Three cycles of least-squares refinement of the scale factor and the positional and isotropic thermal parameters for the nonhydrogen atoms led to a conventional R factor, $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.126$, and a weighted residual, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2} = 0.155$. At this point a program described elsewhere for refinement[10] of the phenyl groups as rigid bodies, with individual isotropic temperature factors assigned to each of the ring atoms, was used. The rigid body parameters were generated from the parameters of the third cycle of refinement, assuming an ideal distance of 1.397 Å from the center of gravity of the phenyl ring to each carbon atom. The hydrogen atoms on the phenyl rings were fixed at positions 1.00 Å beyond the carbon atoms along lines directed from the ring centers through the carbon atoms (each set of 5 H atoms thus forming another rigid body) and each hydrogen atom was assigned an isotropic thermal parameter 1.1 times that of the carbon atom to which it was attached. The other atoms were then refined with anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Several cycles resulted in convergence with $R_1 = 9.4$ and $R_2 = 12.5$. Investigation of a difference Fourier at this point showed large residual electron density in the area of the phenyl groups indicating a significant contribution to sytematic errors resulting from the deficiency in representing phenyl group vibrations. Consequently, all nonhydrogen atoms were refined anisotropically. Due to limitations of core space on the computer the structure was refined in sections with cycles in which parameters for C11-C26 were held constant alternating with cycles in which parameters for C31-C46 were held constant. The hydrogen atoms on the phenyl rings continued to be fixed at calculated distances. An em-

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(8) Computer programs used in this study were: (a) D. P. Shoemaker, MIXG2, calculates diffractometer settings; DISTAN, calculates orthogonal cell coordinates, intra- and intermolecular contacts, and angles; (b) R. C. Elder, PDATA2, corrects MIXG2 output for ϕ_0 and scan width and prints diffractometer setting in convenient format; PUBTAB, prepares compact tabulation of structure factors; (c) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, MIFR -2A, 1962, Fourier summation for Patterson or Fourier maps; (d) W. C. Hamilton, GONO9, used for the absorption correction; (e) C. T. Prewitt, SFLS5, 1967, least-squares refinement of parameters minimizing $\Sigma(w||F_o| - |F_c||^2)$; (f) J. S. Wood, MGEOM, calculates intramolecular bond lengths and angles and standard deviations and best least-squares planes; (g) M. J. Bennett, PMMO, data reduction and σ calculation.

(9) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); (b) R. Mason and G. B. Robertson, "Advances in Structural Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1966, p 57; (c) "International Tables for Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, Table 3.3.2B.

(10) A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6675 (1968).

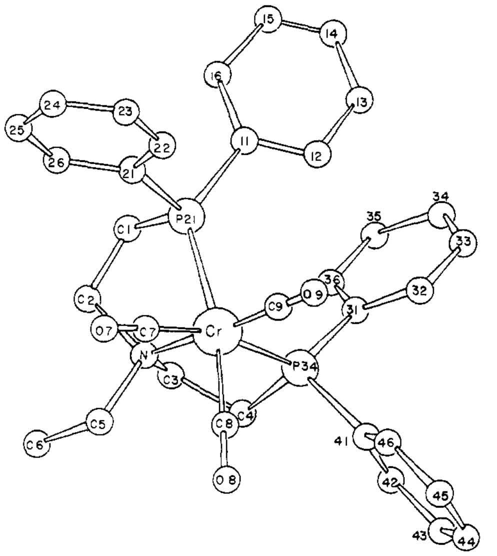

Figure 1. The molecular structure of $Cr(CO)_3(PNP)$ as seen in projection on the (100) crystal plane. The numbering scheme used in all tables is shown.

pirical weighting scheme setting $\sigma = [2.450 + 0.073 \cdot (F_{\text{obsd}} - 20.0)]^{1/2}$ if $F_{\text{obsd}} > 20.0$ and $\sigma = [2.450]^{1/2}$ if $0 < F_{\text{obsd}} < 20.0$ removed the dependence of $w\Delta^2$ on F_{obsd}[11] and immediately reduced the standard deviation of an observation of unit weight from 1.80 to 1.09. The last cycle of this refinement, showing no parameter shift greater than $^1/_2$ of 1 esd for the phenyl carbons and no parameter shift greater than $^1/_5$ of 1 esd for other atoms, gave $R_1 = 7.5\%$ and $R_2 = 9.6\%$. In the final electron-density difference map the standard deviation in the electron density[12] was 0.10 e/Å^3. The highest peak in the difference map was in the vicinity of the Cr atom and contained 0.69 e/Å^3. The final standard deviation of an observation of unit weight was 1.07.

