

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  $\text{CoCl}_2(\text{NO})[\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)_2]_2$ , 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  $\text{CoCl}_2(\text{NO})\text{L}_2$  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  $\nu(\text{NO})$  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  $^{59}\text{Co}$  and  $^{15}\text{N}$  nmr spectra.

**Registry No.**  $\text{CoCl}_2(\text{NO})[\text{P}(\text{C}_2\text{H}_5)_3]_2$ , 38402-81-2;  $\text{CoCl}_2(\text{NO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$ , 36237-02-2;  $\text{CoCl}_2(\text{NO})[\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)_2]_2$ , 38402-83-4;  $\text{CoCl}_2(\text{NO})[\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2]_2$ , 38402-84-5;  $\text{CoCl}_2(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ , 38402-85-6;  $\text{CoCl}_2(\text{NO})[\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3]_2$ , 38402-86-7.

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## Crystal and Molecular Structure of Tris(cyclopentadienyltricarbonylmolybdenum)thallium(III), $\text{Tl}(\text{Mo}(\text{CO})_3(\pi\text{-C}_5\text{H}_5))_3$

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The crystal and molecular structure of a potentially highly conducting complex tris(cyclopentadienyltricarbonylmolybdenum)thallium(III),  $\text{Tl}(\text{Mo}(\text{CO})_3\text{Cp})_3$  (Cp =  $\pi\text{-C}_5\text{H}_5$ ), 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  $119.7^\circ$ . 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  $C_2^1-P1$ ,  $a = 11.131$  (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<sup>3</sup>,  $d_{\text{calcd}} = 2.44$  g/cm<sup>3</sup>. 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,<sup>1</sup> organometallic compounds possessing metal-metal bonds are being extensively studied.<sup>2</sup> The compound  $\text{Tl}(\text{Mo}(\text{CO})_3\text{Cp})_3$  (Cp =  $\pi\text{-C}_5\text{H}_5$ , cyclopentadienyl) was recently prepared by King.<sup>3</sup> 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  $\text{Mo}(\text{CO})_3\text{Cp}$  groups, gave us hope that it would show a high electrical conductivity, as it might meet the requirements of the theory proposed by Little.<sup>4</sup> 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  $\text{Tl}(\text{CH}_3)_3$ ,<sup>5</sup>  $\text{In}(\text{CH}_3)_3$ ,<sup>6</sup> and  $\text{In}(\text{C}_6\text{H}_5)_3$ .<sup>7</sup> For these reasons a crystal structure determination of  $\text{Tl}(\text{Mo}(\text{CO})_3\text{Cp})_3$

(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).

(CO)<sub>3</sub>Cp)<sub>3</sub> was undertaken, prior to the measurement of possible anisotropic physical properties.

### Experimental Section

Tl(Mo(CO)<sub>3</sub>Cp)<sub>3</sub> was prepared according to the literature method<sup>8</sup> and characterized by its infrared spectrum and by elemental analysis. *Anal.* Calcd for C<sub>24</sub>H<sub>15</sub>O<sub>9</sub>Mo<sub>3</sub>Tl: C, 30.1; H, 1.6. Found: C, 30.7; H, 1.6. Crystals suitable for X-ray analysis were obtained by vapor diffusion of pentane into an acetone solution of the compound in a dry nitrogen atmosphere. The red-green crystals are air stable. A needle-shaped crystal of dimensions 0.6 × 0.04 × 0.02 mm was mounted in air with the needle axis along the spindle axis. A series of Weissenberg and precession photographs was taken using Cu Kα radiation. In these photographs no symmetry elements other than a center of symmetry were detected and so the crystal was assigned to the triclinic system. Because of the high linear absorption coefficient for Cu radiation ( $\mu$  233 cm<sup>-1</sup>) all subsequent X-ray work was carried out using Mo Kα radiation ( $\mu$  75.5 cm<sup>-1</sup>). The crystal was transferred to a FACS-1 automatic diffractometer and cell constants were determined in the manner previously described,<sup>8</sup> using 10 reflections in the range 17° ≤ 2θ ≤ 32° and Mo Kα<sub>1</sub> radiation (λ 0.70930 Å) monochromatized from the (002) face of a mosaic graphite crystal. The reduced cell thus obtained has *a* = 11.131 (9), *b* = 17.305 (16), *c* = 6.833 (9) Å; α = 98.59 (5), β = 96.45 (5), γ = 79.51 (5)°; *V* = 1275.6 Å<sup>3</sup>. The Delaunay reduction that led to this cell did not suggest the presence of hidden symmetry elements. An observed density of 2.3 (1) g cm<sup>-3</sup>, obtained by flotation of the material in CH<sub>2</sub>I-CHBr<sub>3</sub> is in fair agreement with that of 2.44 g cm<sup>-3</sup> calculated for two molecules in the unit cell. There was some decomposition of the crystal in the flotation liquid.

