32 *Inorg. Chem.* **1984**, *23*, 32-39

Contribution from Bell Laboratories,
Murray Hill, New Jersey 07974

Metal Tetrathiolenes. 8. Molecular Structures of Two Isostructural Two-Electron Systems: $(Ph_3P)_2(CO)XIr(C_{10}Cl_4S_4)$ (X = Cl, H). The First Member of a Novel Series of Metal Tetrathiolene Complexes

BOON K. TEO* and P. A. SNYDER-ROBINSON

Received February 1, 1983

Recent stereochemical and spectroscopic investigations revealed that tetrathionaphthalene (TTN, $C_{10}H_4S_4$), tetrachlorotetrathionaphthalene (TCTTN, $C_{10}Cl_4S_4$), and tetrathiotetracene (TTT, $C_{18}H_8S_4$) can act as, formally, two-, four-, six-, eight-, and twelve-electron donors when coordinated to one, two, two, three, and four metals, respectively. These five classes of compounds constitute a unified pattern of metal tetrathiolene coordination chemistry that stems from the electronic, steric, and reactivity requirements of the ligands as well as those of the metals. This paper reports the structures of the first member of the series: the one-metal two-electron (2e) systems $(Ph_3P)_2(CO)XIr(TCTTN)\cdot C_6H_6\cdot CH_3CN$ where X = Cl (**1**), H (**2**). Both **1** and **2** (isomorphous) crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$. Cell parameters: $a = 12.434$ (4) Å, $b = 20.312$ (7) Å, $c = 10.888$ (4) Å, $\alpha = 104.05$ (3)°, $\beta = 97.98$ (3)°, $\gamma = 75.48$ (3)°, $V = 2573$ Å^3 for **1**; $a = 12.102$ (4) Å, $b = 19.911$ (7) Å, $c = 10.853$ (7) Å, $\alpha = 101.26$ (4)°, $\beta = 96.79$ (4)°, $\gamma = 80.41$ (3)°, $V = 2519$ Å^3 for **2**. The structures were solved by the heavy-atom method and least-squares refined to the final reliability indices of $R_1 = 6.4\%$, $R_2 = 5.7\%$ for **1** and $R_1 = 6.8\%$, $R_2 = 7.3\%$ for **2**. For both structures, the iridium atom is octahedrally coordinated with two triphenylphosphines (in a trans configuration), two sulfur atoms from the TCTTN ligand, one carbonyl ligand, and one chloride or hydride ligand. As in the case of the two-metal 4e system $(Ph_3P)_4Pt_2(TTN)$, the $IrS_2(CO)X$ plane is not coplanar with the TCTTN plane, a structural feature characteristic among metal tetrathiolenes characterized so far. Though the title compounds are formed via oxidative addition of one of the two sulfur–sulfur bonds of the tetrathiolene ligands to the low-valent iridium(I) compounds, $IrX(CO)(PPh_3)_2$, they are an important member of the series. In other words, since there are two S–S bonds, there is no a priori reason to believe that the reaction will stop at 2e rather than go all the way to the two-metal 4e or 6e systems. Finally, a detailed comparison of the intact sulfur–sulfur bond with those of the ligands revealed a strengthening of the remaining sulfur–sulfur bond upon metal coordination of the first one, thereby providing strong evidence that the second S–S bond is deactivated somewhat toward further oxidative-addition reaction. This latter observation helps explain why 2:1 reactions of $Pt(PPh_3)_4$ with the TTL ligands gave rise to 4e systems with one metal on each side of the ligand whereas similar reactions with Vaska's compounds yielded 6e systems with two metals on one side and none on the other.

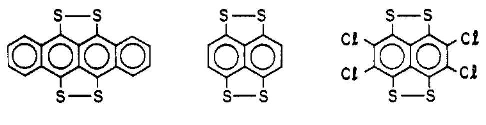
Introduction

Recently we reported the syntheses and characterization of a novel series of metal tetrathiolene complexes[1-7] containing the tetrathiolene ligands portrayed in Chart I.