The independent atom model appears to be significantly better than the rigid body approximation. An R factor test[13] rejected the rigid body model at the 0.995 confidence level but this assumes no systematic errors in the data, which in Hamilton's definition would include the radius of the phenyl rings and the assumption that the phenyl rings are regular hexagons.

Results

All distances and angles and all numbers in the tables are from the independent atom refinement. The final atomic positional parameters are given in Table II. The anisotropic thermal parameters are listed in Table III. The molecular structure is displayed in Figure 1 projected on the *bc* plane. Figure 1 defines the numbering scheme used in the tables. Table IV lists intramolecular distances and Table V gives bond angles. Selected intermolecular distances are listed in Table VI. A list of calculated structure factors and observed structure amplitudes has been deposited with the ASIS–NAPS.[14]

Table II. Atomic Positional Parameters

Atom	*x*	*y*	*z*
Cr	0.24425 (9)	0.16257 (7)	0.06522 (6)
P21	0.2030 (1)	0.0455 (1)	0.0364 (1)
P34	0.1403 (2)	0.1970 (1)	0.1400 (1)
N	0.1232 (4)	0.1886 (3)	−0.0050 (3)
C1	0.0996 (6)	0.0565 (5)	−0.0160 (4)
C2	0.1059 (6)	0.1290 (5)	−0.0501 (4)
C4	0.0546 (6)	0.2446 (5)	0.0889 (4)
C3	0.0367 (6)	0.2040 (5)	0.0260 (4)
C5	0.1497 (6)	0.2544 (5)	0.0416 (4)
C6	0.0837 (7)	0.2759 (5)	0.0970 (5)
C8	0.2856 (6)	0.2541 (5)	0.0715 (4)
C7	0.3226 (6)	0.1580 (5)	0.0033 (4)
C9	0.3346 (6)	0.1355 (5)	0.1211 (4)
O8	0.3208 (5)	0.3093 (3)	0.0750 (3)
O7	0.3766 (4)	0.1603 (4)	−0.0338 (3)
O9	0.3957 (5)	0.1194 (4)	0.1566 (3)
C21	0.2802 (6)	0.0001 (4)	−0.0140 (4)
C26	0.2627 (6)	−0.0100 (5)	−0.0778 (4)
C25	0.3252 (9)	−0.0406 (6)	−0.1140 (5)
C24	0.4021 (9)	−0.0646 (6)	−0.0872 (6)
C23	0.4226 (7)	−0.0595 (5)	−0.0216 (7)
C22	0.3596 (7)	−0.0249 (5)	0.0148 (5)
C11	0.1757 (6)	−0.0296 (4)	0.0869 (4)
C16	0.1598 (6)	−0.0976 (5)	0.0637 (4)
C15	0.1390 (7)	−0.1521 (5)	0.1038 (5)
C14	0.1343 (7)	−0.1393 (6)	0.1679 (5)
C13	0.1511 (8)	−0.0720 (8)	0.1909 (5)
C12	0.1719 (7)	−0.0174 (5)	0.1516 (4)
C41	0.1744 (6)	0.2649 (4)	0.1992 (4)
C42	0.1087 (7)	0.3082 (5)	0.2236 (4)
C43	0.1364 (11)	0.3582 (6)	0.2686 (5)
C44	0.2269 (12)	0.3641 (6)	0.2911 (5)
C45	9.2893 (8)	0.3202 (6)	0.2669 (5)
C46	0.2623 (8)	0.2723 (5)	0.2210 (5)
C31	0.0751 (6)	0.1381 (4)	0.1887 (4)
C32	0.1125 (7)	0.1189 (5)	0.2463 (4)
C33	0.0671 (10)	0.0680 (6)	0.2834 (5)
C34	−0.0154 (10)	0.0432 (6)	0.2611 (7)
C35	−0.0518 (8)	0.0625 (6)	0.2053 (6)
C36	−0.0088 (7)	0.1116 (5)	0.1686 (4)

