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A Bent *vs.* Linear Nitrosyl Paradox. Infrared and X-Ray Photoelectron Spectra of $CoCl_2(NO)L_2$ and Crystal Structure with $L = P(CH_3)(C_6H_5)_2$

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Received August 27, 1972

Infrared, pmr, and X-ray photoelectron spectral data are presented to substantiate the existence of conformational isomers of the nitrosyl complexes $CoCl_2(NO)L_2$. The first isomer A has trigonal-bipyramidal geometry with a linear nitrosyl (NO^+) while the second isomer B is believed to have square-pyramidal geometry with a bent nitrosyl (NO^-) at the apex. A low-temperature crystalline form of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$ containing almost solely isomer A was found to transform partially to B by grinding in preparation for a Nujol mull. Nitrogen 1s electron binding energies suggest an unexpectedly high preference for isomer B at the surface of most solid samples. The crystal and molecular structures of the room-temperature form of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$ have been determined from three-dimensional X-ray data collected at room temperature by counter methods. The material crystallizes with 8 molecules in space group $C_{2h}{}^6$-$C2/c$ of the monoclinic system in a cell of dimensions $a = 16.970$ (14), $b = 17.035$ (9), $c = 18.735$ (8) Å, and $\beta = 108.00$ (2)°. The calculated and observed densities are 1.445 and 1.44(2) g cm^{-3}, respectively. The structure has been solved and refined by conventional means. The final R factor (on F) for the 2428 unique reflections having $F_o{}^2 > 3\sigma(F_o{}^2)$ is 0.046. The resultant structure is of isomer A, a somewhat distorted trigonal bipyramid, and there is no evidence for the coexistence of isomer B in the crystal used in the X-ray analysis.

Introduction

Recently, we presented[3] infrared data on a series of cobalt nitrosyl complexes, $CoCl_2(NO)L_2$, consistent with the existence of conformational equilibria between the two limiting forms of metal-nitrosyl bonding displayed by five-coordinate transition metal nitrosyl complexes, *i.e.*, the so-called bent and linear forms. To substantiate further this hypothesis a single-crystal X-ray structure determination of one of the complexes has been undertaken as well as X-ray photoelectron spectra and further infrared studies. Rather than simplifying the issue the new results have provided an interesting set of contradictions which can only be explained by consideration of the precise nature of the material under investigation and the limitations of the physical techniques used in the investigation.

Experimental Section

Preparations. Preparative reactions involving nitrosyl complexes or air-sensitive phosphines were carried out in degassed solvents under a nitrogen atmosphere using Schlenk-tube techniques. Nitric oxide was prepurified by passage through a silica gel tube cooled to −77°. ^{15}N nitric oxide was supplied by Mallinckrodt.

X-Ray powder patterns were run with Cu Kα radiation (Ni filtered) using 5% NaCl as an internal standard. Melting points are not given since decomposition of the nitrosyl complexes to blue solids occurs prior to melting. A Cahn Faraday electrobalance was used to test for paramagnetism. Grinding samples for solid infrared spectra was done manually with an agate mortar and pestle. Grinding in an inert atmosphere was done in a Vacuum Atmospheres drybox. A Perkin-Elmer Model 457 infrared spectrometer was used and pmr spectra were recorded on Varian A-60 or T-60 models using TMS as internal standard.

The starting complexes $CoCl_2L_2[L = P(C_2H_5)_3$, $P(n\text{-}C_4H_9)_3$, $P(CH_3)_2(C_6H_5)$, $P(CH_3)(C_6H_5)_2$, $P(C_6H_5)_3$, and $P(p\text{-}CH_3C_6H_4)_3]$ were prepared[4] by addition of stoichiometric amounts of the appropriate phosphine to acetone solutions of $CoCl_2 \cdot 6H_2O$ and isolated as intensely blue solids by the addition of hexane. The nitrosyl complexes were prepared by direct reaction of solutions of $CoCl_2L_2$ with nitric oxide essentially following the procedures of Booth and Chatt[4] although solvents and work-ups were altered to accommodate the differing solubilities of the phosphine ligands. The following procedures are typical.

$CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$. (i) Room-Temperature Form. Nitric oxide was bubbled briefly through a saturated dichloromethane solution of 200 mg of $CoCl_2(P(CH_3)(C_6H_5)_2)_2$. Ethanol (60 ml) was added gradually and after several hours the dark brown crystals were filtered, washed with ethanol, and vacuum dried (190 mg, 90%). Pmr in $CDCl_3$: τ 7.5 (t, CH_3, $J_{PH} = 4$ Hz); τ 2.6 (m, C_6H_5). *Anal.* Calcd for $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$: C, 55.75; H, 4.7; N, 2.5; Cl, 12.7. Found: C, 55.45; H, 4.6; N, 2.5; Cl, 12.3. The triphenylphosphine and tri(p-tolyl)phosphine complexes were prepared in a similar manner. *Anal.* Calcd for $CoCl_2(NO)(P(C_6H_5)_3)_2$: C, 63.2; H, 4.4; N, 2.05. Found: C, 62.85; H, 4.5; N, 2.0. Calcd for $CoCl_2(NO)(P(p\text{-}CH_3C_6H_4)_3)_2$: C, 65.2; H, 5.45; N, 1.8. Found: C, 64.95; H, 5.75; N, 1.6.

(ii) Low-Temperature Form. To a suspension of 1 g of $CoCl_2(P(CH_3)(C_6H_5)_2)_2$ in 35 ml of ethanol was added just sufficient dichloromethane to dissolve the blue crystals. Nitric oxide was bubbled briefly through the solution which was then quickly cooled to −77°. After 2 hr 60 ml of cold (−77°) hexane was added and after several hours the light brown crystals were filtered, washed with cold (−77°) ethanol followed by cold hexane, and quickly vacuum dried at room temperature (950 mg, 90%). *Anal.* Calcd for $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$: C, 55.75; H, 4.7; N, 2.5. Found: C, 55.55; H, 4.6; N, 2.5.

$CoCl_2(NO)(P(CH_3)_2(C_6H_5))_2$. An ethanol suspension (10 ml) of 500 mg of $CoCl_2(P(CH_3)_2(C_6H_5))_2$ was treated briefly with a stream of nitric oxide and then left at −10° to crystallize. The dark brown crystals were filtered, washed with cold ethanol, followed by cold hexane, and vacuum dried (400 mg, 80%). The solid was stored in a sealed tube under argon. Pmr in $CDCl_3$: τ 7.95 (t, CH_3, $J_{PH} = 5$ Hz); τ 2.4 (m, C_6H_5). *Anal.* Calcd for $CoCl_2(NO)(P(CH_3)_2(C_6H_5))_2$: C, 44.05; H, 5.1; N, 3.2. Found: C, 44.1; H, 5.1; N, 3.4. The triethylphosphine and tri(n-butyl)phosphine complexes were prepared in a similar manner using hexane as solvent. *Anal.* Calcd for $CoCl_2(NO)(P(C_2H_5)_3)_2$: C, 36.4; H, 7.55; N, 3.55; Cl, 17.9. Found: C, 36.3; H, 7.4; N, 3.85; Cl, 18.2. Calcd for $CoCl_2(NO)(P(C_4H_9)_3)_2$: C, 51.0; H, 9.6; N, 2.5. Found: C, 51.2; H, 9.6; N, 2.55.

Collection and Reduction of Intensity Data. Dark brown, well-formed crystals of $Co(NO)Cl_2(P(CH_3)(C_6H_5)_2)_2$ were grown from acetone at 0°. Preliminary precession photographs using Cu Kα radiation showed Laue symmetry $2/m$, indicating that the crystals belong to the monoclinic system. The extinctions observed, $h0l$ for either h or $l = 2n + 1$, $0k0$ for $k = 2n + 1$, and hkl for $h + k = 2n + 1$ are consistent with either the space group $C2/c$ or the related noncentrosymmetric group Cc.

The crystal selected for data collection was a flat plate of approximate dimensions 0.42 × 0.42 × 0.16 mm. The twelve faces bounding the crystal were identified by optical goniometry as belonging to the $\{010\}$, $\{001\}$, $\{111\}$, and $\{\bar{1}11\}$ forms. In order to minimize multiple diffraction effects,[5] the crystal was mounted so that no symmetry axis was coincident with the spindle axis.

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All measurements were made using a Picker FACS-I computer-controlled four-circle X-ray diffractometer equipped with scintillation counter, pulse height analyzer, and graphite monochromator. Preliminary cell constants and the orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of twelve reflections with 2θ values of 20–25° which had been centered on the Mo $K\alpha_1$ peak, λ 0.70930 Å. The refinement was carried out on a PDP-8/L computer using the logic of the FACS-I system.[6] The mosaicity of the crystal was measured by means of the narrow-source, open-counter, ω-scan technique. At a takeoff angle of 1.1°, the peak widths at half-height of three reflections surveyed were 0.05° or less.

