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The Synthesis and Structure of the Novel Binuclear Iridium-Dithiolene Complex Dicarbonylbis(triphenylphosphine)tris(toluene-3,4-dithiolato)diiridium(III), $\text{Ir}_2(\text{tdt})_3(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$

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The reaction of $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ with toluene-3,4-dithiol, H_2tdt , has been investigated as a means of synthesizing new iridium-dithiolene complexes. In addition to the simple oxidative addition product, two new complexes are formed, one of which has been characterized structurally by single-crystal X-ray methods. $\text{Ir}_2(\text{tdt})_3(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ crystallizes in space group $B\bar{1}$ of the triclinic system in a cell of dimensions $a = 20.43$ (2), $b = 12.39$ (1), $c = 22.05$ (2) Å, $\alpha = 104.73$ (5), $\beta = 95.65$ (5), $\gamma = 89.25$ (5)°, and $V = 5374$ Å³. There are four binuclear units per unit cell ($\rho_{\text{exptl}} = 1.73 \pm 0.03$ g/cm³; $\rho_{\text{calcd}} = 1.76$ g/cm³). The structure was solved by Patterson and Fourier methods and refined by least squares to a final R factor of 0.061 for 3218 observed reflections. The structure of the complex consists of two Ir atoms held together by bridging sulfur atoms of two tdt ligands which are chelated to only one of the iridiums. Each Ir atom is octahedrally coordinated and can be considered as an Ir(III) ion, but the coordination sphere about each differs considerably. As such, the complex represents a new structure type in dithiolene complex chemistry. The Ir-bridging S distances which average 2.465 (11) Å are significantly longer than the Ir-S distances within the chelate rings (average value of 2.383 (10) Å). The Ir-Ir distance is 3.668 (3) Å. A scheme for the formation of this unusual binuclear complex is proposed.

Introduction

Studies of the oxidative addition reactions of thiols with complexes of Ir(I) and Rh(I) have been reported recently by Singer and Wilkinson¹ and by Stiddard and Townsend.² During this same period of time, we have been studying the reaction of toluene-3,4-dithiol, H_2tdt , with $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ as a means of synthesizing new and interesting iridium-dithiolene complexes. Our study reveals that if the reaction between H_2tdt and $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ is allowed to continue beyond the initial oxidative addition step reported previously,¹ several new products are obtained. One of these is an unusual binuclear Ir(III) complex whose complete structural characterization is reported herein.

To date, the only other report of well-characterized iridium-dithiolene complexes has been made by Connelly and McCleverty,³ who examined the reaction of Vaska's complex with bis(perfluoromethyl)dithietene. In their study, these authors isolated two polynuclear complexes of iridium³ but with stoichiometries differing from those reported in the present study.

Experimental Section

Materials.—Toluene-3,4-dithiol (H_2tdt) was purchased from Matheson Coleman and Bell and was used without further purification. Vaska's complex, $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$, was prepared following the method of Collman, *et al.*⁴ Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

Reaction of $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ with H_2tdt .—A 0.47-g (3-mmol) sample of H_2tdt was added to 0.78 g (1 mmol) of $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ dissolved in 30 ml of benzene at room temperature under an atmosphere of nitrogen. The reaction mixture was stirred for about 10 hr, and the pale yellow solid separated was collected by filtration and identified as the initial oxidative addition product $\text{IrHCl}(\text{H}_2\text{tdt})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$, I, reported previously.¹ The brown filtrate was evaporated *in vacuo* to yield a red-brown oil. The oil was dissolved in a minimum volume of CH_2Cl_2 and chromatographed on alumina using a 4:6 v/v mixture of benzene and hexane as eluent. Two bands separated on the column, the first one green and the second orange-red, and these bands were collected separately. The green solution was evaporated to dryness and the residue was recrystallized from

methylene chloride-hexane solution to yield green-black crystals of $\text{Ir}_2(\text{tdt})_3(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$, II. *Anal.* Calcd for $\text{Ir}_2(\text{tdt})_3(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$, II: C, 49.6; H, 3.37. Found: C, 48.9; H, 3.51. Elemental analyses for sulfur were inconsistent for different runs on the same sample.

The orange-red solution, after the removal of solvent under reduced pressure, yielded a red oil. Orange-red crystals, III, were subsequently obtained when a benzene solution of the red oil was allowed to stand for 24 hr after the addition of a small amount of methanol. No unambiguous formulation of this compound is possible at the present time, but it seems likely that III is polynuclear in analogy with Connelly and McCleverty's work.³ *Anal.* Found: C, 50.8; H, 3.27.

The yields of I, II, and III were 60, 8, and 3% (assuming III to be trinuclear), respectively, based on $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$. When the reaction time was increased to 35 hr, the yield of II decreased but the yield of III increased to 10%. Compound I was found to be soluble in dichloromethane and chloroform but insoluble in benzene, hexane, and methanol, while compounds II and III were soluble in benzene, dichloromethane, and chloroform but insoluble in hexane and methanol.

Spectroscopic Measurements.—Infrared spectra were measured on a Perkin-Elmer Model 337 grating spectrophotometer. Unless otherwise noted, the infrared spectra were taken as KBr pellets.

Collection and Reduction of the X-Ray Data for $\text{Ir}_2(\text{tdt})_3(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$.—Green-black crystals of II suitable for single-crystal X-ray studies were grown from methylene chloride-methanol solutions. Single-crystal Weissenberg and precession photographs and optical examinations of the crystals indicated the complex to crystallize in the triclinic system. A convenient nonprimitive cell which gave systematic extinctions of hkl for $h + l = 2n + 1$ was chosen for the structure determination. The systematic absences are consistent with either of the space groups $B1$ or $B\bar{1}$ which represent nonprimitive settings of the triclinic space groups $P1$ (C_1 , no. 1) and $P\bar{1}$ (C_1 , no. 2), respectively.⁵ The lattice constants at room temperature, which were determined from a least-squares refinement⁶ of the angular settings of 14 reflections centered on a Picker four-circle automated diffractometer using Mo $K\alpha$ radiation (λ 0.7107 Å), are $a = 20.43$ (2), $b = 12.39$ (2), $c = 22.05$ (2) Å, $\alpha = 104.73$ (5), $\beta = 95.65$ (5), $\gamma = 89.25$ (5)°, and $V = 5374$ Å³. A De-

(5) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1960, pp 74, 75.

(6) The main programs used in this work were our PICKLST orientation refinement and diffractometer setting program and local versions of Hamilton's GONO9 absorption program, the Busing-Levy ORFLS least-squares program, the Zalkin FORDAP Fourier summation program, the Busing-Martin-Levy ORFFE function and error program, the Dewar FAME scaling program, and the Johnson ORTEP plotting program. Various other local programs were also used. All computing was performed on Brown's IBM 360/67 computer.

(1) H. Singer and G. Wilkinson, *J. Chem. Soc. A*, 2516 (1968).

(2) M. H. B. Stiddard and R. E. Townsend, *ibid.*, 2719 (1970).

(3) N. G. Connelly and J. A. McCleverty, *ibid.*, 1621 (1970).

(4) J. P. Collman, C. T. Sears, and M. Kubota, *Inorg. Syn.*, **11**, 101 (1968).

launay reduction⁷ did not reveal the presence of any symmetry and yielded the following reduced cell parameters: $a = 15.75$ (2), $b = 18.13$ (2), $c = 17.06$ (2) Å, $\alpha = 108.83$ (5), $\beta = 94.30$ (5), $\gamma = 137.77$ (5)°, and $V = 2687$ Å³. An observed density of 1.73 ± 0.03 g/cm³ obtained by the flotation method in methylene iodide-carbon tetrachloride solution agrees with the value of 1.76 g/cm³ calculated for four molecules per unit cell.