Discussion

Although there are considerable deviations from the 90 and 180° angles of an octahedron, which will be discussed below, the CrC_3P_2N skeleton may be crudely described as "octahedral." The configuration is *cis* in agreement with the inference made by Dobson and coworkers[6] from the infrared spectrum in the CO stretching region. The occurrence of this configuration rather than the meridional one is of interest, since it suggests that the relative importance of the various factors influencing configuration may not be easy to predict. Two of the principal factors, namely, π bonding and steric hindrance, work in opposition to each other. In replacing CO groups of an $M(CO)_6$ molecule by ligands which are much poorer π acids, π bonding can be maximized if CO groups are placed *trans* to such substituents rather than *trans* to each other. Thus, $M(CO)_4L_2$ and $M(CO)_3L_3$ are generally most stable in the *cis* configurations, examples being diammine and diphosphine compounds such as $Mo(CO)_4(py)_2$ and $Cr(CO)_4(PR_3)_2$ and the diethylenetriamine compounds $Cr(CO)_3$dien and $Mo(CO)_3$dien.

However, repulsions between nonbonded atoms when the substituents on the coordinated N or P atoms are large might be expected to destabilize the *cis* structures in favor of the *trans* or meridional ones. Indeed, several

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(11) D. W. S. Cruickshank, "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965.

(12) D. W. J. Cruickshank, *Acta Crystallogr.*, **2**, 154 (1949).

(13) W. C. Hamilton, *ibid.*, **18**, 502 (1956).

(14) This table has been deposited as NAPS Document No. 00559 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Table III. Anisotropic Thermal Parameters ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	38.0 (7)	16.5 (4)	13.0 (3)	0.4 (5)	7.2 (4)	0.3 (3)
P21	37.6 (1.2)	16.4 (6)	13.2 (5)	−0.2 (7)	8.5 (7)	−0.2 (5)
P34	42.6 (1.3)	16.8 (7)	11.5 (5)	1.7 (7)	6.4 (6)	−0.5 (5)
N	33 (4)	22 (2)	13 (2)	37.0 (2)	22.0 (2)	22 (2)
C1	36 (5)	23 (3)	19 (2)	−1.0 (3)	0 (3)	0 (2)
C2	54 (6)	20 (3)	14 (2)	−3.0 (3)	5 (3)	−4 (2)
C4	47 (5)	22 (3)	13 (2)	9 (3)	3 (3)	3 (2)
C3	31 (5)	30 (3)	14 (2)	6 (3)	7 (3)	−4 (2)
C5	57 (6)	24 (3)	21 (3)	0 (4)	8 (3)	13 (2)
C6	73 (7)	31 (4)	18 (3)	12 (4)	−1 (4)	6 (3)
C8	61 (6)	21 (3)	13 (2)	2 (4)	16 (3)	3 (2)
C7	31 (4)	23 (3)	17 (2)	−1 (3)	9 (3)	−1 (2)
C9	38 (5)	22 (3)	18 (2)	−1 (3)	8 (3)	−3 (2)
O8	71 (5)	18 (2)	26 (2)	−12 (2)	3 (2)	6 (2)
O7	56 (4)	36 (3)	30 (2)	−2 (3)	24 (3)	−1 (2)
O9	42 (4)	49 (3)	20 (2)	4 (3)	1 (2)	4 (2)
C21	36 (5)	12 (2)	23 (3)	4 (3)	14 (3)	0 (2)
C26	58 (6)	26 (3)	14 (2)	4 (3)	8 (3)	−4 (2)
C25	82 (8)	37 (4)	23 (3)	12 (5)	22 (4)	−2 (3)
C24	96 (10)	25 (4)	33 (4)	−5 (5)	41 (5)	−4 (3)
C23	49 (6)	24 (4)	51 (5)	9 (4)	20 (5)	3 (3)
C22	55 (6)	25 (3)	30 (3)	3 (4)	17 (4)	0 (3)
C11	40 (5)	16 (3)	16 (2)	−2 (3)	9 (3)	4 (2)
C16	50 (6)	25 (3)	20 (2)	−8 (3)	4 (3)	−3 (2)
C15	54 (6)	21 (3)	30 (3)	−6 (3)	1 (4)	3 (2)
C14	56 (6)	28 (4)	28 (3)	3 (4)	11 (4)	10 (3)
C13	103 (9)	37 (4)	17 (3)	15 (4)	18 (4)	7 (3)
C12	85 (8)	22 (3)	15 (2)	6 (4)	9 (4)	3 (2)
C41	51 (5)	15 (3)	12 (2)	−3 (3)	2 (3)	−3 (2)
C42	81 (8)	25 (3)	17 (3)	10 (4)	14 (4)	−4 (2)
C43	137 (12)	22 (4)	21 (3)	14 (5)	31 (5)	−2 (3)
C44	136 (12)	34 (4)	19 (3)	−23 (6)	16 (5)	−9 (3)
C45	85 (8)	38 (4)	20 (3)	−13 (5)	4 (4)	−6 (3)
C46	77 (7)	20 (3)	18 (3)	−6 (4)	8 (4)	−3 (2)
C31	44 (5)	21 (3)	12 (2)	3 (3)	14 (3)	−1 (2)
C32	72 (7)	27 (3)	17 (3)	−13 (4)	8 (3)	−2 (2)
C33	116 (10)	33 (4)	15 (3)	−5 (5)	17 (4)	3 (3)
C34	99 (11)	37 (4)	37 (4)	−22 (6)	34 (6)	−5 (4)
C35	64 (7)	46 (5)	31 (4)	−11 (5)	8 (4)	6 (4)
C36	52 (6)	33 (4)	19 (3)	−4 (4)	10 (3)	3 (2)