Intensity data were collected as previously described.[7,8] Molybdenum radiation was reflected from the (002) face of a graphite crystal, resulting in an incident beam of monochromatized Mo $K\alpha$ radiation. The intensities were measured by the θ–2θ scan technique at a takeoff angle of 2.06°. At this angle the intensity of a reflection is about 80% of the maximum value as a function of the takeoff angle. A symmetric scan range in 2θ was used, the scan ranging from 1.0° below the Mo $K\alpha_1$ peak center to 1.0° above the Mo $K\alpha_2$ peak center. For data with 2θ values of over 36° such a large scan was not necessary, and the range was reduced to 0.6° on either side of the Mo $K\alpha$ peak. The background was measured at each end of the scan. The data were collected in two shells; for those reflections where $0° \leqslant 2\theta$ (Mo $K\alpha_1$) $\leqslant 33°$, the scan rate was 1.0°/min with 20-sec background counts, while for the data $33° \leqslant 2\theta$ (Mo $K\alpha_1$) $\leqslant 44°$, a scan rate of 0.5°/min with 40-sec background counts was used. Attenuators were inserted automatically if the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan; the attenuators used were Cu foils, whose thickness had been chosen to give attenuator factors of approximately 2.3. The pulse height analyzer was set for approximately a 90% window centered on the Mo $K\alpha$ peak. Five standard reflections from diverse parts of reciprocal space were measured after every 100 reflections in the first shell and after every 50 reflections in the second shell to test for crystal decomposition and electronic stability.

The intensities of 3304 reflections were measured for the unique quadrant of reciprocal space with $2\theta \leqslant 44°$; of these, 876 had $I \leqslant 3\sigma(I)$ and were omitted from the refinement. Beyond this point, there were very few reflections of significant intensity. At the end of regular data collection, all 434 reflections of the form $\{hkl\}$ with $2\theta \leqslant 14°$ were measured as an aid in deciding between the space groups $C2/c$ and Cc. All data were processed as previously described;[8] and the values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. The value of p in the formula for the standard deviations of the corrected intensities was chosen as 0.04.

At the end of data collection twelve reflections with 2θ values between 25 and 30° were recentered on the Mo $K\alpha_1$ peak in order to determine the cell constants more accurately. The setting angles for these reflections were used as the observations for the least-squares refinement of the cell constants and the orientation matrix using a modification of the program PICK[7] for the CDC 6400 computer. This refinement resulted in lower standard deviations for the cell constants and in substantially better agreement between observed and calculated values of the setting angles than had been obtained using the FACS-I system. In order to ascertain if this improved agreement significantly changed the orientation matrix used for data collection, the intensities of six reflections of varying χ and ϕ values were measured first using the original FACS-I matrix and then using the one generated by PICK. Averaging over five measurements for each intensity, no significant differences were observed. It has been our experience, however, that data collected using the orientation matrix refined on the CDC 6400 leads to lower agreement factors than data collected using the FACS-I logic for crystal orientation.

The unit cell parameters at 21° are $a = 16.970$ (14), $b = 17.035$ (9), $c = 18.735$ (8) Å, and $\beta = 108.00$ (2)°. The density calculated for eight molecules in the unit cell is 1.445 g/cm³, which agrees well with the experimental density of 1.44 (±0.02) g/cm³ measured by suspension in an aqueous solution of $ZnCl_2$. In the space group $C2/c$, the order of the general position is 8, while in Cc it is 4. Thus if the noncentrosymmetric space group were the correct choice, there would be two independent molecules in the asymmetric unit. A comparison of the intensities of the Friedel pairs showed no differences in intensity significantly larger than those which would be expected on the basis of counting statistics alone; the space group was therefore assumed to be $C2/c$. This choice was confirmed by successful solution of the structure, and by the location of the methyl hydrogen atoms from difference Fourier syntheses.

Solution and Refinement of Structure. The heavy atoms in the structure were located using the MULTAN series of programs for direct-phase determination written by Main, Woolfson, and Germain. Normalized structure factors were computed and the 298 reflections having $E \geqslant 1.70$ were used in the phasing procedure. The highest peaks in the E map calculated from the solution with the highest figure of merit, 1.043, were at the special positions $^1/_4$, $^1/_4$, 0 and 0, y, $^1/_4$, $y = 0.26$. These positions have point symmetry i and m, respectively; if they corresponded to cobalt atoms the molecule would have to be disordered or disproportionated. Placing the cobalt atoms at these locations did not lead to solution of the structure; consequently, an E map was calculated from the set of phases with the second highest figure of merit, 1.041. This map showed the positions of the cobalt, the two chlorine, and the two phosphorus atoms. These atoms were located at general positions, and there was no evidence for a second independent molecule in the asymmetric unit.

Refinement of the structure was carried out by full-matrix least-squares techniques.[9] Throughout the refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and where weight w is $4F_o^2/\sigma^2(F_o^2)$. The agreement factors R_1 and R_2 are defined as $R_1 = \Sigma\| F_o| - |F_c\|/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$. The scattering factors for Cl, P, O, N, and C were taken from the usual tabulation,[10] while those for Co were calculated by Cromer and Waber.[11] The hydrogen scattering factors were those of Stewart, *et al.*[12] The effects of anomalous dispersion were taken into account in the structure factor calculations,[13] the values of $\Delta f'$ and $\Delta f''$ for Co, Cl, and P being those given by Cromer and Liberman.[14]

After two cycles of least-squares refinement of the scale factor and of the positional parameters and temperature factors of the five heavy atoms, the agreement factors R_1 and R_2 were 0.39 and 0.48, respectively. A difference Fourier synthesis based on a subsequent structure factor calculation revealed the positions of the four phenyl rings, the two methyl carbons, and the nitrogen atom. The rings were treated as rigid groups[15,16] of D_{6h} symmetry, d(C–C) = 1.397 Å, in subsequent least-squares refinements. They were assigned group temperature factors, while the nongroup atoms were refined with individual isotropic thermal parameters. Two more cycles of refinement lowered the agreement factors to 0.12 and 0.16, respectively. A second difference synthesis located the oxygen atom; isotropic refinement of all atoms converged with agreement factors of 0.080 and 0.106.

At this point the data were corrected for absorption and decomposition. Even though the linear absorption coefficient of the compound is low, 9.49 cm⁻¹, the absorption correction is important since the crystal has a nonequant habit. Transmission factors ranged from 0.868 to 0.680. A plot of the standard reflections showed a loss of intensity with time. A linear correction corresponding to overall decomposition of 4.5% was applied to the data.

In further refinements, the nongroup atoms were allowed to vibrate anisotropically and the group atoms were given individual isotropic thermal parameters. After two cycles of anisotropic refinement, the hydrogen atom positions around the two methyl groups were located from difference Fourier syntheses. These positions were idealized (d(C–H) = 1.00 Å, H–C–H = 109.5°), as were the hydrogen positions around the phenyl rings (D_{6h} symmetry, d(C–H) = 1.00 Å). Each hydrogen atom was assigned an isotropic temperature factor 1

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[7] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

[8] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 6, 204 (1967).

[9] In addition to various local programs for the CDC 6400 computer, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program; the Busing–Levy ORFFE error function program; and Johnson's ORTEP thermal ellipsoid plotting program. Our local least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program, and Cahen's program AGNOST for absorption corrections includes the Coppens–Leiserowitz–Rabinovich logic for gaussian integration.

[10] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, Table 3.3 1A.

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Table I. Positional, Thermal, and Group Parameters for $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.13484 (4)[b]	0.23427 (4)	0.12697 (4)	0.00254 (3)	0.00228 (3)	0.00221 (3)	0.00020 (2)	0.00059 (2)	0.00000 (2)
P(1)	0.27368 (8)	0.23588 (8)	0.17872 (8)	0.00246 (6)	0.00224 (5)	0.00233 (5)	0.00022 (4)	0.00087 (4)	0.00010 (4)
P(2)	0.00107 (8)	0.24785 (8)	0.05667 (8)	0.00256 (6)	0.00239 (5)	0.00203 (5)	0.00007 (4)	0.00051 (4)	0.00000 (4)
Cl(1)	0.15482 (9)	0.35117 (8)	0.07480 (9)	0.00349 (7)	0.00239 (5)	0.00367 (6)	−0.00001 (5)	0.00081 (5)	0.00060 (4)
Cl(2)	0.15277 (10)	0.13572 (9)	0.05240 (9)	0.00455 (8)	0.00312 (6)	0.00350 (6)	0.00012 (5)	0.00127 (5)	−0.00064 (5)
C(1)	0.3294 (4)	0.2407 (4)	0.1107 (3)	0.0036 (3)	0.0043 (3)	0.0027 (2)	0.0004 (2)	0.0018 (2)	0.0003 (2)
C(2)	−0.0121 (4)	0.2486 (4)	−0.0433 (3)	0.0037 (3)	0.0039 (3)	0.0021 (2)	0.0000 (2)	0.0006 (2)	−0.0001 (2)
N	0.1105 (3)	0.2087 (3)	0.2056 (3)	0.0024 (2)	0.0035 (2)	0.0022 (2)	0.0003 (2)	0.0007 (1)	0.0002 (1)
O	0.0887 (4)	0.1787 (4)	0.2464 (3)	0.0082 (4)	0.0085 (4)	0.0051 (3)	0.0011 (3)	0.0034 (3)	0.0014 (3)