The presence of the short *c* axis further encouraged us to believe that a Tl-Tl interaction was possible in this structure and so collection of data and solution of the structure were pursued. Intensities were collected in the manner described previously<sup>8,9</sup> using monochromatized Mo Kα radiation. The takeoff angle was 3.5°. The counter was positioned 32 cm from the crystal and was preceded by an aperture of dimensions 7 mm × 7 mm. The scan range was from 0.8° below the Kα<sub>1</sub> peak to 0.8° above the Kα<sub>2</sub> peak. The scan rate was 1° in 2θ/min. Background counts of 10, 20, and 40 sec each were taken in the ranges 2.5° ≤ 2θ ≤ 27°, 27° ≤ 2θ ≤ 35°, and 35° ≤ 2θ ≤ 40°, respectively, at the extremes of each scan. Unique intensities (with the exception of the *hk0* Friedel pairs) were collected out to 40° in 2θ. Past that point there was only a small fraction (about 10%) of the reflections above background. A total of 2664 reflections was collected. Throughout the data collection 6 standard reflections were measured at intervals of 75 observations. The intensities of these standards remained constant within counting statistics.

The data were processed in the usual manner<sup>8,9</sup> using a *p* of 0.04. A total of 2060 unique reflections was obtained having  $F_o^2 > 3\sigma(F_o^2)$ , and these were used in subsequent calculations. An analysis of the intensities of the *hk0* Friedel pairs showed an average deviation of 1.4% and provided the first suggestion that the space group is the centrosymmetric one *C*<sub>1</sub><sup>1</sup>-*P*1, rather than its noncentrosymmetric subgroup, *P*1.

Solution and refinement of the structure proceeded by standard methods, with a sharpened, origin-removed Patterson function revealing the positions of the Tl atom and two of the Mo atoms.<sup>10</sup> In subsequent least-squares calculations the function minimized was  $\Sigma w(|F_o| - |F_c|)^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure amplitudes and where the weights *w* are taken as  $4F_o^2/\sigma^2(F_o^2)$ . In all calculations of *F<sub>c</sub>* the atomic scattering factors for the atoms were taken from those compiled by Cromer and Waber.<sup>11</sup> The effects of anomalous dispersion were included in *F<sub>c</sub>*<sup>12</sup> and the values of Δ*f'* and Δ*f''* for Tl and Mo were taken from the calculations of

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

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

(10) In addition to various local programs, Patterson functions and Fourier syntheses were calculated using a local version of Zalkin's FORDAP. Refinement and structure factor calculations were carried out with our least-squares program, NUCLS, which, in its nongroup form, resembles the Busing-Levy ORFLS. Errors in derived quantities were obtained from the Busing-Levy ORFFE program, and drawings were made with the use of Johnson's ORTEP program. Absorption corrections were arrived at by using Cahen's program AGNOST.

(11) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, in press, Table 2.2A.

(12) J. A. Ibers, and W. A. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

Cromer and Liberman.<sup>13</sup> A least-squares refinement of the Tl and two Mo positions found on the Patterson map, followed by a difference Fourier map revealed the positions of the third Mo along with the other nonhydrogen atoms. In subsequent refinements the cyclopentadienyl rings were treated as rigid groups<sup>14</sup> of *D*<sub>5h</sub> symmetry with C-C = 1.42 Å. A refinement in which all nongroup atoms were assigned variable isotropic thermal parameters as was each group, converged to values of the reliability indices *R*<sub>1</sub> and *R*<sub>2</sub> of 0.060 and 0.076, respectively, where  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$  and  $R_2$  (weighted  $R$ ) =  $(\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)^{1/2}$ .

At this point an absorption correction was made. The needle-like crystal has a hexagonal cross section. The girdle faces belong to the forms {100}, {130}, and {120}, and the end faces are of the form {001} (and hence the *c* axis is the spindle axis). The transmission coefficients ranged from 0.728 to 0.800. A further refinement of the isotropic model now led to values of *R*<sub>1</sub> and *R*<sub>2</sub> of 0.055 and 0.069 and these values decreased to 0.049 and 0.061 when the nongroup atoms were allowed to vibrate anisotropically. In subsequent calculations the contributions to *F<sub>c</sub>* of the H atoms of the cyclopentadienyl groups were added. These contributions were based on the known geometry of the C<sub>5</sub>H<sub>5</sub> ring, a C-H distance of 1.0 Å, and *B*(H) = 5.0 Å<sup>2</sup>. In a final cycle of least-squares refinement the C atoms of the cyclopentadienyl groups were assigned individual, variable isotropic thermal parameters. This cycle converged to values of *R*<sub>1</sub> and *R*<sub>2</sub> of 0.030 and 0.036, respectively.