years ago in this laboratory,[15] the compound $Cr(CO)_3$-$[(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2]$ was prepared with the purpose of obtaining a more soluble analog of $Cr(CO)_3$dien. However, the compound with the tetraethyl ligand appeared on the basis of its infrared spectrum to have the meridional configuration. It would seem that this difference must be mainly attributable to repulsions between the ethyl groups in the *cis* configuration.

Since the PNP ligand has the rather bulky $(C_6H_5)_2P$-groups at each end and the P atoms are better π-acid ligands than N atoms, it might seem that a meridional configuration for $Cr(CO)_3(PNP)$ would be preferred. The conflict between this expectation and the indication from the infrared spectrum[6] that the configuration is *cis* provided one reason for investigating the configuration definitively by X-ray diffraction. Since it is now unequivocally shown that the configuration is *cis*, it would seem that the factors determining configuration in this and similar cases may be more complex than the preceding analysis suggests. Alternatively, it is perhaps possible that the *cis* complex is the result of a kinetically rather than thermodynamically controlled stereochemistry in the preparative reaction. Before speculating further on the meaning of the observed *cis* configuration, it would be well to have some evidence on this point.

It is to be noted that rather short nonbonded contacts do indeed occur in the molecule. Table IV, part 3, lists nine C···H contacts between 2.60 and 2.81 Å. All of these would seem to be due, directly or indirectly, to the closeness of the phosphorus atoms, even though the phosphorus atoms have moved away from each other to the extent that the P–Cr–P angle has the very large value of 105°. Some of this angle expansion may in fact be due to repulsion between the $-P(C_6H_5)_2$ groups, but this point must remain unresolved because strains in the chelate rings will also play a role in expanding the P–Cr–P angle.

Strain within the chelate rings, aggravated by the fact that two such rings are fused, shows dramatically in the bond common to both, the Cr–N bond. This bond is astonishingly long, namely, 2.310 (6) Å, in comparison with the Cr–N bonds in $Cr(CO)_3$dien, which have a mean value of 2.185 (4). We believe that strain effects become focused on this bond. The Cr–P bonds are probably inherently stronger than a Cr–N bond even at its optimum distance. Therefore, the Cr–P bonds retain what appear to be normal values (mean: 2.381 (5) Å) when compared to those in $Cr(CO)_4$(diphos) (mean: 2.360 (5) Å), while the Cr–N distance is drastically increased.

By comparison with $Cr(CO)_3$dien, the increase in Cr–N due to strain in the present molecule is 0.125 Å, but this is only a lower limit because there may be a

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(15) F. A. Cotton and A. Musco, unpublished work.