Group	x_c[c]	y_c	z_c	δ	ϵ	η
R11	0.3573 (1)	0.0888 (1)	0.2829 (1)	−1.072 (2)	3.101 (2)	0.486 (2)
R12	0.3393 (2)	0.3775 (2)	0.2959 (2)	−0.970 (4)	2.285 (2)	1.997 (4)
R21	0.1232 (2)	0.1097 (2)	0.4291 (1)	−0.832 (2)	2.978 (3)	−0.263 (3)
R22	0.0818 (2)	0.4054 (2)	0.4054 (1)	2.999 (7)	1.975 (2)	−1.890 (7)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [c] The angles δ, ϵ, and η (in radians) which bring about alignment (except for translation) of an internal system within the group with a fixed external coordinate system are those previously described.[15,16]

Å² larger than that of carbon atom to which it is attached. In subsequent structure factor calculations the contributions of these hydrogen atoms were taken into account. The refinement converged in two cycles to give agreement factors of 0.046 and 0.058 for the 2428 unique reflections having $I > 3\sigma(I)$. The two largest peaks in the final difference Fourier synthesis have heights of 0.98 and 0.96 e/Å³, about one-fifth of a carbon peak, and are associated with the phenyl rings.

Inspection of the data shows that no correction for extinction is necessary, and comparisons of $\Sigma w(|F_o| - |F_c|)^2$ for various classes of reflections based on $|F_o|$, Miller indices, and the scattering angle show no significant trends. The error in a reflection of unit weight is 1.93 e. Of the reflections omitted from the refinement for which $F_o^2 < 3\sigma(F_o^2)$, none had $F_o^2 - F_c^2 > 4.9\sigma(F_o^2)$.

The final least-squares parameters are given in Table I, with the standard deviations of these parameters as derived from the inverse matrix. The parameters of the ring carbon atoms which may be derived from the data in Table I are presented in Table II, together with the thermal parameters as obtained from the last cycle of least-squares refinement. The calculated positions of the methyl hydrogen atoms are given in Table III. The final values of $10|F_o|$ and $10|F_c|$ in electrons are given in Table IV; only the reflections which were used in the refinement are listed in this table.[17]

X-Ray Photoelectron Spectra. Spectra were taken on an AEI ES 100B photoelectron spectrometer, using either a Mg (1253.6 eV) or an Al (1486.6 eV) source of incident radiation. Although the half-width of the Al source is larger than that of the Mg source, the contribution of the line width of the source to the peak is not significant in relation to the errors in the half-widths observed for the nitrogen 1s peaks. In general, the improvement of several tenths of 1 eV in the observed peak widths using Mg Kα radiation did not justify the 50% loss of intensity in going from Al to Mg Kα radiation. Samples were mounted by dusting them onto a thin film of Corning Hyvac silicone grease spread on an aluminum plate. In this way no pressure was applied to the sample during the mounting procedure. An exception was the low-temperature form of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$, which was ground in a mortar and pressed directly onto the aluminum plate prior to taking the spectrum. Since the complex $CoCl_2(NO)(P(CH_3)_2(C_6H_5))_2$ appeared to be air sensitive, the sample, which had been stored under argon, was mounted and transferred to the sample chamber under a nitrogen atmosphere. Spectra were collected digitally under the control of a PDP-8/S computer programmed to perform time averaging. Channel counts were monitored periodically to check on stability of the sample and change of the spectrum with time. In an attempt to reduce crystal decomposition, the spectra were taken at −80 (±10)°. The position of the carbon 1s peak (of the phenyl rings) was measured as an internal standard, the binding energy of the carbon 1s electrons being taken as 285.0 eV.[18]

Table II. Derived Parameters for Ring Carbon Atoms[a]

Atom	x	y	z	B, Å²
R11C1	0.3193 (2)	0.1517 (2)	0.2373 (2)	2.7 (1)
R11C2	0.2727 (2)	0.0863 (2)	0.2442 (2)	3.5 (1)
R11C3	0.3106 (2)	0.0233 (2)	0.2898 (2)	3.8 (1)
R11C4	0.3953 (2)	0.0258 (2)	0.3284 (2)	3.7 (1)
R11C5	0.4419 (2)	0.0912 (2)	0.3215 (2)	4.1 (1)
R11C6	0.4040 (2)	0.1542 (2)	0.2759 (2)	3.7 (1)
R12C1	0.3104 (2)	0.3176 (2)	0.2432 (2)	2.9 (1)
R12C2	0.2844 (2)	0.3212 (2)	0.3071 (2)	3.7 (1)
R12C3	0.3133 (3)	0.3811 (2)	0.3598 (2)	4.5 (1)
R12C4	0.3682 (3)	0.4374 (2)	0.3486 (2)	5.6 (2)
R12C5	0.3942 (3)	0.4337 (2)	0.2848 (3)	6.1 (2)
R12C6	0.3653 (3)	0.3738 (2)	0.2321 (2)	4.7 (1)
R21C1	0.0698 (2)	0.1706 (2)	0.4333 (2)	3.1 (1)
R21C2	0.0420 (2)	0.0929 (2)	0.4264 (3)	4.7 (1)
R21C3	0.0954 (3)	0.0320 (2)	0.4223 (3)	5.6 (2)
R21C4	0.1767 (2)	0.0488 (2)	0.4250 (3)	5.4 (2)
R21C5	0.2045 (2)	0.1264 (3)	0.4319 (3)	5.5 (2)
R21C6	0.1511 (2)	0.1874 (2)	0.4360 (2)	4.2 (1)
R22C1	0.0442 (2)	0.3382 (2)	0.4228 (2)	2.9 (1)
R22C2	0.0672 (3)	0.3995 (2)	0.4748 (2)	3.9 (1)
R22C3	0.1048 (3)	0.4668 (2)	0.4574 (2)	4.9 (1)
R22C4	0.1194 (3)	0.4727 (2)	0.3880 (2)	5.2 (1)
R22C5	0.0964 (3)	0.4114 (2)	0.3360 (2)	5.2 (1)
R22C6	0.0588 (3)	0.3441 (2)	0.3534 (2)	4.0 (1)

[a] C1 is attached to P; other C atoms are numbered in succession so that C4 is para to C1.

Table III. Calculated Hydrogen Positional Parameters

Atom	x	y	z
C(1)H(1)	0.391	0.242	0.137
C(1)H(2)	0.316	0.194	0.076
C(1)H(3)	0.314	0.290	0.080
C(2)H(1)	0.004	0.196	−0.059
C(2)H(2)	−0.070	0.260	−0.072
C(2)H(3)	0.025	0.290	−0.054

The spectra are shown in Figure 1; peak positions and full-width half-maxima (FWHM) derived from these spectra are given in Table V. Experimental data points were fit with theoretical gaussians using the Du Pont 310 curve resolver. For overlapping peaks, deconvolution was carried out using two gaussian peaks of variable position, area, and half-width. Errors on these parameters are less than 0.2 eV, 10%, and 0.2 eV, respectively. In at least two of the complexes, $CoCl_2(NO)(P(CH_3)_2(C_6H_5))_2$ and the room-temperature form of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$, the spectra were observed to change with time, a peak at low binding energy growing in at the expense of one at high binding energy. The signal-to-noise

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(17) Table IV, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1304.

(18) K. Siegbahn, C. Nordin, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johanson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells AB, Uppsala, 1967.

Table V. Photoelectron Data for $CoCl_2(NO)L_2$[a]

Compd	Ir bands (KBr disk or Nujol mull), cm^{-1}	Peak positions,[b] eV	Rel areas	FWHM, eV	Source
$CoCl_2(NO)(P(CH_3)_2(C_6H_5))_2$	1750 m, 1640 s	(403.3, 399.8)	(43, 57)	(1.9, 2.4)	Al
$CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$					
Room-temp form	1735 s, 1640 m	400.8		2.8	Al
		(402.2, 400.5)	(33, 65)	(1.9, 2.1)	
Low-temp form	1750 s	400.7		2.5	Al
		(402.3, 400.4)	(28, 72)	(2.3, 2.1)	
Low-temp form, ground	1750 s, 1640 m	400.7		3.3	Mg
		(401.8, 400.2)	(32, 67)	(2.3, 2.4)	
$CoCl_2(NO)(P(C_6H_5)_3)_2$	1725 m, 1640 s	400.5		2.5	Mg

[a] Values in parentheses taken from deconvoluted spectra. [b] ±0.5 eV in absolute position.