An analysis of  $\Sigma w(|F_o| - |F_c|)^2$  as a function of  $|F_o|$ , scattering angle, and Miller indices indicated no unusual trends. The error in an observation of unit weight is 1.38 e for 232 variables and 2060 observations. The maximum density on a final difference Fourier map is 1.46 e/Å<sup>3</sup>, approximately 25% of the height of a C atom on previous maps. A structure factor calculation for the 369 reflections omitted from the calculations which have  $F_o^2 < 3\sigma(F_o^2)$  reveals that 366 of them have  $|F_o^2 - F_c^2| < 3\sigma(F_o^2)$ . Table I presents the values of 10 $|F_o|$  and 10 $|F_c|$  for the 2060 reflections used in the analysis.<sup>15</sup> The positional and thermal parameters derived from the last cycle of least-squares refinement are given in Table II along with the associated standard deviations, as derived from the inverse matrix. Table III presents the parameters of the C atoms which may be derived from the data of Table II, and Table IV presents the idealized positions of the H atoms.

### Description of the Structure

The crystal structure consists of the packing of discrete molecules of Tl[Mo(CO)<sub>3</sub>Cp]<sub>3</sub>. No crystallographic symmetry is imposed on these molecules. A stereoscopic pair of views of the contents of two unit cells is given in Figure 1. An overall view of the molecule, with the exclusion of hydrogen atoms, is shown in Figure 2 which also displays the labeling scheme. A selection of intramolecular bond distances and bond angles, together with standard deviations derived from the inverse matrix, is given in Tables V and VI. The root-mean-square amplitudes of vibration along the principal axes of vibration for atoms refined anisotropically are given in Table VII. The directions of vibration may be discerned from Figure 2.

The coordination about the thallium atom is trigonal pyramidal with the thallium atom lying -0.586 (1) Å from the plane of the three molybdenum atoms. The best weighted least-squares plane through the thallium atom and three molybdenum atoms is given by the equation 2.442*x* - 1.267*y* + 6.456*z* = 0.3416 Å with the deviations from the plane, in Å, for the Tl, Mo(1), Mo(2), and Mo(3) atoms being -0.1534 (4), 0.109 (1), 0.065 (1), and 0.551 (1) Å, respectively. There is no threefold symmetry about the thallium atom.

The average thallium to molybdenum distance is 2.965 Å.

(13) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(14) See, for example, R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

(15) Table I, a listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm 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-73-1313.

Table II. Positional, Thermal, and Group Parameters for  $\text{Tl}[\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)]_3$ 

Atom	x	y	z	$10^4\beta_{11}^a$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Tl	0.16388 (4) <sup>b</sup>	0.24445 (2)	0.01513 (7)	43.1 (5)	20.1 (2)	158 (1)	-3.9 (2)	20.4 (5)	4.4 (3)
Mo(1)	0.28271 (8)	0.08271 (5)	-0.16049 (14)	44 (1)	20.2 (4)	161 (3)	-4.0 (5)	22 (1)	1.9 (8)
Mo(2)	-0.10439 (9)	0.26174 (6)	0.02781 (15)	44 (1)	24.8 (4)	159 (3)	-0.1 (50)	19 (1)	11.2 (8)
Mo(3)	0.29470 (9)	0.37998 (6)	0.10137 (14)	63.6 (11)	22.9 (4)	133 (3)	-11.4 (5)	13.5 (13)	4.4 (8)
C(1,1)	0.3753 (11)	0.1236 (7)	0.0881 (20)	43 (11)	23 (5)	200 (37)	5 (6)	3 (17)	11 (11)
C(2,1)	0.4454 (12)	0.0692 (7)	-0.2563 (18)	55 (13)	31 (5)	210 (36)	-3 (6)	15 (18)	4 (11)
C(3,1)	0.2514 (10)	0.1618 (7)	-0.3485 (21)	47 (12)	26 (5)	249 (40)	-8 (6)	40 (17)	-20 (12)
C(1,2)	-0.0598 (10)	0.3507 (8)	0.2203 (20)	60 (13)	26 (5)	233 (38)	7 (7)	59 (17)	13 (12)
C(2,2)	-0.0245 (10)	0.1756 (7)	0.1796 (18)	56 (12)	29 (5)	152 (33)	-5 (6)	37 (16)	-6 (11)
C(3,2)	-0.2311 (12)	0.2660 (8)	0.2115 (19)	61 (13)	52 (7)	153 (35)	-2 (7)	-21 (19)	17 (12)
C(1,3)	0.1437 (13)	0.4099 (7)	-0.0693 (19)	85 (14)	24 (5)	183 (35)	-11 (7)	10 (19)	22 (11)
C(2,3)	0.3974 (12)	0.2980 (8)	-0.0645 (19)	67 (13)	38 (6)	176 (35)	-17 (7)	19 (18)	-4 (12)
C(3,3)	0.3521 (12)	0.4469 (8)	-0.0632 (19)	107 (15)	40 (6)	174 (35)	-38 (8)	.04 (19)	11 (12)
O(1,1)	0.4359 (8)	0.1412 (5)	0.2288 (15)	79 (10)	50 (5)	238 (28)	8 (5)	-15 (14)	-17 (9)
O(2,1)	0.5408 (8)	0.0620 (5)	-0.3124 (14)	66 (10)	52 (5)	295 (29)	-5 (5)	66 (14)	-9 (9)
O(3,1)	0.2316 (9)	0.2029 (6)	-0.4719 (14)	133 (12)	48 (4)	214 (26)	-19 (6)	1 (14)	46 (10)
O(1,2)	-0.0435 (9)	0.4056 (6)	0.3304 (16)	126 (12)	34 (4)	364 (33)	-11 (6)	85 (16)	-37 (10)
O(2,2)	0.0178 (8)	0.1247 (5)	0.2756 (13)	95 (10)	35 (4)	210 (25)	-3 (5)	19 (12)	38 (8)
O(3,2)	-0.3081 (9)	0.2679 (7)	0.3117 (16)	75 (10)	96 (7)	303 (33)	1 (7)	70 (16)	57 (12)
O(1,3)	0.0573 (9)	0.4323 (5)	-0.1693 (15)	107 (11)	43 (4)	319 (31)	-11 (6)	-29 (16)	48 (10)
O(2,3)	0.4673 (8)	0.2530 (6)	-0.1550 (15)	83 (10)	46 (4)	373 (32)	-28 (5)	79 (15)	-35 (10)
O(3,3)	0.3874 (11)	0.4872 (7)	-0.1556 (15)	217 (16)	79 (6)	258 (30)	-96 (9)	-5 (18)	52 (11)
Group	$x_c^c$	$y_c$	$z_c$	$\delta$			$\epsilon$		
R(1)	0.1950 (5)	-0.0110 (3)	-0.1932 (8)	-1.861 (18)			1.911 (5)		
R(2)	-0.1731 (5)	0.2675 (3)	-0.2752 (8)	-2.315 (5)			2.769 (6)		
R(3)	0.3284 (5)	0.4086 (3)	0.3970 (8)	-1.716 (5)			2.958 (6)		