Tetrathionaphthalene (TTN, $C_{10}H_4S_4$),[8] tetrachlorotetrathionaphthalene (TCTTN, $C_{10}Cl_4S_4$),[9] and tetrathiotetracene (TTT, $C_{18}H_8S_4$)[10] possess three attractive features that make this class of organic compounds excellent ligands in organometallic chemistry. First, they are strictly planar with extensive π-electron delocalization. Second, each of these molecules has two S–S bonds, one on each side of the molecule, suitable for oxidative addition(s) to low-valent transition-metal complexes. And finally, upon coordinating to two metal complexes, each of these ligands presumably can accommodate up to a total of four (formal) electrons.

Stereochemical and spectroscopic investigations[1-7] revealed that these ligands can act as, formally, two-, four-, six-, eight-, and twelve-electron donors when coordinated to one, two, two, three, and four metals, respectively (cf. Figures 1 and 2 of ref 7). (This simple electron-counting scheme is based on the ligands being considered as neutral entities.) These five classes of compounds constitute a unified pattern of metal tetrathiolene coordination chemistry that stems from the electronic, steric, and reactivity requirements of the ligands as well as those of the metals.[7]

Chart I



TTT TTN TCTTN

This paper reports the structures of the first member of the series: the one-metal two-electron (2e) systems $(Ph_3P)_2(CO)XIr(TCTTN)$ where X = Cl (**1**), H (**2**). For both structures, the iridium atom is octahedrally coordinated with two triphenylphosphines (in a trans configuration), two sulfur atoms from the TCTTN ligand, one carbonyl ligand, and one chloride or hydride ligand. As in the case of the two-metal 4e system $(Ph_3P)_4Pt_2(TTN)$, the $IrS_2(CO)X$ plane is not coplanar with the TCTTN plane. This latter structural feature seems to be characteristic among metal tetrathiolenes characterized so far. Furthermore, though the title compounds are formed via oxidative addition of one of the two sulfur–sulfur bonds of the tetrathiolene ligands to the low-valent iridium(I) compounds, $IrX(CO)(PPh_3)_2$, they are an important member of the series. In other words, since there are two S–S bonds rather than one, there is no a priori reason to believe that the reaction will stop at 2e rather than go all the way to the two-metal 4e[3] or 6e[4] systems. Even with one S–S bond as in hexachloronaphtho[1,8-*cd*]-1,2-dithiole, $C_{10}Cl_6S_2$,[11] it is not always possible to make the mononuclear oxidative-ad-

---

(1) Teo, B. K.; Wudl, F.; Marshall, J. H.; Kruger, A. *J. Am. Chem. Soc.* **1977**, *99*, 2349.

(2) Teo, B. K.; Wudl, F.; Hauser, J. J.; Kruger, A. *J. Am. Chem. Soc.* **1977**, *99*, 4862.

(3) Teo, B. K.; Snyder-Robinson, P. A. *Inorg. Chem.* **1978**, *17*, 3489.

(4) Teo, B. K.; Snyder-Robinson, P. A. *J. Chem. Soc., Chem. Commun.* **1979**, 255.

(5) Teo, B. K.; Snyder-Robinson, P. A. *Inorg. Chem.* **1979**, *18*, 1490.

(6) Teo, B. K. "Inorganic Compounds with Unusual Properties—II; King, R. B., Ed.; American Chemical Society: Washington, DC, 1979; Adv. Chem. Ser. No. 173, p 364.

(7) Teo, B. K.; Snyder-Robinson, P. A. *Inorg. Chem.* **1981**, *20*, 4235.

(8) Wudl, F.; Schaffer, D. E.; Miller, B. *J. Am. Chem. Soc.* **1976**, *98*, 252.

(9) Klingsberg, E. *Tetrahedron* **1972**, *28*, 963.

(10) Marshalk, C.; Stumm, C. *Bull. Soc. Chim. Fr.* **1948**, *15*, 418.

(11) Thelin, J. H. U.S. Patent 2905-695, 1960; *Chem. Abstr.* **1960**, *54*, 5602.