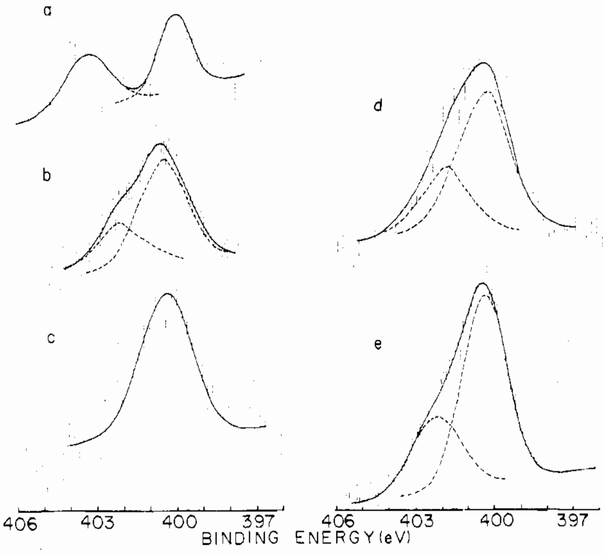

Figure 1. Nitrogen 1s region of X-ray photoelectron spectra: (a) $CoCl_2(NO)(P(CH_3)_2(C_6H_5))_2$; (b) $CoCl_2(NO)(PCH_3(C_6H_5)_2)_2$, room-temperature form; (c) $CoCl_2(NO)(P(C_6H_5)_3)_2$; (d) $CoCl_2(NO)(PCH_3(C_6H_5)_2)_2$, low-temperature form, ground; (e) $CoCl_2(NO)(PCH_3(C_6H_5)_2)_2$, low-temperature form, unground. In deconvoluted spectra, both individual components and resulting peak envelopes are shown.

ratio for the envelope of the two peaks increases with number of counts, but the deconvolution becomes more difficult as one of the signals diminishes in intensity. In these cases, the peak positions and FWHM were taken from the spectra which showed the best resolution.

Results and Discussion

For a series of complexes, $CoCl_2(NO)L_2$, both solution and solid-state infrared spectra exhibit two peaks assigned to an NO stretching mode (Table VI). Since the νNO frequencies are little changed going from solution to solid we suppose the molecular structures giving rise to these bands are not seriously different in the two phases. The most reasonable explanation for the origin of these two bands is that each represents a discrete coordination geometry, the higher ν(NO) arising from a trigonal-bipyramidal complex having a linear nitrosyl, A, and the lower ν(NO) from a square-pyramidal complex with a bent nitrosyl, B. Within the oxidation state formalism it is convenient to label A as an NO^+ complex of Co(I) and B as an NO^- complex of Co(III). In solution the two forms, A and B, are thought to be in rapid, dynamic equilibrium

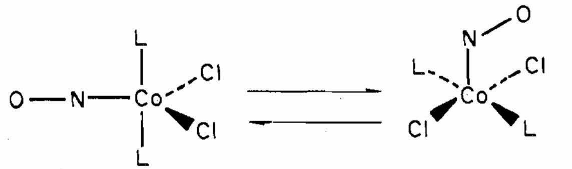

Table VI. Infrared Data on Cobalt Nitrosyl Complexes

No.	Compd	ν(NO), cm^{-1} [a]
1	$CoCl_2(NO)(P(C_2H_5)_3)_2$	1720 w, 1650 s (1720 m), (1640 s)
2	$CoCl_2(NO)(P(n\text{-}C_4H_9)_3)_2$	1750 s, 1650 s (1720 m), (1650 s)
3	$CoCl_2(NO)(P(CH_3)_2(C_6H_5))_2$	1760 m, 1650 s (1750 m), (1640 s)
4	$CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$ (room-temp form)	1750 m, 1650 s 1725,[b] 1620 s[b] (1735 s), (1640 m)
5	$CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$ (low-temp form)	1750 m, 1650 s (1750 s)[c] (1750 s), (1640 m)
6	$CoCl_2(NO)(P(C_6H_5)_3)_2$	1715 m, 1655 s (1725 m), (1640 s) (1685 m),[b] (1603 s)[b]
7	$CoCl_2(NO)(P(p\text{-}CH_3C_6H_4)_3)_2$	1712 s, 1650 w (1710 m), (1650 s)

[a] All spectra recorded in CH_2Cl_2 solution except those in parentheses, which were determined in KBr pellets. [b] ^{15}N peaks.
[c] Negligibly ground sample as Nujol mull.

In the solid state each form should be frozen by the crystal lattice. A model for the proposed Co(III) structure B exists in $IrCl_2(NO)(P(C_6H_5)_3)_2$, which has been shown[19] by X-ray diffraction to exhibit a square-pyramidal coordination geometry with a bent NO at the apex. The nitrosyl stretching frequency[20] is low, 1560 cm^{-1}, and a single similar ν(NO) is observed in solution. Lacking a structural analog of A we chose to examine the solid-state structure of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$, **4**, which on the basis of its solid-state ir spectrum appeared to exhibit a major proportion (>85%) of the form represented by A. An X-ray diffraction structure of a single crystal of **4** revealed *only* the presence of form A. On the other hand, X-ray photoelectron spectra and infrared evidence suggest the presence of significant amounts of form B in solid samples of **4**. This paradox is discussed later on.

Infrared Spectra. Several experimental observations corroborate the presence of two distinct complexes A and B in solution and presumably in the solid state. The assignment of ν(NO) was confirmed by ^{15}N substitution for **4** and **6** (Table VI) and in accord with the general observation that bent nitrosyls have somewhat low stretching frequencies the lower of the two NO bands is assigned to B. The solution infrared spectrum of **4** was measured over the temperature range +30 to −70°. At room temperature the 1640-cm^{-1} band is slightly more intense (Figure 2d) but as the temperature is lowered (Figure 2e) the 1750-cm^{-1} band increases at the expense of the 1640-cm^{-1} band in a smooth reversible manner. The summation of absorbances remained constant within experimental error throughout this temperature range

[19] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 10, 1035 (1971).
[20] C. A. Reed and W. R. Roper, *J. Chem. Soc. A*, 3054 (1970).

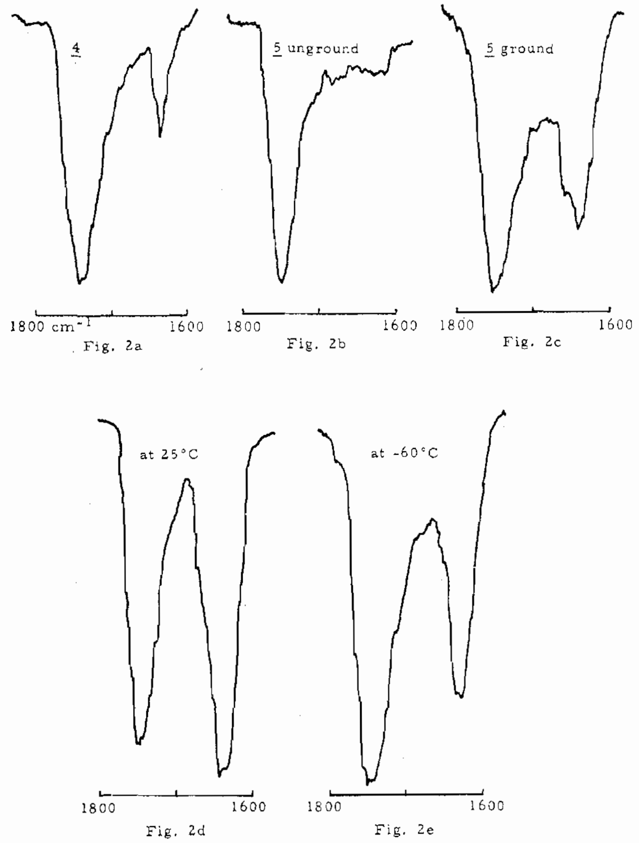

Fig. 2a Fig. 2b Fig. 2c

Fig. 2d Fig. 2e

Figure 2. Infrared spectra of various forms of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$ in the ν(NO) region. Spectra 2a and 2b recorded as Nujol mulls, 2c as a KBr disk, and 2d and 2e in dichloromethane.

ruling out a concentration-dependent equilibrium. Throughout the series **1-6**, the relative intensities of the two NO bands in solution are dependent on the nature of phosphine—the lower band predominating as the phosphine becomes more basic. This is consistent with the proposed equilibrium of A and B, the more basic ligands stabilizing the bent nitrosyl cobalt(III) form, B. The greater stability toward air oxidation of the complexes having more basic phosphines is also consistent with this hypothesis.

The air-stable complexes, **1** and **2**, exhibited monomeric molecular weights but reliable data could not be obtained for the other air-sensitive complexes. Within experimental error the ratio of the ν(NO) absorbances of **4** remained constant throughout a fourfold dilution further ruling out a monomer-dimer concentration-dependent equilibrium as the origin of the two ν(NO) bands. Conductivity measurements on **4** in CH_2Cl_2 showed it to be a nonelectrolyte ruling out ionization as the cause of the two ν(NO) bands. Both the dimethylphenylphosphine and methyldiphenylphosphine complexes **3** and **4** display a single well-resolved methyl 1:2:1 triplet consistent with the presence of trans phosphine groups. This precludes cis-trans isomers and indicates rapid equilibration of A and B on the pmr time scale. Cooling to −80° does not freeze out two methyl signals in either **3** or **4**. Collapse of the triplet with added free phosphine occurs with **3** but not **4**; presumably the less bulky $P(CH_3)_2(C_6H_5)$ confers greater substitution lability on **3**. The complexes when prepared free of starting materials are diamagnetic in both the solid state and solution, excluding the possibility of a spin equilibrium giving rise to two NO frequencies as has been observed for Fe(NO)(salen).[21] Several of the complexes show a number of bands in the far-infrared region 300-400 cm^{-1} attributable to ν(Co-Cl) but without comparison to series of bromide or iodide analogs we could not make unambiguous assignments.