The crystal used for the intensity data collection was of approximate dimensions $0.24 \times 0.11 \times 0.11$ mm (the longest dimension being in the c^* direction). The crystal was mounted on a glass fiber in the a^* direction and aligned accurately on a precession camera. After the crystal was transferred to the diffractometer, its mosaic spread was determined from open-counter, narrow-source ω scans⁸ through several strong reflections and found to have an average value of 0.5° . The intensity data were collected by the θ - 2θ scan technique using Zr-filtered Mo K α radiation. A takeoff angle of 1.5° was used for the data collection with a counter opening of 5×5 mm. Each reflection was scanned from -0.8 to $+1.0^\circ$ of the calculated 2θ value for the reflection at a scan rate of $1^\circ/\text{min}$. The background was counted for 10 sec at each end of the scan range. The maximum 2θ value for the reflections which were measured was 45° . Pulse height analysis designed to accept 90% of the diffracted Mo K α radiation was employed. The intensities of four strong reflections were measured after every 100 reflections to check on crystal and electronic stability. No systematic variation of these standards was observed, although the standards did deviate as much as 8% from their mean values.

The intensities of 7226 independent reflections was measured and these were then corrected for the usual Lorentz and polarization factors to yield a set of F_o^2 values where F_o is the observed structure factor amplitude. Of the 7226 independent reflections measured, 3271 were assumed to be statistically reliable, having $F_o^2 > 1.5\sigma(F_o^2)$. For the absorption correction, the six faces of the crystal were identified by optical goniometry and their identification was confirmed with the diffractometer settings for the corresponding reflections. The six faces were 100, $\bar{1}00$, $0\bar{1}2$, $01\bar{2}$, $0\bar{1}0$, and 120 . W. C. Hamilton's GONO9 absorption program was used for the absorption correction. The linear absorption for $\text{Ir}_2(\text{tdt})_3(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ is 55.65 cm⁻¹, and for this crystal, the transmission coefficients range from 0.26 to 0.68.

Solution and Refinement of the Structure.—The centrosymmetric space group $B\bar{1}$ was initially assumed to be the correct one for the structure. This assumption received support from the distribution of normalized structure factors⁹ calculated using Dewar's FAME program and appears to be justified ultimately by the successful solution and refinement of the structure described herein. With four molecules per unit cell and no crystallographic symmetry imposed on the molecule, all atoms can occupy general positions of the space group. A simple survey of the diffraction data showed that in addition to the centering conditions for nonzero reflection, only those reflections with h even and l even possessed significantly large intensities, and this pattern was taken to indicate that the iridium atoms occupied positions different by approximately 0.5 in either the x or z coordinates. This notion was confirmed as the positions of the two Ir atoms were easily determined from a three-dimensional Patterson function map. A difference Fourier map based on phases obtained from the two Ir atom contributions revealed the positions of eight more atoms, which were taken to be either the sulfur or phosphorus atoms. The positional parameters of all ten atoms

along with individual isotropic temperature factors assigned to them were refined through two cycles of least squares. The positions of all of the carbon and oxygen atoms were then determined from a number of difference Fourier maps based on phases obtained from the refined positions of the located atoms. It was only after the location of the ring carbon atoms that the positions of the phosphorus and sulfur atoms could be differentiated.

The trial structure was refined using a least-squares procedure. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weights w were assigned as $4F_o^2/\sigma^2(F_o^2)$ and the standard deviations σ were estimated from counting statistics¹⁰ according to the formula

$$\sigma(F_o^2) = \frac{1}{TLp} (C + \frac{1}{2}(t_c/t_b)^2(B_1 + B_2) + (0.03I)^2)^{1/2}$$

where Lp is the Lorentz-polarization factor, T is the transmission coefficient, C is the total integrated count obtained in time t_c , B_1 and B_2 are the background counts, each obtained in time t_b , and I is the net integrated count. The iridium, sulfur, phosphorus, carbon, and oxygen atom scattering factors used were those tabulated by Cromer and Waber.^{11a} The effects of anomalous scattering were included in the calculated structure factors with values of $\Delta f'$ and $\Delta f''$ for Ir, P, and S taken from Cromer's tabulation.^{11b} Only those reflections with F_o^2 greater than $1.5\sigma(F_o^2)$ were included in the refinement and in the calculation of the discrepancy indices R ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) and R' ($= (\sum w \cdot (|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$).

In all refinements the phenyl groups were treated as rigid groups (D_{6h} symmetry, C-C = 1.392 Å) using the program BUGLES, a local version of the group least-squares program written by Ibers and Doedens.¹² In the initial round of calculations, all non-group atoms were assigned individual isotropic temperature factors and each group was also assigned a single isotropic temperature factor. This refinement of 183 positional and thermal parameters and one variable scale factor after four cycles of refinement converged to discrepancy factors R and R' of 0.135 and 0.158, respectively. A difference Fourier map at this stage indicated considerable anisotropic thermal motion about the heavy atoms. Refinement was therefore continued assuming the ellipsoidal anisotropic thermal model for all heavy atoms (Ir, S, P).

Before the final round of calculations a number of reflections which were affected by errors due to incorrect punching, white radiation streaks, and unusually high background counts were eliminated. Because of computer limitations, the anisotropic refinement was carried out in blocks, with the parameters of two of the three tdt ligands and the group parameters varied on alternate cycles. This refinement converged to discrepancy factors of 0.060 and 0.061, respectively. However, an examination of the bond distances and angles calculated for the structure based on this refinement indicated that the carbon atoms of the carbonyl groups had refined to positions that were chemically unreasonable.¹³ It was therefore decided to hold these positional parameters fixed at more chemically reasonable values obtained from a difference Fourier map based on a refinement in which the CO groups were omitted. This refinement converged after three cycles to a conventional R factor of 0.061 and a weighted R factor R' 0.063 for 3218 reflections above 1.5σ . The final estimated standard deviation of an observation of unit weight is 1.08.

In the final difference Fourier map, the highest peak had a value of 1.14 e/Å³ or approximately 50% of the height of a carbon atom in this structure. There were four such peaks having

(7) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1960, p 530.

(8) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10.

(9) I. L. Karle, K. S. Dragoinette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965); as quoted in G. H. Stout and L. H. Jensen, "X-Ray Structure Determination—A Practical Guide," Macmillan, New York, N. Y., 1968, p 320. The experimental distribution of the normalized structure factors $|E|$ together with theoretical values for the centrosymmetric and noncentrosymmetric cases is as follows

	Exptl	Theoret	
		Centro-symmetric	Noncentro-symmetric
Av $ E ^2$	0.984	1.000	1.000
Av $ E^2 - 1 $	1.109	0.968	0.736
Av $ E $	0.718	0.798	0.886
$ E > 1, \%$	29.98	32.00	37.00
$ E > 2, \%$	6.02	5.00	1.80
$ E > 3, \%$	0.21	0.30	0.01

(10) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(11) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965);

(b) D. T. Cromer, *ibid.*, **18**, 17 (1965).