<sup>a</sup> The form of the thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . <sup>b</sup> Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant figures. <sup>c</sup>  $x_c, y_c, z_c$  are the fractional coordinates of the ring center;  $\delta, \epsilon, \eta$  (in radians) have been defined previously.<sup>13</sup>

Table III. Derived Parameters for Ring Carbon Atoms

Ring atom	x	y	z	$B, \text{\AA}^2$
R(1)C(1)	0.1895 (7) <sup>b</sup>	-0.0036 (5)	-0.0157 (8)	3.5 (2)
R(1)C(2)	0.2863 (6)	-0.0501 (5)	-0.1221 (11)	3.5 (2)
R(1)C(3)	0.2569 (7)	-0.0425 (5)	-0.3269 (10)	3.8 (3)
R(1)C(4)	0.1004 (6)	0.0327 (5)	-0.1546 (11)	2.9 (2)
R(1)C(5)	0.1420 (7)	0.0086 (5)	-0.3469 (9)	3.9 (3)
R(2)C(1)	-0.2664 (6)	0.3074 (4)	-0.1990 (14)	3.9 (3)
R(2)C(2)	-0.2415 (7)	0.2232 (4)	-0.2365 (14)	3.9 (3)
R(2)C(3)	-0.1220 (7)	0.2003 (4)	-0.3025 (14)	4.1 (3)
R(2)C(4)	-0.1623 (8)	0.3364 (4)	-0.2419 (14)	4.2 (3)
R(2)C(5)	-0.0731 (6)	0.2702 (5)	-0.3059 (14)	4.1 (3)
R(3)C(1)	0.2298 (6)	0.4515 (4)	0.4053 (14)	3.5 (2)
R(3)C(2)	0.3410 (7)	0.4740 (4)	0.3701 (14)	3.7 (2)
R(3)C(3)	0.4349 (5)	0.4061 (5)	0.3721 (14)	3.8 (3)
R(3)C(4)	0.2548 (6)	0.3697 (4)	0.4289 (14)	3.7 (2)
R(3)C(5)	0.3816 (7)	0.3417 (4)	0.4084 (14)	3.7 (2)

<sup>a</sup>  $B$  is the refined isotropic thermal parameter for the individual ring carbon atoms. <sup>b</sup> The estimated standard deviations are derived from those of the group parameters.

Table IV. Idealized Coordinates of the Ring Hydrogen Atoms<sup>a</sup>

Ring atom	x	y	z
R(1)H(1) <sup>b</sup>	0.185	0.003	0.132
R(1)H(2)	0.362	-0.082	-0.063
R(1)H(3)	0.309	-0.068	-0.437
R(1)H(4)	0.022	0.069	-0.122
R(1)H(5)	0.099	0.026	-0.474
R(2)H(1)	-0.344	0.341	-0.151
R(2)H(2)	-0.297	0.187	-0.215
R(2)H(3)	-0.079	0.145	-0.337
R(2)H(4)	-0.154	0.394	-0.232
R(2)H(5)	0.009	0.273	-0.347
R(3)H(1)	0.148	0.487	0.411
R(3)H(2)	0.351	0.528	0.347
R(3)H(3)	0.523	0.404	0.351
R(3)H(4)	0.194	0.337	0.455
R(3)H(5)	0.426	0.286	0.418

<sup>a</sup> All atoms have  $B = 5.0 \text{\AA}^2$ . <sup>b</sup> R(1)H(1) is bonded to C(1) in ring 1.