One interesting experiment was the isolation of two crystalline forms of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$, the first, **4**, at room temperature having two ν(NO) frequencies (*ca.* 1750, 1650 cm^{-1}) (the single-crystal structure of this form has been determined) and the second, **5**, isolated at low temperature (−77°), having only a single ν(NO) frequency at 1750 cm^{-1} corresponding solely to the NO^+ complex (Figure 2a and 2b, respectively). More interesting, however, was the observation that grinding this low-temperature form, **5**, in preparation for a Nujol mull, induced the appearance of the 1650-cm^{-1} band. In fact, rigorous grinding followed by pressing into a KBr pellet effects approximately 30% conversion to the low-ν(NO) isomer corresponding to a considerably greater 1650:1750 ratio than that of the room-temperature form which is not detectably pressure sensitive. This effect is displayed in Figure 2b and 2c. The two crystalline forms have quite different X-ray powder patterns and the powder pattern of the *heavily ground* low-temperature form, **5**, showed low resolution with a high background typical of partially amorphous material. We suspect that a pressure-triggered isomerization from the NO^+ to the NO^- isomer occurs upon grinding and that the attendant stereochemical change destroys some crystallinity. The photoelectron spectra, discussed in detail below, indicate that the isomerization is largely a surface phenomenon. That a sample of **5** ground at low temperature has the same solid infrared spectrum as one ground at room temperature implicates a pressure- rather than a temperature-induced isomerization and that solution spectra of ground and unground **5** are identical with one another and with the spectrum of **4** rules out the possibility of decomposition giving rise to the 1650-cm^{-1} band. Atmospheric considerations were also ruled out by grinding **5** and preparing a Nujol mull in an inert atmosphere; the ir spectrum was identical with one prepared in air. Pressure-induced changes in an infrared spectrum have been mentioned[22] but the magnitude of the ν(NO) shift (100 cm^{-1}) in this case indicates a gross stereochemical change rather than a change merely in crystal packing. In spite of the metastable nature of this low-temperature crystal form **5**, we believe the coordination geometry to be quite similar to that found in the room-temperature form, **4**, described in detail below.

Description of the Structure of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$. The structure consists of discrete, well-separated molecules of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$. The shortest cobalt-cobalt contact is 7.049 (3) Å and there is only one hydrogen-hydrogen distance shorter than 2.4 Å. The molecules are arranged in pairs in the unit cell such that the nitrosyl ligands are directed toward one another across the twofold axis. The separation between the symmetry-related oxygen atoms of the nitrosyls is 3.054 (13) Å, 0.2 Å greater than the sum of the van der Waals radii. The N-O· · ·O angle is 126.2 (5)°. A stereoscopic view of the arrangement about the twofold axis is given in Figure 3; the unit cell is shown in Figure 4.

The geometry of the complex is illustrated in Figure 5. Principal distances and angles and their standard deviations are given in Table VII. These bond distances may be corrected for thermal motion using the "riding" and "inde-

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(21) A. Earnshaw, E. A. King, and L. F. Larkworthy, *J. Chem. Soc. A*, 2459 (1969).

(22) H. J. Buttery, S. F. A. Kettle, G. Keeling, P. J. Stamper, and I. Paul, *J. Chem. Soc. A*, 3148 (1971).

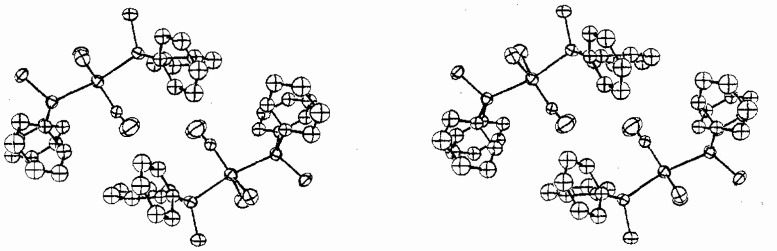

Figure 3. A stereoscopic view of the arrangement of the molecules about the crystallographic twofold axis. The shapes of the atoms in this and the following drawings represent 50% probability contours of thermal motion. Hydrogen atoms are omitted for the sake of clarity.

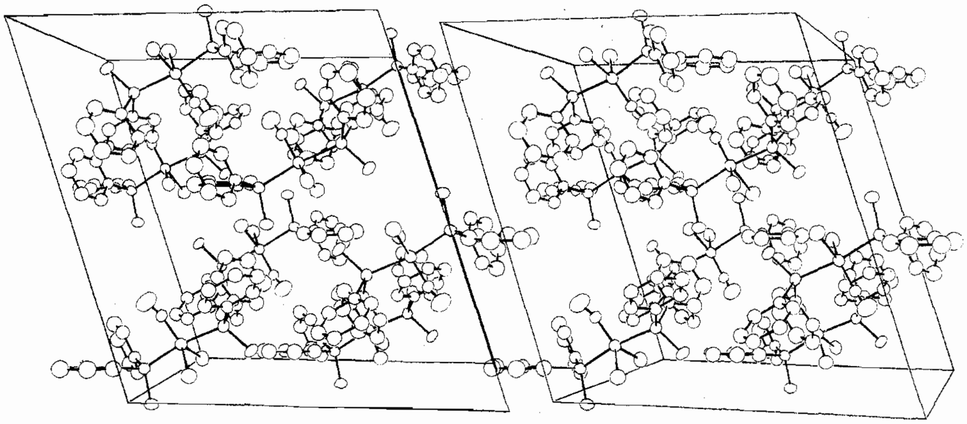

Figure 4. A stereoscopic view of the unit cell of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$. The *x* axis is horizontal, the *z* axis is vertical, and the *y* axis points into the paper.

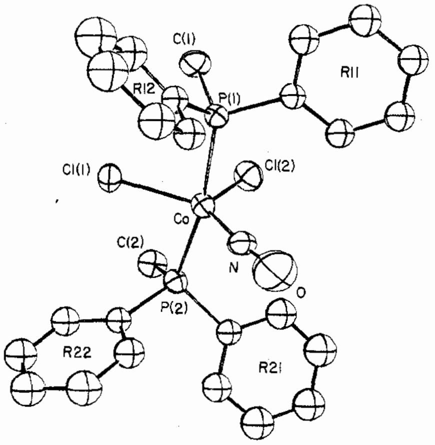

Figure 5. A view of the molecule $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$.

pendent" models of Busing and Levy.[23] However, differences between bond lengths remain essentially the same when either of these corrections is applied. The root-mean-square amplitudes of vibration along the principal axes of thermal vibration for the atoms which were refined anisotropically are given in Table VIII. The directions of the principal axes can be discerned at least approximately from the figures.

The coordination of the cobalt atom is trigonal bipyramidal with the two phosphine ligands axial and the chloride and nitrosyl ligands equatorial. The ligands are arranged so that the molecule has approximate mirror symmetry. The cobalt-phosphorus distances of 2.254 (2) and 2.257 (2) Å are essentially equal and are similar to the cobalt-phosphorus bond distances found in other five-coordinate complexes of cobalt (*cf.* $CoH(N_2)(P(C_6H_5)_3)_3$,[24] 2.192 (6) Å; $CoBr_2(PH(C_6H_5)_2)_3$,[25] 2.20 (2) Å; $Co(CF_2CF_2H)(CO)_3(P(C_6H_5)_3)$,[26] 2.27 (1) Å). The geometry of the ligands within the equatorial plane, however, is significantly distorted from the ideal trigonal arrangement. A view of the molecule showing this plane is given in Figure 6.