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

(13) The positional and isotropic thermal parameters obtained from this refinement for the carbonyl ligand atoms are

Atom	x	y	z	$B, \text{Å}^2$
CO(1)C	0.310 (1)	-0.019 (2)	-0.094 (1)	3.0 (5)
CO(1)O	0.370 (1)	0.008 (2)	-0.091 (1)	6.0 (4)
CO(2)C	0.258 (2)	0.027 (4)	0.155 (2)	9.6 (12)
CO(2)O	0.277 (1)	-0.040 (2)	0.189 (1)	7.4 (7)

These parameters lead to the following bond distances and angles which we judged to be chemically unreasonable: Ir(1)-CO(1)C, 1.56 (3) Å; Ir(2)-CO(2)C, 1.73 (5) Å; CO(1)C-CO(1)O, 1.30 (3) Å; CO(2)C-CO(2)O, 1.29 (5) Å; Ir(1)-CO(1)C-CO(1)O, 167 (2)°; Ir(2)-CO(2)C-CO(2)O, 151 (3)°.

TABLE I
 FINAL PARAMETERS FOR $\text{Ir}_2(\text{tdt})_3(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$

Atomic Positional and Isotropic Thermal Parameters				
Atom ^a	x^b	y^b	z^b	B^c
Ir(1)	0.2402 (1) ^d	-0.0615 (1)	-0.0845 (1)	<i>e</i>
Ir(2) ^f	0.2529 (1)	0.0681 (1)	0.0855 (1)	<i>e</i>
S(1)	0.3667 (5)	0.0775 (9)	0.0724 (5)	<i>e</i>
S(2)	0.2526 (5)	-0.1136 (10)	0.0163 (5)	<i>e</i>
S(3)	0.2185 (4)	0.0252 (8)	-0.1665 (4)	<i>e</i>
S(4)	0.1258 (5)	-0.1027 (9)	-0.0907 (4)	<i>e</i>
S(5)	0.1366 (4)	0.0401 (8)	0.0818 (4)	<i>e</i>
S(6)	0.2316 (5)	0.1239 (8)	-0.0103 (4)	<i>e</i>
P(1)	0.2460 (5)	-0.2433 (8)	-0.1529 (4)	<i>e</i>
P(2)	0.2555 (5)	0.2540 (10)	0.1524 (5)	<i>e</i>
C(1)	0.391 (1)	-0.063 (3)	0.047 (1)	5.2 (7)
C(2)	0.453 (1)	-0.088 (3)	0.051 (1)	6.1 (8)
C(3)	0.469 (2)	-0.211 (3)	0.028 (2)	7 (1)
C(4)	0.419 (2)	-0.283 (3)	0.009 (1)	7.1 (8)
C(5)	0.355 (2)	-0.268 (3)	0.009 (1)	5.3 (7)
C(6)	0.340 (1)	-0.146 (3)	0.027 (1)	5.0 (8)
C(7)	0.454 (2)	-0.380 (4)	-0.011 (2)	18 (1)
C(8)	0.136 (2)	0.002 (3)	-0.188 (1)	6.0 (8)
C(9)	0.102 (2)	0.035 (3)	-0.243 (2)	9 (1)
C(10)	0.040 (2)	0.019 (3)	-0.263 (2)	7.9 (9)
C(11)	0.004 (2)	-0.032 (3)	-0.234 (2)	7.1 (9)
C(12)	0.023 (2)	-0.069 (3)	-0.177 (2)	7.0 (8)
C(13)	0.094 (1)	-0.051 (3)	-0.157 (1)	5.2 (7)
C(14)	-0.069 (3)	-0.084 (5)	-0.267 (2)	14 (2)
C(15)	0.106 (1)	0.122 (3)	0.027 (1)	5.2 (7)
C(16)	0.036 (2)	0.141 (3)	0.025 (1)	6.4 (8)
C(17)	0.015 (2)	0.200 (3)	-0.024 (2)	6.4 (1)
C(18)	0.050 (2)	0.244 (3)	-0.059 (2)	7.7 (9)
C(19)	0.117 (2)	0.217 (3)	-0.055 (1)	6.3 (8)
C(20)	0.143 (2)	0.156 (3)	-0.011 (1)	5.2 (8)
C(21)	-0.045 (2)	0.246 (4)	-0.024 (2)	12 (1)
CO(1)C ^g	0.326	-0.021	-0.088	4.9 (8)
CO(2)C ^g	0.265	0.020	0.157	9 (1)
CO(1)O	0.374 (1)	0.013 (2)	-0.091 (1)	6.7 (6)
CO(2)O	0.277 (1)	-0.040 (2)	0.190 (1)	7.9 (7)

Anisotropic Thermal Parameters ^h						
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir(1)	27 (1)	53 (2)	17 (1)	0 (1)	0 (0)	4 (1)
Ir(2)	26 (1)	52 (2)	19 (1)	8 (1)	-2 (0)	1 (1)
S(1)	33 (3)	75 (10)	32 (3)	-7 (4)	1 (2)	-2 (4)
S(2)	37 (4)	112 (14)	24 (3)	6 (5)	-1 (2)	-3 (5)
S(3)	43 (3)	77 (9)	24 (2)	-21 (4)	-2 (2)	4 (4)
S(4)	29 (3)	75 (10)	22 (3)	-4 (4)	3 (2)	-1 (4)
S(5)	38 (3)	78 (9)	26 (2)	-3 (4)	4 (2)	2 (4)
S(6)	38 (3)	39 (9)	17 (3)	-18 (4)	-4 (2)	7 (4)
P(1)	30 (3)	40 (10)	18 (3)	-12 (5)	1 (2)	6 (4)
P(2)	41 (4)	82 (14)	22 (4)	13 (6)	0 (3)	2 (5)

Group Positional Parameters						
Group	X_0^i	Y_0	Z_0	ϕ^j	θ	ρ
R1	0.134 (1)	-0.297 (1)	-0.271 (1)	2.69 (1)	-2.72 (1)	2.29 (1)
R2	0.384 (1)	-0.300 (1)	-0.211 (1)	-1.36 (3)	-2.07 (1)	1.87 (3)
R3	0.230 (1)	-0.445 (1)	-0.085 (1)	1.14 (2)	-2.59 (1)	-0.57 (1)
R4	0.295 (1)	0.253 (1)	0.299 (1)	1.05 (1)	-2.74 (1)	-1.49 (1)
R5	0.115 (1)	0.375 (1)	0.144 (1)	-0.46 (2)	2.67 (1)	-0.01 (1)
R6	0.359 (1)	0.425 (1)	0.127 (1)	1.79 (4)	1.86 (1)	2.21 (4)

^a In our labeling scheme C(1), C(6), C(8), C(13), C(15), and C(20) are the benzene carbon atoms of the tdt ligands bonded to S(1), S(2), S(3), S(4), S(5), and S(6), respectively. C(7), C(14), and C(21) are methyl carbons of the tdt ligands bonded to C(4), C(11), and C(17), respectively. ^b x , y , z are in fractional coordinates. ^c Isotropic thermal parameters in \AA^2 . ^d Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures. ^e Atoms refined anisotropically. ^f The vector between Ir(1) and the centrosymmetrically related atom of Ir(2) (positional parameters -0.2529, -0.0681, -0.0855) is (0.4931, 0.0066, 0.0010), thus verifying that the two independent Ir atoms occupy positions differing by approximately 0.5 in their x coordinates as construed from the intensity patterns. ^g The positional parameters were held fixed. ^h The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The anisotropic thermal parameters given are times 10^4 . ⁱ X_0 , Y_0 , Z_0 are the fractional coordinates of the ring centers. ^j The angles ϕ , θ , ρ (in radians) have been defined previously. See, for example, R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

values of ca. $1 \text{ e}/\text{\AA}^3$, and all of these were located near the iridium and sulfur atoms. The rest of the peaks were below $0.56 \text{ e}/\text{\AA}^3$. Although the thermal parameters for two of the tdt methyl carbons were relatively large, there were no indications on the final difference Fourier map of any disorder in their positions.