Using covalent radius values of 1.62 Å for Mo(O)<sup>16</sup> and 1.45

(16) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 185 (1966).

Table V. Interatomic Distances (Å)

Atoms	Distance	Atoms	Distance
Tl-Mo(1)	3.001 (3)	C(1,3)-O(1,3)	1.151 (14)
Tl-Mo(2)	2.955 (3)	C(2,3)-O(2,3)	1.155 (14)
Tl-Mo(3)	2.938 (2)	C(3,3)-O(3,3)	1.152 (14)
Av Tl-Mo	2.965	Av C-O	1.154 (8)
Mo(1)-C(1,1)	1.992 (14)	Mo(1)-R(1)C(1)	2.351 (8)
Mo(1)-C(2,1)	1.956 (13)	Mo(1)-R(1)C(2)	2.344 (8)
Mo(1)-C(3,1)	1.973 (15)	Mo(1)-R(1)C(3)	2.344 (9)
Mo(2)-C(1,2)	1.970 (15)	Mo(1)-R(1)C(4)	2.356 (8)
Mo(2)-C(2,2)	1.963 (14)	Mo(1)-R(1)C(5)	2.351 (8)
Mo(2)-C(3,2)	1.976 (15)		
Mo(3)-C(1,3)	1.968 (14)	Mo(2)-R(2)C(1)	2.343 (9)
Mo(3)-C(2,3)	1.953 (14)	Mo(2)-R(2)C(2)	2.331 (9)
Mo(3)-C(3,3)	1.959 (14)	Mo(2)-R(2)C(3)	2.351 (9)
Av Mo-C <sup>a</sup>	1.968 (12)	Mo(2)-R(2)C(4)	2.369 (9)
C(1,1)-O(1,1)	1.146 (13)	Mo(2)-R(2)C(5)	2.374 (9)
C(2,1)-O(2,1)	1.148 (13)	Mo(3)-R(3)C(1)	2.367 (9)
C(3,1)-O(3,1)	1.159 (14)	Mo(3)-R(3)C(2)	2.343 (9)
C(1,2)-O(1,2)	1.150 (14)	Mo(3)-R(3)C(3)	2.329 (9)
C(2,2)-O(2,2)	1.173 (13)	Mo(3)-R(3)C(4)	2.368 (9)
C(3,2)-O(3,2)	1.148 (14)	Mo(3)-R(3)C(5)	2.345 (9)
		Av Mo-RC	2.351 (9)

<sup>a</sup> A number in parentheses associated with an average quantity is the standard deviation of a single observation.

Å for Tl (obtained from the Tl-C distance in  $\text{Tl}(\text{CH}_3)_3$  and a C radius of 0.77 Å), a Tl-Mo single-bond distance of 3.07 Å is calculated. This is 0.10 Å longer than the observed bond distance. Such a shortening of the metal-metal bond length is also observed for the tin to molybdenum bond in the compound  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]\text{SnCl}$ .<sup>17</sup> This shortening is not observed in  $[\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)]_2$  where the metal-metal interaction is between two molybdenum atoms with a formal oxidation state of zero.<sup>18</sup>

(17) J. E. O'Connor and E. J. Corey, *J. Amer. Chem. Soc.*, **89**, 3930 (1967).

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

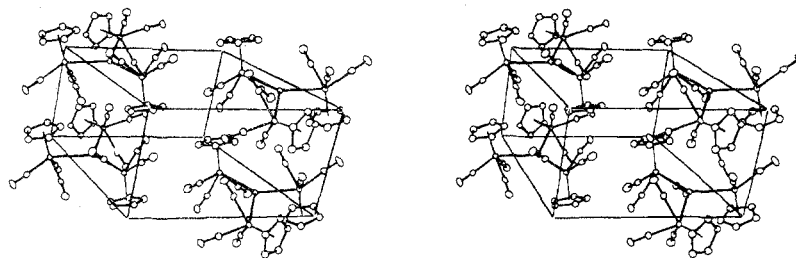


Figure 1. A stereoscopic view of two unit cells of  $\text{Tl}(\text{Mo}(\text{CO})_3\text{Cp})_3$ . Hydrogen atoms have been omitted for the sake of clarity. The other atoms are drawn at their 50% probability levels. In this drawing  $x$  goes from right to left,  $z$  from bottom to top, and  $y$  into the paper. The unit cell is doubled in the  $z$  direction.