The two cobalt-chlorine distances of 2.289 (2) and 2.264 (2) Å differ by over ten standard deviations, although they

Table VII. Selected Distances (Å) and Angles (deg) in $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$

Co-Co	7.049 (3)	P(1)-Co-P(2)	168.2 (1)
Co-P(1)	2.254 (2)	P(1)-Co-Cl(1)	84.3 (1)
Co-P(2)	2.257 (2)	P(1)-Co-Cl(2)	87.3 (1)
Co-Cl(1)	2.289 (2)	P(1)-Co-N	97.5 (2)
Co-Cl(2)	2.264 (2)	P(2)-Co-Cl(1)	85.2 (1)
Co-N	1.705 (5)	P(2)-Co-Cl(2)	91.1 (1)
N-O	1.076 (6)	P(2)-Co-N	93.6 (2)
Co-O	2.757 (6)	Cl(1)-Co-Cl(2)	108.4 (1)
P(1)-C(1)	1.808 (5)	Cl(1)-Co-N	134.3 (2)
P(1)-R11C1	1.826 (4)	Cl(2)-Co-N	117.3 (2)
P(1)-R12C1	1.822 (4)	Co-N-O	164.5 (5)
P(2)-C(2)	1.816 (6)	Co-P(1)-C(1)	113.7 (2)
P(2)-R21C1	1.831 (4)	Co-P(1)-R11C1	116.2 (1)
P(2)-R22C1	1.815 (4)	Co-P(1)-R12C1	113.1 (1)
P(1)-P(2)	4.487 (4)	C(1)-P(1)-R11C1	104.0 (3)
P(1)-Cl(1)	3.048 (2)	C(1)-P(1)-R12C1	106.7 (2)
P(1)-Cl(2)	3.118 (2)	R11C1-P(1)-R12C1	101.9 (2)
P(1)-N	3.000 (5)	Co-P(2)-C(2)	112.5 (2)
P(1)-O	3.856 (7)	Co-P(2)-R21C1	116.1 (1)
P(2)-Cl(1)	3.078 (3)	Co-P(2)-R22C1	112.3 (1)
P(2)-Cl(2)	3.226 (3)	C(2)-P(2)-R21C1	103.6 (2)
P(2)-N	2.912 (5)	C(2)-P(2)-R22C2	106.7 (3)
P(2)-O	3.602 (6)	R21C1-P(2)-R22C2	104.7 (2)
Cl(1)-Cl(2)	3.693 (3)		
Cl(1)-N	3.688 (5)		
Cl(1)-O	4.739 (7)		
Cl(2)-N	3.402 (5)		
Cl(2)-O	4.168 (6)		

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[23] W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 17, 142 (1964).

[24] B. R. Davis, N. C. Payne, and J. A. Ibers, *Inorg. Chem.*, 8, 2719 (1969).

[25] J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, 5, 879 (1966).

[26] J. B. Wilford and H. M. Powell, *J. Chem. Soc. A*, 2092 (1967).

Table VIII. Principal Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Co	0.175 (1)	0.186 (1)	0.197 (1)
P(1)	0.171 (2)	0.184 (2)	0.196 (2)
P(2)	0.176 (2)	0.187 (2)	0.194 (2)
Cl(1)	0.179 (2)	0.214 (2)	0.256 (2)
Cl(2)	0.197 (2)	0.245 (2)	0.252 (2)
C(1)	0.169 (9)	0.226 (8)	0.258 (8)
C(2)	0.182 (9)	0.225 (8)	0.240 (8)
N	0.175 (7)	0.188 (7)	0.229 (7)
O	0.244 (8)	0.315 (8)	0.377 (8)

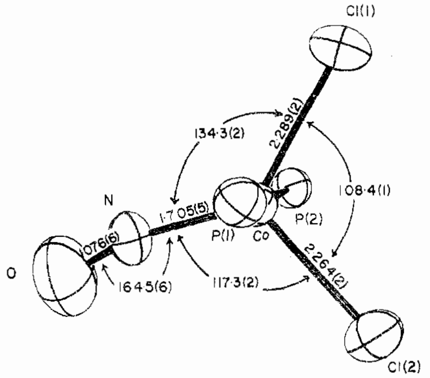

Figure 6. The inner coordination sphere of the molecule viewed perpendicular to the equatorial plane of the trigonal bipyramid.

are both in the range observed for cobalt–chlorine bond distances in five- and six-coordinate complexes (*cf.* [Co(NH_3)$_5$Cl]Cl_2,[27] 2.286 (2) Å; [Co(en)$_2$$Cl_2$]$S_2O_6$·$H_2O$,[28] 2.224 (12) and 2.235 (12) Å; $CoCl_2$(terpy),[29] 2.28 (2) and 2.30 (1) Å). In addition, the bond angles between the three equatorial ligands are significantly distorted from the ideal value of 120°. The chlorine atom further from the cobalt is shifted away from the nitrosyl ligand toward the other chlorine atom such that the N-Co-Cl(1) angle is enlarged to 134.3 (2)° and the Cl(1)-Co-Cl(2) angle is contracted to 108.4 (1)°.

The coordination of the nitrosyl ligand may be classified as linear, leading to formulation of the compound as an NO^+ complex of Co(I). Supporting this assignment is the cobalt-nitrogen distance of 1.705 (5) Å, which is equal to the average of all metal-nitrogen distances in NO^+ complexes.[30] The Co-N-O bond angle of 164.5 (6)°, however, shows a deviation of 15° from linearity and is the smallest M-N-O angle observed for any five-coordinate complex of NO^+.[30] The nitrogen-oxygen distance of 1.076 (6) Å can be lengthened to 1.147 (7) Å by applying the correction for "riding motion" of Busing and Levy.[23]

All angles and distances associated with the rings and methyl groups are in the range of those observed for other phosphine complexes. There are no unusual interactions between ring carbons or hydrogens and other atoms. The shortest hydrogen-hydrogen intermolecular contact is 2.305 Å and is between the R12H4 and R21H2 atoms.

Discussion of the Structure. Since the results of this crystal structure determination apparently contradict the infrared spectral data, it is important to consider whether there is any possibility that there could be two independent molecules in the unit cell differing in the mode of coordination of the nitrosyl ligand. In the refinement of the data it was assumed that the space group is *C*2/*c* with the molecule lying on a general eightfold position. If the correct space group were the noncentrosymmetric subgroup *Cc*, the general position would be of order 4, and there would be two independent molecules in the cell. There is, however, no reason to believe that the space group is noncentrosymmetric. Examination of the intensities of the Friedel pairs shows that there are no differences larger than those that would be expected on the basis of counting statistics alone, and the distributions of the magnitudes of the normalized structure factors closely follow the theoretical distribution for a centrosymmetric structure.[31] The success of the refinement of the structure also indicates that the correct space group was chosen. The final agreement factor is low, and the anisotropic thermal parameters are reasonable, showing no unusual elongations such as might be expected if an inversion center had been imposed on a noncentrosymmetric atom distribution. The location of the methyl hydrogen atoms in the difference Fourier synthesis strongly suggests that the space group which was chosen is correct.

It is also necessary to examine the possibility that the unit cell could contain a statistical disorder of molecules with two types of nitrosyl coordination and to estimate an upper limit to this disorder. From experience with other five-coordinate nitrosyl complexes, it is expected that the change from linear to bent NO coordination would be accompanied by a change in the coordination geometry from trigonal bipyramidal to square pyramidal. There are no known complexes of bent NO^- with trigonal-bipyramidal geometry. A comparison of this complex with the iridium complex $IrCl_2(NO)(P(C_6H_5)_3)_2$, which has been shown[19] to be a square pyramid with an Ir-N-O angle of 123.4 (20)°, shows what types of atomic displacements are necessary to transform a trigonal bipyramid into a square pyramid. The P-M-P angles in the two complexes are very similar; in the cobalt complex the angle is 168.2 (1)°, while in the iridium molecule it is 170.2 (1)°. The Cl-M-Cl angles, however, are very different, being 108.4 (1)° in the cobalt complex and 157.4 (1)° in the iridium. Thus while a change in the nitrosyl ligand and a concomitant change in the coordination geometry would not necessarily change the overall shape of the molecule since the positions of the bulky phosphine ligands would not have to be altered, it should be accompanied by a large shift in the chlorine atoms in the direction of wide bending of the Cl-Co-Cl angle. Since these changes in the chlorine atom positions and in the Co-N-O angle would probably not affect the packing of the molecules significantly, it could be argued that the square-pyramidal NO^- complex could exist within the crystal as a disordered molecule. If this were the case, there should be peaks in the final difference Fourier synthesis corresponding to the positions of the chlorines in the square-pyramidal complex. A careful inspection of the final difference map revealed no peaks significantly above background in the vicinity of possible ligand sites around the iridium atom; the maximum electron density observed was 0.20 (±0.07) e/Å^3. From a consideration of the peak height of the chlorine atom in a Fourier map phased from the calculated structure factors, the upper limit on the disorder of the chlorine atoms would be 0.5%. Therefore, it may be concluded that a square-pyramidal complex of NO^- does not exist as an impurity in the crystal studied.

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(27) G. G. Messmer and E. L. Amma, *Acta Crystallogr., Sect. B*, 24, 417 (1968).

(28) O. Foss and K. Maroy, *Acta Chem. Scand.*, 19, 2219 (1965).

(29) E. Goldschmied and N. C. Stephenson, *Acta Crystallogr., Sect. B*, 26, 1867 (1970).

(30) For a recent review of monomeric transition metal nitrosyl complexes see B. A. Frenz and J. A. Ibers, "MTP International Review of Science," Physical Chemistry (Series 1), Vol. 11, 1972, p 33.

(31) I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, 19, 713 (1965).