The parameters obtained in the last cycle of refinement are

taken as the final parameters for the structure and are given in Table I along with their estimated standard deviations as obtained from the appropriate inverse matrix. Table II lists the fractional coordinates of the ring carbon atoms, which are derived from the data of Table I. A table of the F_0 and $|F_c|$ values (in electrons $\times 10$) for the 3218 reflections included in the refine-

TABLE II
DERIVED POSITIONAL AND ISOTROPIC THERMAL PARAMETERS
FOR GROUP CARBON ATOMS

Group atoms ^a	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
R(1)C(1)	0.184 (1)	-0.277 (2)	-0.221 (1)	5.0 (7)
R(1)C(2)	0.182 (1)	-0.217 (2)	-0.267 (1)	6.2 (9)
R(1)C(3)	0.132 (1)	-0.238 (2)	-0.316 (1)	5.0 (7)
R(1)C(4)	0.084 (1)	-0.318 (2)	-0.320 (1)	7.0 (9)
R(1)C(5)	0.085 (1)	-0.377 (2)	-0.274 (1)	6.4 (8)
R(1)C(6)	0.135 (1)	-0.357 (2)	-0.225 (1)	5.6 (7)
R(2)C(1)	0.324 (1)	-0.275 (5)	-0.187 (1)	4.9 (7)
R(2)C(2)	0.327 (1)	-0.320 (4)	-0.251 (1)	5.0 (7)
R(2)C(3)	0.387 (1)	-0.345 (2)	-0.275 (1)	6.8 (8)
R(2)C(4)	0.445 (1)	-0.325 (5)	-0.235 (1)	7.7 (9)
R(2)C(5)	0.442 (1)	-0.280 (4)	-0.170 (1)	7.4 (9)
R(2)C(6)	0.382 (1)	-0.255 (2)	-0.146 (1)	6.5 (9)
R(3)C(1)	0.236 (1)	-0.360 (2)	-0.114 (1)	5.7 (7)
R(3)C(2)	0.279 (1)	-0.450 (2)	-0.125 (1)	4.8 (7)
R(3)C(3)	0.273 (1)	-0.535 (2)	-0.095 (1)	6.7 (8)
R(3)C(4)	0.224 (1)	-0.531 (2)	-0.055 (1)	6.7 (8)
R(3)C(5)	0.181 (1)	-0.441 (2)	-0.045 (1)	6.6 (8)
R(3)C(6)	0.187 (1)	-0.356 (2)	-0.074 (1)	6.3 (10)
R(4)C(1)	0.275 (1)	0.255 (2)	0.237 (1)	4.4 (6)
R(4)C(2)	0.332 (1)	0.201 (2)	0.250 (1)	5.1 (7)
R(4)C(3)	0.353 (1)	0.199 (2)	0.312 (1)	5.9 (8)
R(4)C(4)	0.315 (1)	0.252 (2)	0.361 (1)	7.4 (9)
R(4)C(5)	0.258 (1)	0.306 (2)	0.347 (1)	6.4 (8)
R(4)C(6)	0.238 (1)	0.307 (2)	0.285 (1)	6.0 (8)
R(5)C(1)	0.176 (1)	0.325 (2)	0.149 (1)	4.0 (6)
R(5)C(2)	0.122 (1)	0.284 (2)	0.170 (1)	5.4 (7)
R(5)C(3)	0.061 (1)	0.333 (2)	0.165 (1)	7.2 (9)
R(5)C(4)	0.053 (1)	0.424 (2)	0.139 (1)	6.7 (8)
R(5)C(5)	0.107 (1)	0.466 (2)	0.118 (1)	7.3 (9)
R(5)C(6)	0.169 (1)	0.417 (2)	0.124 (1)	5.8 (7)
R(6)C(1)	0.316 (4)	0.347 (4)	0.138 (1)	4.4 (6)
R(6)C(2)	0.354 (2)	0.417 (2)	0.188 (1)	5.3 (7)
R(6)C(3)	0.397 (2)	0.495 (4)	0.177 (1)	6.9 (8)
R(6)C(4)	0.402 (4)	0.503 (4)	0.116 (1)	5.9 (7)
R(6)C(5)	0.364 (2)	0.433 (2)	0.066 (1)	5.8 (8)
R(6)C(6)	0.321 (2)	0.355 (4)	0.077 (1)	5.8 (10)

^a R(1)C(1), R(2)C(1), and R(3)C(1) are attached to P(1) and R(4)C(1), R(5)C(1), and R(6)C(1) are attached to P(2); other carbon atoms are numbered in succession so that R(X)C(4) is para to R(X)C(1). The errors are derived from estimated errors in the group parameters.

ment is available.¹⁴ The root-mean-square amplitudes of vibration for those atoms that were refined anisotropically are included in Table III.

TABLE III
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermed	Max
Ir(1)	0.187 (4)	0.210 (4)	0.239 (3)
Ir(2)	0.179 (4)	0.201 (3)	0.265 (3)
S(1)	0.210 (16)	0.269 (12)	0.303 (14)
S(2)	0.216 (16)	0.270 (13)	0.328 (17)
S(3)	0.195 (14)	0.254 (13)	0.324 (11)
S(4)	0.202 (14)	0.241 (13)	0.272 (14)
S(5)	0.219 (13)	0.265 (13)	0.287 (13)
S(6)	0.138 (23)	0.195 (15)	0.302 (12)
P(1)	0.213 (18)	0.244 (18)	0.316 (18)
P(2)	0.154 (24)	0.206 (17)	0.263 (13)

Results

Spectroscopic Studies.—Infrared spectral data for the iridium tdt complexes are present in Table IV. In all

(14) The table 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, by referring to code number INORG-72-1385. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

TABLE IV
INFRARED SPECTRAL DATA FOR NEW Ir-tdt COMPLEXES^a

I	
3055 m, ^b 2240 s, 2025 vs, 1485 vs, 1435 vs, 1182 m, 1160 m, 1092 vs, 1072 vs, 1026 w, 998 w, 875 w, 835 w, 745 vs, 709 vs, 692 vs, 580 m, 538 sh, 528 vs, 512 sh, 460 w, 425 w	
II	
3047 m, 2915 w, 2855 w, 2053 vs, 2035 vs, 1572 w, 1480 s, 1453 s, 1432 s, 1245 m, 1185 m, 1106 w, 1088 s, 1026 w, 998 w, 870 w, 800 m, 750 m, 708 s, 692 vs, 550 sh, 532 vs, 512 w, 500 w	
III	
3050 m, 2960 sh, 2915 m, 2860 w, 2050 vs, 1585 s, 1485 s, 1455 vs, 1435 vs, 1380 m, 1245 m, 1204 w, 1185 m, 1106 w, 1090 s, 1030 s, 995 w, 865 m, 808 s, 742 s, 706 vs, 695 vs, 546 sh, 532 vs, 516 w, 502 w, 450 w	

^a Spectra taken as KBr pellets. The values given are in cm⁻¹. L = P(C₆H₅)₃. ^b Key: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