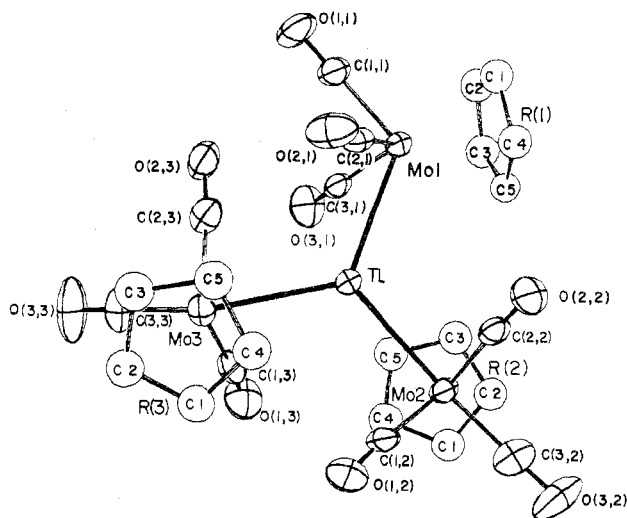


Figure 2. An overall view of the  $\text{Tl}(\text{Mo}(\text{CO})_3\text{Cp})_3$  molecule showing the labeling scheme and the vibrational ellipsoids at their 50% probability level. Hydrogen atoms on the cyclopentadienyl ring have been omitted for the sake of clarity.

Table VI. Bond Angles (deg)

Atoms	Angle	Atoms	Angle
Mo(1)-Tl-Mo(2)	113.92 (6)	C(1,2)-Mo(2)-C(2,2)	97.6 (5)
Mo(2)-Tl-Mo(3)	122.66 (6)	C(2,2)-Mo(2)-C(3,2)	80.4 (5)
Mo(3)-Tl-Mo(1)	122.61 (6)	C(3,2)-Mo(2)-C(1,2)	82.5 (5)
Av Mo-Tl-Mo	119.73	C(1,3)-Mo(3)-C(2,3)	105.2 (5)
C(1,1)-Mo(1)-Tl	67.4 (3)	C(2,3)-Mo(3)-C(3,3)	80.6 (5)
C(2,1)-Mo(1)-Tl	119.2 (3)	C(3,3)-Mo(3)-C(1,3)	79.6 (5)
C(3,1)-Mo(1)-Tl	66.3 (3)	Mo(1)-C(1,1)-O(1,1)	174.0 (9)
C(1,2)-Mo(2)-Tl	76.4 (3)	Mo(1)-C(2,1)-O(2,1)	179.4 (10)
C(2,2)-Mo(2)-Tl	71.6 (3)	Mo(1)-C(3,1)-O(3,1)	174.1 (10)
C(3,2)-Mo(2)-Tl	142.0 (3)	Mo(2)-C(1,2)-O(1,2)	174.5 (10)
C(1,3)-Mo(3)-Tl	71.4 (3)	Mo(2)-C(2,2)-O(2,2)	176.4 (9)
C(2,3)-Mo(3)-Tl	73.9 (3)	Mo(2)-C(3,2)-O(3,2)	172.2 (11)
C(3,3)-Mo(3)-Tl	134.1 (4)	Mo(3)-C(1,3)-O(1,3)	175.6 (10)
C(1,1)-Mo(1)-C(2,1)	80.5 (5)	Mo(3)-C(2,3)-O(2,3)	173.5 (10)
C(2,1)-Mo(1)-C(3,1)	79.7 (5)	Mo(3)-C(3,3)-O(3,3)	178.2 (11)
C(3,1)-Mo(1)-C(1,1)	110.1 (5)	Av Mo-C-O	175.3 (22)

The dimensions and geometry of the " $\text{Mo}(\text{CO})_3\text{Cp}$ " groups do not differ from those found in a variety of other  $\text{Mo}(\text{CO})_3\text{Cp}$  derivatives. A comparison with other structures involving this group is shown in Table VIII.

The geometry around the thallium atom is fairly distorted, as it lacks a threefold symmetry and the Mo-Tl-Mo angles deviate considerably from  $120^\circ$ . Such deviations are also observed in the similar but simpler organometallics  $\text{Tl}(\text{CH}_3)_3$ ,<sup>5</sup>  $\text{In}(\text{CH}_3)_3$ ,<sup>6</sup> and  $\text{In}(\text{C}_6\text{H}_5)_3$ .<sup>7</sup> In these compounds, the polymeric nature of the crystalline material is given as explanation for the distortions. But in  $\text{Tl}[\text{Mo}(\text{CO})_3\text{Cp}]_3$ , the closest intermolecular Tl-Mo distance is greater than 6.5 Å, which is too large to account for the distortion. Moreover, all intermolecular Mo-Mo distances are greater than 5.5