Table IV. Interatomic Distances, Å

	1. Bond Distances		
Cr–P21	2.375 (2)	C1–C2	1.551 (12)
Cr–P34	2.387 (3)	C3–C4	1.547 (12)
Cr–N	2.310 (6)	C5–C6	1.533 (14)
Cr–C7	1.822 (9)		
Cr–C8	1.832 (9)	C7–O7	1.167 (11)
Cr–C9	1.804 (9)	C8–O8	1.163 (11)
		C9–O9	1.181 (11)
P21–C1	1.849 (9)		
P34–C4	1.848 (9)	N–C2	1.487 (11)
P21–C11	1.825 (8)	N–C3	1.516 (11)
P21–C21	1.828 (9)	N–C5	1.530 (11)
P34–C31	1.841 (9)		
P34–C41	1.839 (8)		
P–C (aromatic)	Av 1.833 (4)		
	2. Phenyl Ring Distances		
C11–C12	1.400 (12)	C31–C32	1.359 (13)
C12–C13	1.376 (15)	C32–C33	1.440 (15)
C13–C14	1.374 (16)	C33–C34	1.368 (20)
C14–C15	1.393 (15)	C34–C35	1.321 (19)
C15–C16	1.383 (14)	C35–C36	1.394 (16)
C16–C11	1.385 (12)	C36–C31	1.384 (13)
Av, ring 1	1.385 (9)	Av, ring 3	1.378 (28)
C21–C22	1.376 (13)	C41–C42	1.403 (14)
C22–C23	1.417 (16)	C42–C43	1.384 (15)
C23–C24	1.410 (19)	C43–C44	1.402 (23)
C24–C25	1.323 (18)	C44–C45	1.370 (19)
C25–C26	1.377 (15)	C45–C46	1.368 (14)
C26–C21	1.376 (12)	C46–C41	1.364 (15)
Av, ring 2	1.380 (18)	Av, ring 4	1.382 (13)
Grand average, all ring C–C:	1.381 (3)		
	3. Shorter Nonbonded Contacts		
C1–H26	2.60	C21–H16	2.78
C4–H42	2.78	C11–H32	2.71
C4–H36	2.75	C31–H12	2.64
C8–H46	2.81	C32–H12	2.61
C9–H46	2.71		

Table V. Bond Angles, Degrees

P21–Cr–P34	105.0 (1)	Cr–P21–C1	103.3 (3)	C11–C12–C13	120.1 (9)
P21–Cr–C7	86.3 (3)	Cr–P21–C11	128.9 (3)	C12–C13–C14	121.0 (1.0)
P21–Cr–C9	94.2 (3)	Cr–P21–C21	114.7 (3)	C13–C14–C15	119.2 (1.0)
P21–Cr–N	81.7 (2)	C11–P21–C21	99.8 (4)	C14–C15–C16	120.3 (9)
N–Cr–C7	93.0 (3)	C1–P21–C11	103.7 (4)	C15–C16–C11	120.5 (9)
N–Cr–C8	95.2 (3)	C1–P21–C21	103.5 (4)	C16–C11–C12	118.9 (8)
P34–Cr–N	82.0 (2)	Cr–P34–C4	101.1 (3)	C21–C22–C23	119.7 (1.0)
P34–Cr–C8	85.7 (3)	Cr–P34–C31	127.1 (3)	C22–C23–C24	117.9 (1.0)
P34–Cr–C9	97.2 (3)	Cr–P34–C41	119.0 (3)	C23–C24–C25	121.6 (1.2)
C7–Cr–C8	82.4 (4)	C31–P34–C41	99.5 (4)	C24–C25–C26	120.0 (1.1)
C8–Cr–C9	89.4 (4)	C4–P34–C31	104.7 (4)	C25–C26–C21	121.4 (9)
C7–Cr–C9	88.7 (4)	C4–P34–C41	102.3 (4)	C26–C21–C22	119.3 (8)
P21–Cr–C8	168.1 (3)	Cr–N–C2	110.4 (5)	C41–C42–C43	118.1 (1.1)
P34–Cr–C7	166.7 (3)	Cr–N–C3	114.0 (5)	C42–C43–C44	121.5 (1.1)
N–Cr–C9	175.4 (3)	Cr-N-C5	106.5 (5)	C43–C44–C45	119.0 (1.3)
		C2–N–C5	108.7 (6)	C44–C45–C46	119.5 (1.2)
P21–C1–C2	108.3 (6)	C3–N–C5	108.9 (6)	C45–C46–C41	122.5 (9)
C1–C2–N	112.1 (7)	C2–N–C3	108.2 (6)	C46–C41–C42	119.4 (8)
N–C3–C4	111.7 (7)			C31–C32–C33	119.6 (1.0)
P34–C4–C3	109.8 (6)	P21–C11–C12	118.6 (7)	C32–C33–C34	118.8 (1.0)
N–C5–C6	115.5 (8)	P21–C11–C16	122.5 (7)	C33–C34–C35	121.2 (1.1)
		P21–C21–C22	116.8 (7)	C34–C35–C36	120.7 (1.2)
		P21–C21–C26	123.9 (7)	C35–C36–C31	120.4 (9)
Cr–C7–O7	174.0 (8)	P34–C31–C32	118.0 (7)	C36–C31–C32	119.0 (9)
Cr–C8–O8	172.9 (7)	P34–C31–C36	122.9 (7)	Av	120.0 (2)
Cr–C9–O9	177.6 (8)	P34–C41–C42	119.4 (6)		
		P34–C41–C46	121.1 (6)		