TABLE V

PRINCIPAL INTRAMOLECULAR DISTANCES (Å) AND ANGLES (DEG)			
Ir(1)-Ir(2)	3.668 (3)	P(1)-Ir(1)-S(2)	98.3 (4)
Ir(1)-S(2)	2.457 (12)	P(1)-Ir(1)-S(3)	94.1 (3)
Ir(1)-S(3)	2.332 (10)	P(1)-Ir(1)-S(4)	84.7 (3)
Ir(1)-S(4)	2.381 (10)	P(1)-Ir(1)-S(6)	177.5 (3)
Ir(1)-S(6)	2.474 (10)	P(1)-Ir(1)-CO(1)C	95.7
Ir(2)-S(1)	2.379 (10)	S(2)-Ir(1)-S(3)	166.9 (4)
Ir(2)-S(2)	2.377 (11)	S(2)-Ir(1)-S(4)	87.7 (4)
Ir(2)-S(5)	2.396 (9)	S(2)-Ir(1)-S(6)	79.7 (3)
Ir(2)-S(6)	2.384 (10)	S(2)-Ir(1)-CO(1)C	99.4
Ir(1)-P(1)	2.380 (10)	S(3)-Ir(1)-S(4)	89.1 (3)
Ir(2)-P(2)	2.397 (11)	S(3)-Ir(1)-S(6)	87.8 (3)
Ir(1)-CO(1)C	1.85	S(3)-Ir(1)-CO(1)C	83.6
Ir(2)-CO(2)C	1.83	S(4)-Ir(1)-S(6)	93.8 (3)
S(1)-S(2)	3.26 (2)	S(4)-Ir(1)-CO(1)C	172.7
S(3)-S(4)	3.31 (1)	S(6)-Ir(1)-CO(1)C	86.0
S(5)-S(6)	3.30 (1)	P(2)-Ir(2)-S(1)	91.8 (4)
CO(1)C-CO(1)O	1.07	P(2)-Ir(2)-S(2)	177.8 (5)
CO(2)C-CO(2)O	1.17	P(2)-Ir(2)-S(5)	95.9 (3)
S(1)-C(1)	1.77 (3)	P(2)-Ir(2)-S(6)	95.1 (4)
S(2)-C(6)	1.84 (3)	P(2)-Ir(2)-CO(2)C	86.8
S(3)-C(8)	1.71 (3)	S(1)-Ir(2)-S(2)	86.7 (4)
S(4)-C(13)	1.80 (3)	S(1)-Ir(2)-S(5)	170.8 (3)
S(5)-C(15)	1.83 (3)	S(1)-Ir(2)-S(6)	87.1 (4)
S(6)-C(20)	1.86 (3)	S(1)-Ir(2)-CO(2)C	95.4
C(1)-C(2)	1.31 (3)	S(2)-Ir(2)-S(5)	85.4 (3)
C(2)-C(3)	1.52 (4)	S(2)-Ir(2)-S(6)	83.1 (3)
C(3)-C(4)	1.33 (4)	C(2)-Ir(2)-CO(2)C	94.9
C(4)-C(5)	1.30 (4)	S(5)-Ir(2)-S(6)	87.3 (3)
C(5)-C(6)	1.50 (4)	S(5)-Ir(2)-CO(2)C	89.9
C(6)-C(1)	1.42 (4)	S(6)-Ir(2)-CO(2)C	176.7
C(7)-C(4)	1.39 (5)	Ir(1)-S(2)-Ir(2)	98.7 (5)
C(8)-C(9)	1.48 (4)	Ir(1)-S(6)-Ir(2)	98.0 (4)
C(9)-C(10)	1.30 (4)	Ir(1)-CO(1)C-CO(1)O	172
C(10)-C(11)	1.27 (4)	Ir(2)-CO(2)C-CO(2)O	159
C(11)-C(12)	1.46 (4)	Ir(1)-S(4)-C(13)	102 (1)
C(12)-C(13)	1.48 (4)	S(4)-C(13)-C(8)	121 (2)
C(13)-C(8)	1.43 (4)	Ir(1)-S(3)-C(8)	104 (1)
C(14)-C(11)	1.65 (6)	S(3)-C(8)-C(13)	123 (3)
C(15)-C(16)	1.45 (4)	Ir(2)-S(1)-C(1)	105 (1)
C(16)-C(17)	1.47 (4)	S(1)-C(1)-C(6)	118 (2)
C(17)-C(18)	1.33 (5)	Ir(2)-S(2)-C(6)	100 (1)
C(18)-C(19)	1.40 (4)	S(2)-C(6)-C(1)	124 (3)
C(19)-C(20)	1.43 (4)	Ir(2)-S(5)-C(15)	101 (1)
C(20)-C(15)	1.32 (4)	S(5)-C(15)-C(20)	124 (3)
C(17)-C(21)	1.33 (5)	Ir(2)-S(6)-C(20)	102 (1)
P(1)-R(1)C(1)	1.84 (2)	S(6)-C(20)-C(15)	121 (3)
P(1)-R(2)C(1)	1.82 (2)	Ir(1)-S(2)-C(6)	104 (1)
P(1)-R(3)C(1)	1.87 (2)	Ir(1)-S(6)-C(20)	106 (1)
P(2)-R(5)C(1)	1.86 (2)	Ir(1)-P(1)-R(1)C(1)	116 (1)
P(2)-R(5)C(1)	1.85 (2)	Ir(1)-P(1)-R(2)C(1)	115 (1)
P(2)-R(6)C(1)	1.80 (2)	Ir(1)-P(1)-R(3)C(1)	114 (1)
		Ir(2)-P(2)-R(4)C(1)	112 (1)
		Ir(2)-P(2)-R(5)C(1)	113 (1)
		Ir(2)-P(2)-R(6)C(1)	116 (1)

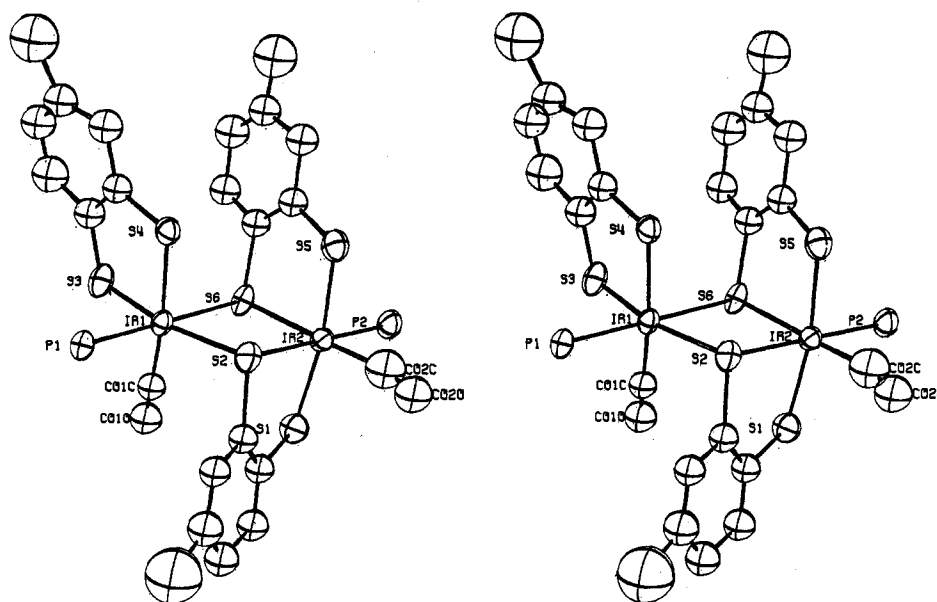


Figure 1.—A stereoscopic drawing of the inner coordination geometry of the $\text{Ir}_2(\text{tdt})_3(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ complex. The phenyl rings of the triphenylphosphine ligands are omitted for clarity.