Table VII. Root-Mean-Square Amplitudes of Vibration (Å)<sup>a</sup>

Atom	Min	Intermed	Max
Tl	0.1531 (9)	0.1719 (8)	0.1950 (8)
Mo(1)	0.153 (2)	0.172 (2)	0.199 (2)
Mo(2)	0.155 (2)	0.185 (2)	0.203 (2)
Mo(3)	0.171 (2)	0.173 (2)	0.202 (2)
C(1,1)	0.14 (2)	0.20 (2)	0.22 (2)
C(2,1)	0.18 (2)	0.21 (2)	0.23 (2)
C(3,1)	0.15 (2)	0.18 (2)	0.27 (2)
C(1,2)	0.14 (2)	0.20 (2)	0.26 (2)
C(2,2)	0.15 (2)	0.20 (2)	0.22 (2)
C(3,2)	0.16 (2)	0.22 (2)	0.28 (2)
C(1,3)	0.16 (2)	0.21 (2)	0.23 (2)
C(2,3)	0.19 (2)	0.19 (2)	0.25 (2)
C(3,3)	0.18 (2)	0.20 (2)	0.29 (2)
O(1,1)	0.20 (1)	0.21 (1)	0.32 (1)
O(2,1)	0.16 (2)	0.26 (1)	0.30 (1)
O(3,1)	0.19 (2)	0.27 (1)	0.29 (1)
O(1,2)	0.18 (2)	0.26 (1)	0.33 (1)
O(2,2)	0.18 (1)	0.23 (1)	0.26 (1)
O(3,2)	0.17 (2)	0.26 (1)	0.38 (1)
O(1,3)	0.21 (1)	0.25 (1)	0.30 (1)
O(2,3)	0.18 (1)	0.22 (1)	0.34 (1)
O(3,3)	0.17 (2)	0.25 (1)	0.43 (1)

<sup>a</sup> Figure 2 provides an indication of the directions of these principal axes of vibration.

Table VIII. Distances (Å) between Adjacent Atoms in the  $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3$  Group of (A)  $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3]_2$ ,<sup>a</sup> (B)  $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3(\text{C}_2\text{H}_5)$ ,<sup>b</sup> (C)  $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3(\text{CH}_2\text{CO}_2\text{H})$ ,<sup>c</sup> (D)  $[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]_2[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3]\text{SnCl}$ ,<sup>d</sup> and (E)  $\text{Tl}[\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)]_3$ <sup>e</sup>

Atoms	A	B	C	D	E
Mo-C(ring)	2.35	2.38 (2)	2.37 (2)	2.35 (5)	2.351 (9)
Mo-C(carbonyl)	1.96	1.96	1.99 (2)	1.96 (4)	1.968 (12)
C-O	1.16	1.15	1.15 (3)	1.20 (6)	1.154 (8)
C-C(ring)	1.42	1.43 (4)	1.42 (3)	1.45 (8)	1.42
Mo-ring center		2.04	2.01		2.02

<sup>a</sup> Reference 18. <sup>b</sup> M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963). <sup>c</sup> J. K. P. Ariyaratne, A. M. Bierrium, M. L. H. Green, C. K. Prout, and M. G. Swanwick, *J. Chem. Soc. A*, 1309 (1969). <sup>d</sup> Reference 17. <sup>e</sup> This work.

Å and the intramolecular Mo-Mo distances are of the order of 5.0 Å. This casts doubt on the conjecture that the proximity of the molybdenum atoms brings about the decomposition of  $\text{Tl}[\text{Mo}(\text{CO})_3\text{Cp}]_3$  in solution, according to the equilibrium  $\text{Tl}[\text{Mo}(\text{CO})_3\text{Cp}]_3 \rightleftharpoons [\text{CpMo}(\text{CO})_3]_2 + \text{Tl}[\text{Mo}(\text{CO})_3\text{Cp}]$  as suggested by King.<sup>3</sup>

In addition, inter- and intramolecular atomic contacts (including hydrogen atoms) were computed to see whether such interactions could account for the distortions. No systematic close interactions of  $\text{H} \cdots \text{H}$  contacts  $\leq 2.0$  Å were found. Also, no intermolecular contacts less than 3.6 Å between the carbon or oxygen atoms and thallium were found. Distances of up to 3.4 Å have been used previously as providing evidence for weak intermolecular interactions in similar organometallics.<sup>7</sup>

The only other structure of a similar system was recently

reported by Robinson and Schussler for the compound In[Co(CO)<sub>4</sub>]<sub>3</sub>.<sup>19</sup> The InCo<sub>3</sub> moiety is reported to be trigonal and planar.