lengthening of the Cr–N bonds in Cr(CO)$_3$dien itself due to ring strain. The three Cr–N bonds in Cr(CO)$_3$dien are of equal length within experimental error, but perhaps here the effects of ring strain are distributed evenly over the three.

The structure of a complex containing the related ligand ((C$_6$H$_5$)$_2$PCH$_2$CH$_2$)$_2$NH has recently been reported,[16] and it is interesting to observe that some similar bond length anomalies are found here also. The two P, the N, and one of the Br atoms of Ni(PNP)Br$_2$ (where PNP is here used for the ligand with H instead of C$_2$H$_5$ on N) occupy the basal positions of a square-pyramidal, low-spin Ni(II) complex. While the Ni–N distance of 2.01 Å might superficially appear "normal," proper consideration shows that it is in fact $\geq$0.1 Å "too long." It has been shown[17] that for low-spin square-coordinated Ni(II), the Ni–O distances are some 0.17 Å shorter than in high-spin octahedral Ni(II) complexes with comparable ligands. This has been attributed to the absence of Ni–O antibonding d electrons in the square complex. An entirely analogous situation should prevail in Ni(PNP)Br$_2$, and a "normal" Ni–N distance should be some 0.17 Å shorter than that in high-spin octahedral Ni(II) amine complexes. This has actually been observed in structural studies of certain Lifschitz salts[18] in which it is found that Ni–N distances in the high-spin square species are 1.89 Å, a difference of 0.16 ± 0.02 Å. Thus, the actual Ni–N distance in Ni(PNP)Br$_2$ appears to be at least 0.1 Å "too long." From another point of view, the Ni–Br bond length may be taken as normal, since it is not subject to any obvious strain effects. The difference between the single bond radii[19] of Br and N is 0.44 Å, whereas the observed Ni–Br and Ni–N distances differ by only 0.32 Å, again suggesting the Ni–N distance is "too long," by ~0.12 Å.

In view of the large strain effects leading to appreciable deviations of bond angles from ideal octahedral values and the drastic stretching of the Cr–N bond, it is clear that no detailed analysis of Cr–C bond lengths in terms of the π acidity of the P or N atom *trans* to each would be justified. The Cr–C bonds approximately

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[16] P. L. Orioli and L. Sacconi, *Chem. Commun.*, 1310 (1968).

[17] F. A. Cotton and J. J. Wise, *Inorg. Chem.*, 5, 1200 (1966).

[18] S. C. Nyburg and J. S. Wood, *ibid.*, 3, 468 (1964).

[19] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 224.