compounds, the carbonyl stretch is observed around 2050 cm^{-1} as compared with $\nu(\text{CO})$ of 1965 cm^{-1} in the parent Ir(I) complex.¹⁵ This shift to higher frequencies is consistent with the notion that the Ir(I) ion is being oxidized in this series of reactions and that the more highly oxidized iridium ion is less able to back-donate electron density into the π^* orbitals of the carbonyl. Similar shifts have been observed in other oxidative addition products of Vaska's complex.¹⁶ The binuclear complex II shows two sharp carbonyl bands at 2054 and 2035 cm^{-1} indicating the presence of at least two carbonyl ligands, while the mononuclear complex I and the trinuclear complex III each exhibit only one carbonyl stretching frequency at 2025 and 2050 cm^{-1} , respectively. An additional band at 2240 cm^{-1} in the mononuclear complex is assigned as $\nu(\text{Ir}-\text{H})$.¹

Description of the Structure of $\text{Ir}_2(\text{tdt})_3(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$.—The crystal structure of complex II as determined from the single-crystal X-ray analysis consists of the packing of discrete binuclear molecules. The two iridium atoms of the molecule are held together by bridging sulfur atoms of two tdt ligands chelated to one of the iridium atoms. A perspective drawing of the inner coordination geometry of the complex is presented in Figure 1, and all important intramolecular distances and angles are tabulated in Table V. The $\text{Ir}\cdots\text{Ir}$ distance of $3.668(3)\text{ \AA}$ is considerably longer than the $\text{Ir}-\text{Ir}$ distances of 2.714 \AA found in the pure metal¹⁷ and $2.68(2)\text{ \AA}$ observed in $\text{Ir}_4(\text{CO})_{12}$ ¹⁸ where direct metal-metal bonding exists. Thus any possibility of significant metal-metal interaction in the present case can be ruled out.

The coordination geometry about each iridium atom is effectively that of an octahedron, but the composition of ligands about each iridium is quite different. Ir(1) is surrounded by one chelating tdt ligand, a triphenylphosphine, a carbonyl, and two bridging sulfur atoms, while Ir(2) is coordinated to two chelating tdt

ligands, a triphenylphosphine, and a carbonyl. One sulfur atom from each of the tdt ligands chelated to Ir(2) also functions as a bridge to Ir(1). There are three significantly different Ir-S distances in the present structure. The longest involves the Ir(1)-bridging S distances which average $2.456(11)\text{ \AA}$, while the shortest is the Ir(1)-S(3) distance of $2.332(10)\text{ \AA}$ which is trans to one of the sulfur bridges. The other Ir-S distances within the metal-dithiolene chelate rings do not differ significantly from each other and average $2.383(10)\text{ \AA}$. These values may be compared with an Ir-S single-bond distance of $2.488(10)\text{ \AA}$ found in the complex $\text{IrCl}(\text{SO}_2)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$,¹⁹ in which no metal- SO_2 π bonding exists. We thus conclude that the Ir(1)-bridging S bonds are strictly σ interactions of approximately unit bond order and that the relative shortness of the other Ir-S bonds in the structure is indicative of some metal \rightarrow ligand π bonding between the filled Ir d_π orbitals and the vacant π^* functions of the tdt ligands.

The four-atom Ir_2S_2 bridging unit deviates significantly from planarity. In Table VI, the least-squares planes through different portions of the structure including the Ir_2S_2 moiety are tabulated along with the deviations of the atoms from their respective planes. The dihedral angle between the planes defined by the Ir(1)-S(6)-Ir(2) and Ir(1)-S(2)-Ir(2) parts of the four-membered bridging unit is found to be $6.8(8)^\circ$. Within the coordination spheres of the individual Ir atoms, deviations from perfect octahedral coordination are found to occur in the bond angles but this is probably due to the unsymmetrical nature of the coordinating ligands. The intraligand S-Ir-S angles average $87.7(3)^\circ$ and the average intraligand S \cdots S distance in the molecule is $3.29(1)\text{ \AA}$.

The five-membered metal-chelate rings which contain the bridging sulfur atoms deviate significantly from planarity (see Table VI). The deviations may be described as a cracking of the chelate rings about an axis joining the two sulfur atoms such that the dihedral angle between the IrS_2 plane and the S_2C_2 plane

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TABLE VI
WEIGHTED LEAST-SQUARES PLANES AND THE DISTANCES
OF THE ATOMS FROM THEIR RESPECTIVE PLANES^a

Atom	Distance, Å	Atom	Distance, Å
Ir ₂ S ₂ Bridging Unit: 20.31x + 1.54y - 2.69z = 5.0 (Triclinic Coordinates)			
Ir(1)	0.004 (2)	S(2)	-0.10 (1)
Ir(2)	0.005 (2)	S(6)	-0.08 (1)
Metal-Chelate Ring 1: 1.68x - 6.94y + 20.43z = 1.69 (Triclinic Coordinates)			
Ir(2)	0.007 (2)	C(1)	0.36 (3)
S(1)	-0.13 (1)	C(6)	0.44 (3)
S(2)	-0.15 (1)		
Metal-Chelate Ring 2: -3.95x + 8.99y + 10.33z = -2.37			
Ir(1)	-0.001 (2)	C(8)	-0.09 (3)
S(3)	0.02 (1)	C(13)	-0.08 (3)
S(4)	0.02 (1)		
Metal-Chelate Ring 3: -2.00x + 10.26y + 7.27z = 0.81 (Triclinic Coordinates)			
Ir(2)	0.004 (2)	C(15)	0.42 (3)
S(5)	-0.08 (1)	C(20)	0.42 (3)
S(6)	-0.08 (1)		
tdt Ligand 1: -3.28x - 4.34y + 21.90z = 4.36 (Triclinic Coordinates)			
S(1)	0.00 (1)	C(4)	0.01 (3)
S(2)	-0.02 (1)	C(5)	0.14 (3)
C(1)	-0.03 (3)	C(6)	0.06 (3)
C(2)	-0.03 (3)	C(7)	-0.12 (4)
C(3)	-0.05 (4)		
tdt Ligand 2: -5.46x + 9.31y + 9.08z = -2.46 (Triclinic Coordinates)			
S(3)	-0.01 (1)	C(11)	0.01 (3)
S(4)	-0.01 (1)	C(12)	0.09 (3)
C(8)	0.03 (3)	C(13)	0.05 (3)
C(9)	0.03 (4)	C(14)	-0.37 (5)
C(10)	0.03 (4)		
tdt Ligand 3: 2.81x + 8.65y + 10.78z = 1.61 (Triclinic Coordinates)			
S(5)	-0.00 (1)	C(18)	0.01 (3)
S(6)	-0.00 (1)	C(19)	0.00 (3)
C(15)	0.03 (3)	C(20)	0.01 (3)
C(16)	-0.03 (3)	C(21)	0.13 (4)
C(17)	-0.10 (4)		

^a Least-squares planes calculated according to W. C. Hamilton, *Acta Crystallogr.*, **14**, 185 (1961).