### Discussion

The initial purpose of this structure determination was to investigate the red-green dichroic appearance of the crystals of Tl[Mo(CO)<sub>3</sub>Cp]<sub>3</sub>. King<sup>3</sup> had conjectured that the dichroism associated with this compound is similar to that observed in planar complexes of rhodium(I), iridium(I), and platinum(II) which can form "stacked" polymeric crystal structures with metal-metal bonding on an axis perpendicular to the square plane. Consequently, to account for the dichroism he invoked a thallium to thallium interaction (the trigonal planes of molecules stacked one on top of the other) extending along the crystal. An optical study of the crystals was conducted by us with the aid of a polarizing microscope. Maximum extinctions were observed along the needle axis, which coincides with the *c* axis of the crystal. Though this was promising, the closest thallium to thallium distance observed from the complete structure determination is 6.833 Å along the *c* axis. A *c*-axis projection shows an approximate

(19) W. R. Robinson and D. P. Schussler, *Proc. Int. Conf. Coord. Chem.*, 14, 7 (1972).

parallel arrangement of the cyclopentadiene rings about the molybdenum atoms but the distances are too large to invoke electron delocalization. Though the crystals of Tl[Co(CO)<sub>4</sub>]<sub>3</sub> were reported to be deep red to black in color, no mention of their optical properties was made. Hence, without the aid of further microspectrophotometric studies on these crystals, little can be said about the reasons for their dichroic nature. With hindsight, the visually observed fluorescent nature of the solutions of Tl[Mo(CO)<sub>3</sub>Cp]<sub>3</sub> suggests a molecular phenomenon for the observed colors rather than of an extended crystalline nature.

Attempts to obtain some single-crystal conductivity measurements in order to detect any relationships between the axis of prominent dichroism and possible anisotropic conduction failed since the crystals were too small and too brittle for such measurements.

Registry No. Tl(Mo(CO)<sub>3</sub>(π-C<sub>5</sub>H<sub>5</sub>))<sub>3</sub>, 37325-09-0.

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## Structure of *trans*-Dihydridotetrakis(diethyl phenylphosphonite)ruthenium(II)

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The crystal structure of *trans*-dihydridotetrakis(diethyl phenylphosphonite)ruthenium(II), RuH<sub>2</sub>[(C<sub>6</sub>H<sub>5</sub>)P(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, has been determined by X-ray techniques using counter data. The ruthenium atom coordination is distorted from an idealized *D<sub>4h</sub>* model (equatorial phosphines, axial hydrogens) in favor of a flattened equatorial RuP<sub>4</sub> tetrahedron with axial hydride hydrogen atoms. The phosphorus atoms are 0.37 Å from the equatorial plane with an average Ru-P distance of 2.272 (4) Å. The hydride hydrogen atoms were located and their positions refined giving a Ru-H distance of 1.60 (8) Å. The idealized molecular symmetry of the Ru coordination polyhedron is *S<sub>4</sub>*(4); there is space group imposed *C<sub>2</sub>*(2) molecular symmetry. The shape of the RuP<sub>4</sub> tetrahedron arises primarily from steric effects. The structure is compared with the *cis*-FeH<sub>2</sub>[(C<sub>6</sub>H<sub>5</sub>)P(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> structure. Crystals are monoclinic, space group *C2/c* (*Z* = 4), with cell dimensions of *a* = 20.157 (10), *b* = 12.359 (6), *c* = 18.506 (9) Å, and β = 92.76 (6)°. The structure was refined by least squares to a conventional *R* of 0.074 for 1751 observed reflections.

### Introduction

Numerous six-coordinate iron and ruthenium dihydrides are stereochemically nonrigid in solution yielding abundant stereochemical information from X-ray and nmr studies.<sup>1-4</sup> The best characterized example of fluxional behavior in six-coordinate MH<sub>2</sub>L<sub>4</sub> complexes is *cis*-FeH<sub>2</sub>[(C<sub>6</sub>H<sub>5</sub>)P(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>. Structural and mechanistic data<sup>1-5</sup> have been presented for this complex. The iron-phosphorus geometry in this molecule is significantly distorted in the solid state toward a tetrahedron.<sup>5</sup> The fluxional behavior in solution has been

interpreted in terms of a novel "tetrahedral tunneling" mechanism in which the hydrogen atoms traverse the faces of a pseudo phosphorus tetrahedron.<sup>1-3</sup>

An analogous series of ruthenium complexes<sup>2,4</sup> have been prepared which are also fluxional in solution, but with larger barriers to rearrangement than in the iron complexes. The fluxional behavior and the size of the barrier to rearrangement with bulky phosphine ligands are certainly influenced, if not controlled, by steric effects. The crystal structure of *trans*-dihydridotetrakis(diethyl phenylphosphonite)-ruthenium(II), RuH<sub>2</sub>[(C<sub>6</sub>H<sub>5</sub>)P(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, was determined to establish the nature of the ruthenium coordination, in particular the distortion from idealized octahedral models. Parallel work on the nmr interpretation of RuH<sub>2</sub>L<sub>4</sub> complexes was reported recently.<sup>4</sup> Data (X-ray and nmr) have also been reported recently for the interesting example of fluxional eight-coordinate MoH<sub>4</sub>L<sub>4</sub> complexes.<sup>6</sup>

### Experimental Section

The preparation of RuH<sub>2</sub>[(C<sub>6</sub>H<sub>5</sub>)P(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> was reported

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