From an inspection of the principal axes of the thermal ellipsoids, it is evident that the major vibrational mode of the nitrosyl ligand is a bending one. Similarly, it is observed that the principal motion of the chlorine atoms involves bending of the Cl-Co-Cl angle. The rms amplitudes of vibration of these atoms, however, are all less than 0.4 Å. Any dynamic interconversion of the linear and bent forms of nitrosyl coordination accompanied by change of coordination geometry would be expected to result in much larger displacements.

The conclusion that there is no appreciable concentration of a second form of nitrosyl disordered in the crystal studied leaves the question of the origin of the second, lower frequency, nitrosyl stretching band unanswered. The evidence for the existence of two types of nitrosyl coordination in solution is strong, and since the two forms will not necessarily be equally soluble, it would not be surprising if one of the two forms were preferentially precipitated. However, extensive precipitation of a second crystalline form is questionable on several counts. The solid material appears homogeneously crystalline and the intensity ratios of the two ν(NO) bands in Nujol mull spectra do not change noticeably when $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$, **4**, is recrystallized from different solvents. Also, X-ray powder diffraction patterns of bulk samples of **4** reveal no peaks which cannot be indexed using the unit cell found in the single-crystal analysis. It should be noted, however, that the powder pattern does not exclude the possibility of coprecipitation of a second complex either as amorphous material or as crystals whose powder diffraction peaks accidentally coincide with the strong peaks of the predominating form.

It is possible that molecules with the ligand coordinated as NO^- exist either as disorder on the surface of the crystals of the NO^+ form of the complex or as a disorder within the lattice of *some* of these crystals. Random disorder at the surface of the crystals would not be detectable by X-ray diffraction as it would only increase the level of the background. It is, however, hard to believe that surface disorder alone could fully account for the intensity of the lower frequency band. Although no significant disorder within the lattice was observed in this study, the possibility of such disorder in other crystals is not excluded. For data collection a well-formed crystal was chosen; crystals with significant amounts of disorder might very well be small or poorly formed and hence passed over.

An alternative explanation for the presence of two nitrosyl bands in solid state is factor group splitting arising from the interaction of the two nitrosyl ligands which are in close proximity across the twofold axis. The separation of 100 cm^{-1} between the two bands observed for this series of complexes, however, is large for such an effect. Carbonyl factor group splittings are generally in the order of 20 cm^{-1} or less.[32] In addition, the correspondence between the solution and solid-state spectra over a range of complexes with differing phosphine ligands suggests that the origin of the two nitrosyl stretching bands is the same in both phases. An infrared spectrum of the single crystal used for data collection might resolve this controversy. Unfortunately the dimensions of crystals used for X-ray structure determination do not make such an experiment feasible.

X-Ray Photoelectron Spectra. In order to characterize these compounds further in the solid state, the binding energies of the 1s electrons of nitrogen were measured using X-ray photoelectron spectroscopy.[18] The binding energies of the core electrons of nitrogen show substantial chemical shifts with change in chemical environment, and the half-widths of nitrogen peaks are relatively narrow, about 2 eV, allowing resolution of peaks which are separated by a few electron volts. Since the change in electron density at the nitrogen atom between the formally NO^+ and NO^- states of the ligand should be significant, we hoped to be able to observe two nitrogen 1s peaks in the photoelectron spectra of these compounds. Observation of two such types of nitrogen atoms would be further supporting evidence for the existence of conformational isomers involving two forms of nitrosyl coordination.

The resolution of two nitrogen 1s peaks separated by about 2 eV in the complexes $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$ and $CoCl_2(NO)(P(n\text{-}C_4H_9)_3)_2$ has been reported by Finn and Jolly,[33] the higher binding energy peak being assigned to the nitrosyl ligand in the NO^+ form and the lower to the NO^- form, in accordance with the observed variation of the nitrogen 1s binding energy with the formal charge[34] on the nitrogen atom. They did not, however, discuss the relative intensities of the two contributions. If the two peaks correspond to the two forms of nitrosyl coordination, the areas under the peaks should reflect the ratio of the two conformational isomers and should also correlate with the intensities of the two nitrosyl stretching bands in the infrared spectra. We therefore studied the X-ray photoelectron spectra of three of the compounds in the series $CoCl_2(NO)L_2$, where $L = P(C_6H_5)_3$, $P(CH_3)_2(C_6H_5)$, and $P(CH_3)(C_6H_5)_2$, in an attempt to resolve two nitrogen 1s binding energy peaks and to relate them to the infrared spectra. Inasmuch as the relative intensities of the two nitrosyl stretching bands in these complexes vary considerably, the compounds should provide a good test of the correlation of results from infrared and photoelectron spectroscopy. In the third compound, both crystalline forms were studied. Since the vibrational spectrum of the low-temperature crystals changes with grinding, spectra were taken both of samples which had been subjected to grinding and of those to which no pressure had been applied.

Results. Resolution of two closely spaced peaks is very strongly affected by their relative intensities; the more equal the intensities, the greater the chance of observing two individual peaks rather than a shoulder on one broadened, asymmetric peak. Therefore, on the basis of the nitrosyl stretching bands we expected that the best chance for observing two resolved nitrogen peaks was in the dimethylphenylphosphine complex **3**. As in the infrared spectrum, two peaks of approximately equal magnitude were indeed found (Figure 1a), although with time the peak at lower binding energy increased at the expense of the higher one. The separation of 3.5 eV between the two peaks is larger than the separations reported by Finn and Jolly,[33] but the binding energy values are still within the range found for nitrosyl complexes.

With our spectrometer the spectrum of the room-temperature form of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$, **4**, showed not two bands, but a broad asymmetric peak (Figure 1b) which could be deconvoluted to give two peaks in about the same positions reported by Finn and Jolly.[33] It was also observed that the spectrum changed with time, the shoulder on the high binding energy side becoming less distinct and finally

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[32] H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc. A*, 471 (1970).

[33] P. Finn and W. L. Jolly, *Inorg. Chem.*, 11, 893 (1972).

[34] D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, 8, 2642 (1969).

disappearing. Visual examination of the sample after irradiation revealed a brown to greenish color change indicating that some decomposition had taken place.

The low-temperature form of the $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$, **5**, was also studied. This compound is of special interest since the infrared spectrum taken in a Nujol mull with minimal grinding shows only one band, while a second band develops with more extensive grinding, the final spectrum resembling that of the room-temperature form. It was expected, therefore, that the photoelectron spectra of ground and unground complex would show analogous differences. In fact, grinding the sample seems only to broaden the peak, leaving its position unchanged. Before grinding, the nitrogen 1s peak is found to be slightly asymmetric (Figure 1) with a relatively small half-width of 2.5 eV, while afterward the FWHM was increased to 3.3 eV. Subtraction of the line width of the X-ray source (assumed to be gaussian) from the line width of the signal results in half-widths for the two peaks of 2.2 and 3.2 eV, respectively. In both cases, the peaks show asymmetry toward the side of higher binding energy. Since the peaks are expected to be either gaussian or lorentzian and since any effects from uneven charging of the sample should make the peak tail to the low-energy side (as is seen in the $CoCl_2(NO)(P(CH_3)_2(C_6H_5))_2$ spectrum),[35] it may be concluded that the asymmetry arises from the presence of a second nitrogen 1s contribution. In spite of the half-widths in the spectra of the ground and unground samples, there is no significant difference in the relative areas of the two peaks in the deconvoluted spectra leading to the conclusion that within the error of the deconvolution process, grinding does not change the relative contributions of the two forms of nitrosyl coordination.

Unlike the other two compounds, the $P(C_6H_5)_3$ derivative has a solid-state infrared spectrum in which the lower frequency nitrosyl stretching band predominates. In contrast to the previously described spectra, the photoelectron spectrum (Figure 1e) of this compound shows no evidence for the presence of a second peak. The line shape is almost symmetric except for the slight tailing to lower binding energy characteristic of unevenly charged samples.[35] The peak is adequately fit by a single gaussian curve, and while the line width of 2.5 ev is larger than that assigned to the components of the peaks of the other compounds, the peak is not abnormally broad.

Discussion. While there are definitely two nitrogen 1s peaks in the $CoCl_2(NO)(P(CH_3)_2(C_6H_5))_2$ complex and while there is good evidence for the existence of two peaks in the various $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$ samples, it is not possible to correlate successfully the positions and intensities of these peaks with the information from the infrared spectra. From the intensities of the nitrosyl stretching bands in the solid-state infrared spectra, it is inferred that the NO^- form of the complex is dominant in the $P(C_6H_5)_3$ derivative but that the NO^+ form is prevalent in all the other three samples, almost exclusively so in the unground low-temperature form of $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$. In the photoelectron spectra, however, we were surprised to find that the peak at lower binding energy, which is presumably associated with the NO^- form of coordination, is more intense in every case. The information from the two forms of spectroscopy, therefore, appears to be in disagreement.

It is important to consider the possibility that the smaller peak at higher binding energy is an impurity peak. Photoelectron spectroscopy measures the composition of the surface of the sample only; the escape depth of the photoelectrons is at most 50 Å. Transmission infrared spectroscopy, on the other hand, measures the bulk properties of the material. Species stabilized at the surface of the sample are not necessarily representative of the total composition and may not even be observed in the infrared spectrum. Furthermore, the surface is much more susceptible either to reaction with the atmosphere or to decomposition from X-ray exposure.