is 25 (1)° for the chelate ring containing S(1) and S(2) and 22 (1)° for the chelate ring containing S(5) and S(6). Similar deviations from planarity within the chelate rings have been observed in the trigonal-prismatic complexes Mo(S₂C₂H₂)₃²⁰ and Mo(Se₂C₂(CF₃)₂)₃²¹ where the corresponding dihedral angles are 18 and 18.6 (5)°, respectively. In discussing the structure of Mo(S₂C₂H₂)₃, Smith, *et al.*,²⁰ suggested that a rehybridization of the sulfur atoms from sp² to intermediate sp²-sp³ hybridization may be responsible for the nonplanarity of the chelate rings in that structure. In the present study, a p²-sp³ hybridization of the bridging sulfur atoms clearly seems more appropriate on the basis of the bond angles around these atoms, and such a hybridization change should manifest itself in other bond parameters within the chelate rings. The two intrachelate ring S-C distances involving the bridging S atoms average a relatively long 1.85 (3) Å, while the other S-C distances (excluding S(3)-C(8)) average 1.80 (3) Å. Unfortunately, this difference is only possibly significantly different. The S(3)-C(8) distance of

(20) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Amer. Chem. Soc.*, **87**, 5798 (1965).

(21) C. G. Pierpont and R. Eisenberg, *J. Chem. Soc. A*, 2285 (1971).

1.71 (3) Å is significantly shorter than the others and this shortening is probably associated with the factors which serve to produce the short Ir(1)-S(3) distance noted above. In general, S-C distances within complexes of substituted benzenedithiolate ligands average 1.76-1.77 Å²²⁻²⁴ or approximately 0.06 Å longer than the S-C distances found in other dithiolene complex structures.²⁵

The Ir-P distances in the structure average 2.388 (10) Å, which may be compared with values of 2.407 (3), 2.343 (5), 2.411 (2), and 2.367 (2) Å found in the representative iridium(III) complexes IrCl(NO)(CO)(P(C₆H₅)₃)₂⁺,²⁶ IrCl(SO₂)(CO)(P(C₆H₅)₃)₂,¹⁹ *mer*-IrCl₃(CO)(P(C₆H₅)₃)₂,²⁷ and IrCl₂(NO)(P(C₆H₅)₃)₂,²⁸ respectively. The geometry of the triphenylphosphine ligands is as expected.

A view of the packing of the binuclear complex II is presented in Figure 2. The closest intermolecular contacts in the structure are between centrosymmetrically related CO(2)O atoms at a distance of 2.89 Å, and several other intermolecular contacts between CO(2)O and different phenyl ring carbon atoms are observed below 3.5 Å (CO(2)O...R(4)C(4), 3.14 Å; CO(2)O...R(C)C(5), 3.25 Å; CO(2)O...R(4)C(3), 3.30 Å). These short intermolecular contacts appear to account for the apparent nonlinearity of the Ir(2)-CO(2)C-CO(2)O moiety as found after fixing the CO(2)C position in the structure. However, the constraints imposed on the calculated model and the large estimated standard deviations of the carbonyl oxygen positional parameters do not permit any more definitive conclusions to be drawn. No other intermolecular contacts (excluding hydrogens) are found below 3.6 Å and they are therefore not tabulated.

Discussion

The complex Ir₂(tdt)₃(CO)₂(P(C₆H₅)₃)₂ represents an interesting and novel structure type in dithiolene complex chemistry in that the chemical environments about the two Ir atoms differ. The complex is held together by bridging sulfur atoms through S→M coordinate bonding. While the bridging function of the dithiolene ligands has been observed previously in systems such as Co₂(S₂C₂(CF₃)₂)₄,²⁹ [Fe₂(S₂C₂(CN)₂)₄]²⁻,³⁰ and [Co₂(S₂C₆Cl₄)₄]²⁻,²³ these dimers are symmetrical systems, in contrast with the present study, in that the metal atoms within each dimer possess identical chemical environments. Moreover, this is the first example in which the ligand tdt has been found to exhibit the bridging mode of coordination.

The observed diamagnetism of complex II,³¹ the similar carbonyl stretching frequencies for the different CO ligands, the lack of a metal-metal bond, and the

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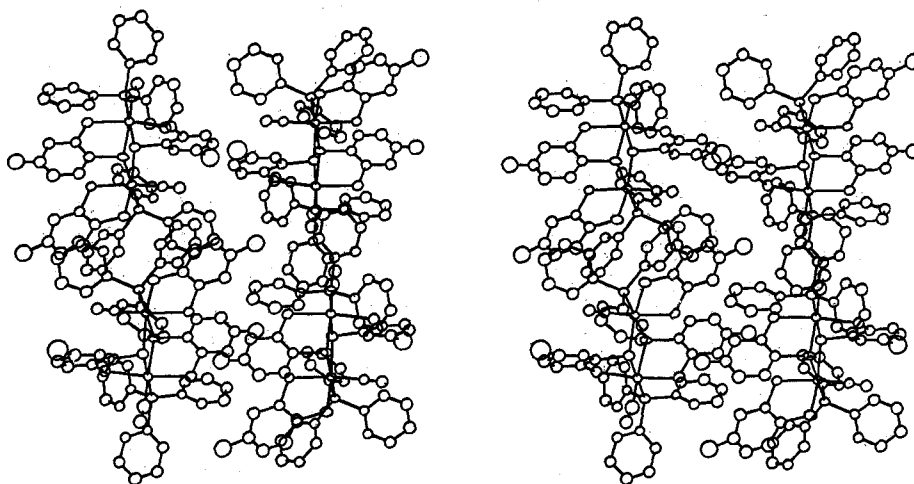


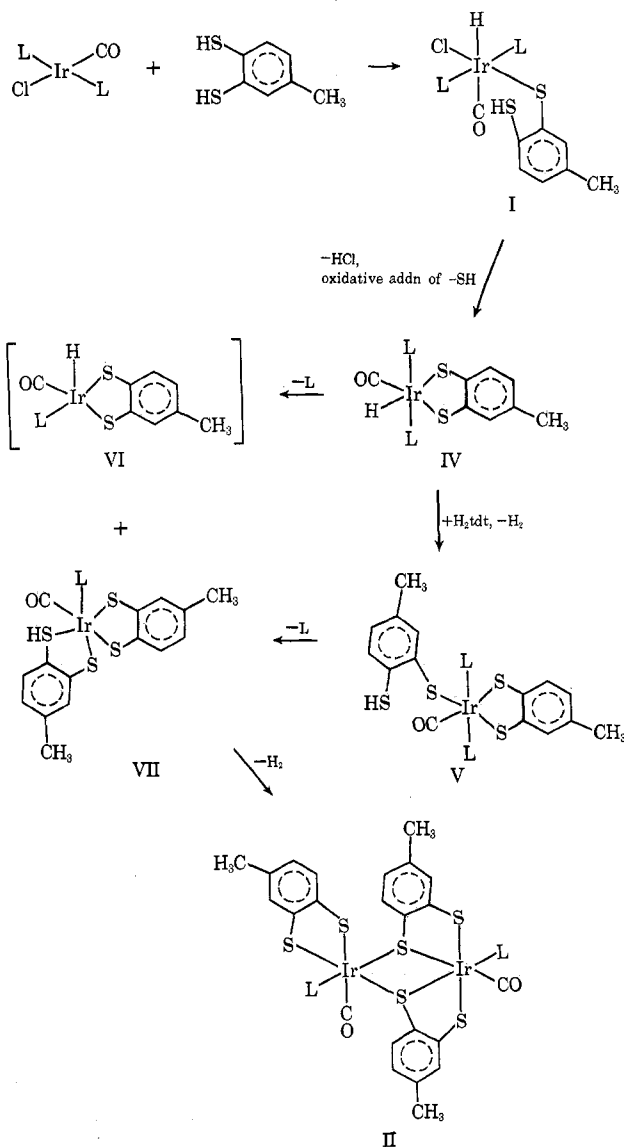
Figure 2.—A stereoscopic drawing of the packing of $\text{Ir}_2(\text{tdt})_3(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ molecules in the ac plane. The view is approximately down the b axis with the positive a direction vertical in the drawing.