Table VI. Closest Intermolecular Contacts

Atoms	Vector between molecules	Distance, Å
H16–O8	$^1/_2 - x,\ ^1/_2 + y,\ -z$	2.57
H36–O8	$^1/_2 + x,\ ^1/_2 - y,\ z$	2.62
H23–O7	$-x,\ -y,\ -z$	2.67
H24–O9	$-x,\ -y,\ -z$	2.66
H13–O9	$^1/_2 - x,\ -y,\ ^1/_2 - z$	2.63
H35–H26	$-x,\ -y,\ -z$	2.52
H44–H26	$x,\ ^1/_2 - y,\ ^1/_2 + z$	2.53
H33–H22	$^1/_2 - x,\ -y,\ ^1/_2 - z$	2.50

trans to the P atoms have lengths of 1.822 (9) and 1.832 (9) Å while the one approximately *trans* to N is perhaps slightly shorter, 1.804 (9) Å. This might have been expected, qualitatively, on the basis of π acidity considerations, but cannot be meaningfully analyzed quantitatively.

Other bond distances and angles in this molecule are normal. Thus the C–O distances are 1.16–1.18 Å, the P–C distances are in the range 1.825–1.849 Å, and the C–C distances in the phenyl rings average 1.381 Å.

A New Bonding Model for Olefinic and Acetylenic Complexes of Transition Metals

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Abstract: Semiempirical one-electron molecular orbital calculations were performed for a series of platinum–acetylene and –olefin complexes. The results indicate that the Dewar–Chatt–Duncanson model can be modified and extended to include the acetylenic complexes. A consistent hybridization scheme, dp^2, is developed to explain the chemical and physical properties of these complexes.

Since the discovery of Zeise's salt, olefin and acetylene complexes of transition metals have presented an anomalous chemistry of great interest. Although the chemistry is well developed, a coherent theory of bonding in these complexes is still lacking. Recent attempts at explaining chemical behavior have led to invoking one argument or the other depending on the properties to be explained.

The most acute question is whether to represent the bonding in olefinic and acetylenic metal complexes as being one of two extreme types: (1) a doubly σ bonded cyclopropyl type structure, or (2) a dative bond involving π orbitals on the organic moiety.[2a] The Dewar–Chatt–Duncanson (DCD) model of bonding for olefinic complexes[2b] has successfully synthesized these two viewpoints. The model involves donation of olefin π electrons to an sp^2 metal hybrid which is synergically opposed by d back donation to the olefin π antibonding orbital.

The bonding in acetylenic complexes remains to be satisfactorily explained. The σ bond–π bond dichotomy has led to an artificial rather than an actual distinction between the two modes of bonding.[3] Thus a consistent picture of bonding for these compounds would be very useful.

Semiempirical one-electron molecular orbital calculations were therefore performed for a series of zerovalent platinum complexes in order to determine the most probable mode of bonding. The model compounds were $(PH_3)_2(CH_3C{\equiv}CCH_3)Pt$, $(PH_3)_2(CH_3C{\equiv}CH)Pt$, and $(PH_3)_2[(CN)_2C{=}C(CN)_2]Pt$, in both square-planar and pseudotetrahedral configurations.

The calculations were performed and a hybridization scheme consistent with the more general theoretical approach was derived. The scheme explains the observed physical and chemical properties and also has the virtue of an easy pictorialization.

Method

The molecular orbitals were determined as a linear combination of atomic orbitals by solution of the secular equation

$$HC = SCE \tag{1}$$

where H is the effective Hamiltonian matrix, S the overlap matrix, E the diagonal matrix of molecular orbital energies, and C the matrix of LCAO coefficients. The diagonal H matrix elements, H_{ii}, were taken as the neutral atom VSIP. The off-diagonal H matrix elements, H_{ij}, were evaluated according to Cusachs and Cusachs[4]

$$-H_{ii} = \text{VSIP} \tag{2}$$

$$H_{ij} = {}^1/_2(H_{ii} + H_{jj})S_{ij}(2 - |S_{ij}|) \tag{3}$$

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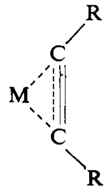
(1) NDEA predoctoral fellow.

(2) (a) R. Ugo, *Coord. Chem. Rev.*, 3, 319 (1968); (b) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 18c, 79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(3) (a) J. A. Pople, *Quart. Rev.* (London), 11, 273 (1957); (b) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, 46, 3879 (1968), and references therein. It is noteworthy that these authors have concluded from mainly chemical arguments that these complexes should be regarded as platinum(0) complexes and they suggest representing them as



This in our opinion is the least misleading representation yet proposed.

(4) L. C. Cusachs and B. B. Cusachs, *J. Phys. Chem.*, 71, 1060 (1967).