If the smaller peak at higher binding energy is an impurity, it must either be a contaminant coprecipitated with the cobalt nitrosyl complex or it must arise from reaction of the sample with the atmosphere since it is most intense at the start of the scanning. The binding energy of this peak is at a position such that the nitrogen is in either a nitrosyl or a nitrite group.[34] Although the reaction of coordinated NO with oxygen to give coordinated NO_2^- is known, it has been reported only in solution in complexes of NO^- stabilized by Schiff base type ligands.[36] These peaks at higher binding energy occur in all the samples except the $P(C_6H_5)_3$ derivative. These samples were crystalline with apparently clean faces when they were put into the sample chamber. Further reaction within the chamber is unlikely since the pressure was 10^{-6} Torr and the temperature of the sample holder was −80°. Further evidence that this peak does not arise from reaction with air is the observation that the peak is most intense in the spectrum of the $CoCl_2(NO)(P(CH_3)_2(C_6H_5))_2$ complex. Very careful precautions were taken with this compound to keep it under an inert atmosphere during transfer to the spectrometer. Finally, if the signal were due to an impurity, it would seem probable that it should not decrease with time; in the samples studied, the peak shows either constant or decreasing intensity.

In the absence of any direct correlation between the intensities of the peaks in the photoelectron and infrared spectra, we suggest that the NO^- form of nitrosyl coordination which corresponds to the peak at lower binding energy is favored on the surface of the sample and that in some cases this stabilization may be dependent upon exposure to X-rays or vacuum. This hypothesis would explain the observation that the relative fractions of the NO^+ and NO^- forms of the ground and unground $CoCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$, **5**, are the same while the infrared spectra show a considerably increased concentration of the NO^- form in the ground sample. As the NO^- is the favored form on the surface, grinding either introduces more surface area into the infrared sample or distorts the bulk properties of the material. Similar results indicating surface layer isomerization of a platinum-olefin complex observed by photoelectron spectroscopy have been reported by Clark and Briggs.[37] An electrostatic field at the surface enhanced by grinding as well as by charging during the photoelectron spectral measurement could also favor form B which should have a greater dipole moment than A.

Since decomposition and surface effects appear to be

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[35] If charging of the sample occurs because of depletion of the surface of the sample of electrons and if charge neutralization of the sample occurs by migration of electrons from the sample backing, then the surface of the sample will have the highest charge. Since the detected photoelectron intensity decays exponentially with depth into the sample, one would expect the integrated intensity as a function of potential to peak toward lower kinetic energy (higher binding energy) and that the "tail" of the distribution would be on the high kinetic energy (low binding energy) side of the peak.

[36] S. Clarkson and F. Basolo, Abstracts, XIVth International Conference on Coordination Chemistry, Toronto, June 1972, p 193.

[37] D. T. Clark and D. Briggs, *Nature* (*London*), 237, 15 (1972).

important in these complexes, we conclude that it is not possible to compare successfully the intensities from the infrared and photoelectron spectra. Nor is it possible, except in the complex $CoCl_2(NO)(P(CH_3)_2(C_6H_5))_2$, to resolve unequivocally two nitrogen 1s peaks. There is good evidence, however, for the existence of two contributions to the observed peaks. Therefore, we conclude that the photoelectron spectra are consistent with the hypothesis of conformational isomerism involving change in the formal oxidation state of the nitrosyl ligand.

Conclusions

Further experiments are warranted to clarify our earlier hypothesis that a dynamic intramolecular redox equilibrium exists in solutions of $CoCl_2(NO)L_2$ complexes. The proposed structure A has now been confirmed by X-ray diffraction but in the cobalt series structure B remains to be established. Hopefully for some member of the series both forms will be found in the same unit cell or at least each form of the complex will be characterized in two different cells. Comparison of the spectral data for fully characterized single crystals and their corresponding solutions is essential to resolve the present paradox. The infrared and photoelectron spectral indications of the uncharacterized form B in a single crystal of **4**, which is shown by X-ray diffraction to contain only A, is perplexing. Solid-state splitting affording two such widely separated infrared bands in a single crystal of **4** is possible but very unlikely in view of the presence of low-frequency peaks in solid spectra for the whole series as well as the close correspondence between the solution and solid ν(NO) frequencies. The failure of photoelectron spectra to resolve this dilemma seems to derive from the fact that this technique samples only the surface, of which our understanding is far from complete. The interconversion of these two forms may be unusually sensitive to external forces.

Future efforts will be focused on a search for a single-crystal containing the uncharacterized form B as well as on a solution study of ^{59}Co and ^{15}N nmr spectra.

Registry No. $CoCl_2(NO)[P(C_2H_5)_3]_2$, 38402-81-2; $CoCl_2(NO)[P(n\text{-}C_4H_9)_3]_2$, 36237-02-2; $CoCl_2(NO)[P(CH_3)_2(C_6H_5)]_2$, 38402-83-4; $CoCl_2(NO)[P(CH_3)(C_6H_5)_2]_2$, 38402-84-5; $CoCl_2(NO)[P(C_6H_5)_3]_2$, 38402-85-6; $CoCl_2(NO)[P(p\text{-}CH_3C_6H_4)_3]_2$, 38402-86-7.

Acknowledgments. We are pleased to acknowledge support of this work by National Science Foundation Grants No. GP20273X and GP28134 and NATO Grant No. 504, as well as a predoctoral fellowship for C. P. B. from the National Institutes of Health. Acknowledgment is also made to the donors of the Petroleum Research Func, administered by the American Chemical Society, for partial support of this research. We thank D. Cahen for powder pattern interpretations.

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Crystal and Molecular Structure of Tris(cyclopentadienyltricarbonylmolybdenum)thallium(III), $Tl(Mo(CO)_3(\pi\text{-}C_5H_5))_3$

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Received November 27, 1972

The crystal and molecular structure of a potentially highly conducting complex tris(cyclopentadienyltricarbonylmolybdenum)thallium(III), $Tl(Mo(CO)_3Cp)_3$ ($Cp = \pi\text{-}C_5H_5$), has been determined from three-dimensional X-ray data collected by counter techniques. The coordination around the central thallium atom is trigonal pyramidal with an average Tl–Mo bond distance of 2.965 Å and an average Mo–Tl–Mo bond angle of 119.7°. Individual Tl–Mo bond distances and Mo–Tl–Mo bond angles differ significantly from these average values. The Tl is 0.586 (1) Å out of the plane of the three Mo atoms. No other metal–metal interactions are observed. Crystal data are as follows: triclinic, space group C_i^1-$P\bar{1}$, $a = 11.131$ (9) Å, $b = 17.305$ (16) Å, $c = 6.833$ (9) Å, $\alpha = 98.59$ (5)°, $\beta = 96.45$ (5)°, $\gamma = 79.51$ (5)° (temperature 22°), $Z = 2$; $d_{\text{obsd}} = 2.3$ (1) g/cm^3, $d_{\text{calcd}} = 2.44$ g/cm^3. The structure was refined using 2060 independent reflections for which $F_o^2 > 3\sigma(F_o^2)$ and the refinement converged to a conventional R factor (on F) of 0.030.

Introduction

With the current interest in anisotropic properties of solids,[1] organometallic compounds possessing metal-metal bonds are being extensively studied.[2] The compound $Tl(Mo(CO)_3Cp)_3$ ($Cp = \pi\text{-}C_5H_5$, cyclopentadienyl) was recently prepared by King.[3] Crystals of the compound were found to be dichroic and King suggested the possibility of metal-metal interactions. That this compound could have a stacked arrangement of the molecules with Tl–Tl interactions, and also carry the highly polarizable $Mo(CO)_3Cp$ groups, gave us hope that it would show a high electrical conductivity, as it might meet the requirements of the theory proposed by Little.[4] Moreover, the coordination about the Tl atom could be novel, as at the inception of this work no structures of organometallic complexes of Tl or In had been reported other than those for $Tl(CH_3)_3$,[5] $In(CH_3)_3$,[6] and $In(C_6H_5)_3$.[7] For these reasons a crystal structure determination of Tl(Mo-

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(1) See, for example, K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969); M. J. Minot and J. H. Perlstein, *Phys. Rev. Lett.*, **26**, 371 (1971).

(2) See, for example, L. K. Monteith, L. F. Ballard, C. G. Pitt, B. K. Klein, L. M. Slifkin, and J. P. Collman, *Solid State Commun.*, **6**, 301 (1968).

(3) R. B. King, *Inorg. Chem.*, **9**, 1936 (1970).

(4) W. A. Little, *Phys. Rev. A*, **134**, 1416 (1964).

(5) G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc. A*, 28 (1970).

(6) E. L. Amma and R. E. Rundle, *J. Amer. Chem. Soc.*, **80**, 4141 (1958).

(7) J. F. Malone and W. S. McDonald, *Chem. Commun.*, 591 (1969).