near equality of chemically similar distances in the two coordination spheres strongly suggest that each iridium in II is best formulated as an Ir(III) ion. This conclusion leads us to view the complex as a chelate in which the bidentate monoanionic "ligand" $\text{Ir}(\text{tdt})_2(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)^-$ is coordinated to $\text{Ir}(\text{tdt})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)^+$. A possible reaction sequence by which the binuclear complex II is formed is given in Scheme I. The first step, as suggested by Singer and Wilkinson,¹ is the oxidative addition of one of the thiol groups of H_2tdt to Vaska's compound resulting in the formation of I. Reductive elimination of a molecule of HCl followed by the oxidative addition of the second $-\text{SH}$ group of the ligand leads to the formation of intermediate IV. A completely analogous product has recently been obtained by Stiddard and Townsend² from the reaction of Vaska's compound and $\text{H}_2\text{S}_2\text{C}_6\text{F}_4$ although they viewed a different route for the elimination of HCl . We then suggest that IV may either undergo a substitution reaction with a molecule of H_2tdt , thereby forming V with loss of a molecule of hydrogen, or dissociate a phosphine to give the coordinatively unsaturated intermediate VI. Substitution of one of the phosphines of V by the remaining uncoordinated thiol to give VII and its reaction with VI yields the binuclear complex II. We note that this scheme is only speculative at the present time.

While no systematic study of bridge-splitting reactions in the present case was carried out, attempts to reduce the binuclear complex with NaBH_4 and hydrazine were made. In each case, the CH_2Cl_2 solution of the complex turned from green to orange-red. The addition of $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$ to the reaction solution followed by the removal of solvent and recrystallization afforded a product which we tentatively identify as the $(\text{C}_2\text{H}_5)_4\text{N}^+$ salt of the conjugate base of VII—*i.e.*, the proposed bidentate ligand $[\text{Ir}(\text{tdt})_2(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)]^-$. No evidence for the formation of $\text{Ir}^{\text{I}}\text{tdt}$ complexes was obtained. Further work in this area is in progress.

It is interesting to compare the results which we have obtained in this study with the results obtained by Connelly and McCleverty,³ who carried out the reaction of Vaska's complex with the heterocyclic system bis(perfluoromethyl)dithietene. These authors isolated two polynuclear compounds, one of which is

SCHEME I
PROPOSED REACTION SEQUENCE FOR THE
FORMATION OF $\text{Ir}_2(\text{tdt})_3(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$



formulated as $\text{Ir}_2(\text{S}_2\text{C}_2(\text{CF}_3)_2)_3(\text{P}(\text{C}_6\text{H}_5)_3)_2$ and the other as $\text{Ir}_3(\text{S}_2\text{C}_2(\text{CF}_3)_2)_3(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$. The latter may

be analogous to complex III, whose formulation is uncertain at the present time. A structural study of III is clearly needed and will be carried out. It is not clear at this stage why the carbonyl ligands which are present in II are not also present in the binuclear compound reported by Connelly and McCleverty,³ but a possible reason could be in the relative π acidities of the two ligands $S_2C_2(CF_3)_2$ and tdt. The former is a stronger π acid which may be able to withdraw enough electron density from the vicinity of the iridium atom

to make the carbonyl ligand more susceptible to dissociation. With the weaker π -acid ligand tdt, the carbonyl ligands are retained in the binuclear species.

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Structural Studies of Organonitrogen Compounds of the Transition Elements.

V. The Structure of μ -2,3-[2,3-Diazabicyclo[2.2.1]heptane]diyl-bis(tricarbonyliron), $C_5H_8N_2Fe_2(CO)_6$, an Iron Carbonyl Complex of a Bicyclic Aliphatic Azo Compound

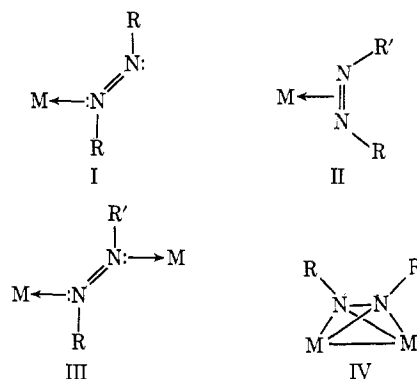
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The crystal and molecular structure of $C_5H_8N_2Fe_2(CO)_6$, an iron carbonyl adduct of 2,3-diazabicyclo[2.2.1]hept-2-ene, has been determined by a single-crystal X-ray analysis. This compound crystallizes in space group $P2_1/c$ of the monoclinic system, with eight molecules in a unit cell of dimensions $a = 9.118$ (4), $b = 22.210$ (2), $c = 13.787$ (7) Å, $\beta = 92.78$ (2)°. Observed and calculated densities are 1.75 (2) and 1.79 g/cm³, respectively. Least-squares refinement, based upon 2513 independent observed counter data, converged to a conventional R factor of 0.056. The two discrete crystallographically independent $C_5H_8N_2Fe_2(CO)_6$ molecules have nearly identical configurations, with two $Fe(CO)_3$ groups linked by the two ligand nitrogen atoms through Fe–N–Fe bridges and also by an iron–iron bond of length 2.490 (2) Å. A N–N bond is retained in the complex; its length of 1.404 (9) Å is close to that expected for a single bond. Iron–nitrogen distances range from 1.906 (7) to 1.937 (7) Å. Both molecules exhibit small but significant departures from C_s - m symmetry.

Introduction

The coordination chemistry of the azo group has become a matter of considerable interest. Much of this interest stems from the potential intermediacy of metal complexes of diimide, the simplest azo compound, in the biological nitrogen-fixation process. Even apart from this, it is of interest to define the various possible modes of coordination of simple azo compounds ($R-\ddot{N}=\ddot{N}-R'$), to examine the factors influencing which of these modes will be adopted in a particular instance, and to compare the $-\ddot{N}=\ddot{N}-$ grouping with the closely related $>C=\ddot{N}-$ and $>C=C<$ functions. Excluding cases in which the azo link is completely ruptured, four principal modes of coordination have been demonstrated to result from the reactions of simple azo compounds with transition metal systems: coordination through the lone pair of a single nitrogen atom (I), π coordination (II), and two types of bridging configuration (III and IV). Structures of type I in which coordination of the azo ligand is solely through one nitrogen lone pair have been proposed in a number of instances,^{1–3} but to date no X-ray studies confirming such structures have been reported. Coordination of a single nitrogen of the azo group is often observed in



chelate structures containing a metal–carbon,^{4–9} metal–oxygen,^{10,11} or metal–nitrogen¹¹ bond to an atom of R or R'. Structurally characterized examples of the other types of coordination include (II) a recently reported nickel(0)–azobenzene adduct,¹² (III) the

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