0020-1669/84/1323-0032$01.50/0

dition product $(Ph_3P)_2M(C_{10}Cl_6S_2)$.[12] For example, the reaction of equimolar amounts of $C_{10}Cl_6S_2$, which has one S–S bond, with $Pd(PPh_3)_3$ or $Pt(PPh_3)_4$, produced $(Ph_3P)_2M(C_{10}Cl_6S_2)$ where M = Pd, Pt, whereas the corresponding reaction with [Ni(cycloocta-1,5-diene)$_2$] in the presence of PPh_3 led to $(Ph_3P)_3Ni_3(C_{10}Cl_6S_2)_3$.[12] Finally, a detailed comparison of the intact sulfur–sulfur bond with those of the ligands revealed a strengthening of the remaining sulfur–sulfur bond upon metal coordination of the first one. This observation helps explain why 2:1 reactions of $Pt(PPh_3)_4$ with the TTL ligands gave rise to 4e systems[3] with one metal on each side of the ligand whereas similar reactions with Vaska's compounds yielded 6e systems[4] with two metals on one side and none on the other side.

Experimental Section

The title compounds were prepared and characterized as described in our previous paper.[7] All operations were performed in an argon-filled Vacuum Atmospheres drybox.

(a) Crystal Growth. All solvents used in the crystal-growing process were freshly distilled under nitrogen. In particular, benzene and acetonitrile were freshly distilled from CaH_2. To a saturated benzene solution was added a small amount of acetonitrile, and the mixture was allowed to slowly evaporate under nitrogen, thereby producing crystals suitable for X-ray diffraction studies.

The density of several crystals was measured to be 1.67 and 1.64 g/cm^3 for $(Ph_3P)_2(CO)XIr(TCTTN)$ where X = Cl and H, respectively, by the flotation method (CCl_4/1,3-dibromopropane). These values are in good agreement with the corresponding values of 1.664 and 1.654 g/cm^3 calculated on the basis of two units of $((C_6H_5)_3P)_2(CO)XIr(C_{10}Cl_4S_4)\cdot C_6H_6\cdot CH_3CN$ per unit cell ($Z = 2$; cf. Table I). The ordered solvent molecules were found and successfully refined in the structural analysis (vide infra).

(b) X-ray Diffraction Measurements. The crystal data were measured, and the X-ray diffraction data were collected and reduced to structure factors at the Molecular Structure Corp., College Station, TX. These data are summarized in Table IA,B, respectively.

(c) Solution and Refinement of Structures. Solution and least-squares refinement of the structures were done at Bell Laboratories. The structure was solved by the heavy-atom technique. There are two molecules per unit cell (triclinic, space group $P\bar{1}$ or $P1$). The asymmetric unit consists of one molecule, one benzene, and one acetonitrile. An analysis of a three-dimensional Patterson map (MAP program)[14] yielded the positions of the iridium atom. A few cycles of Fourier synthesis[14,15] revealed the positions of all non-hydrogen atoms (60 and 59 for $(Ph_3P)_2(CO)XIr(TCTTN)$ with X = Cl (**1**) and H (**2**), respectively). Least-squares refinements[15-18] (ORFLS2 program) on the positional and isotropic thermal parameters gave rise to the R (discrepancy) values listed in Table IC. The conversion and the subsequent least-squares refinements of the anisotropic thermal parameters of the non-phenyl atoms yielded $R_1 = 9.5\%$ and $R_2 = 11.3\%$ for **1** and $R_1 = 8.8\%$ and $R_2 = 11.5\%$ for **2**. A difference Fourier map at this point revealed nine atoms corresponding to the two ordered solvent molecules: C47–C52 as benzene and C53, C54, N as acetonitrile. A few more cycles of such anisotropic–isotropic least-squares refinements (anisotropic for non-phenyl non-solvent non-hydrogen atoms and isotropic for phenyl and solvent atoms) yielded the final conventional discrepancy values[18] $R_1 = 6.4\%$ and $R_2 = 5.7\%$ for **1** and $R_1 = 6.8\%$ and $R_2 = 7.3\%$ for **2**. All solvent atoms are weighted as unity. The final positional and thermal parameters, with errors

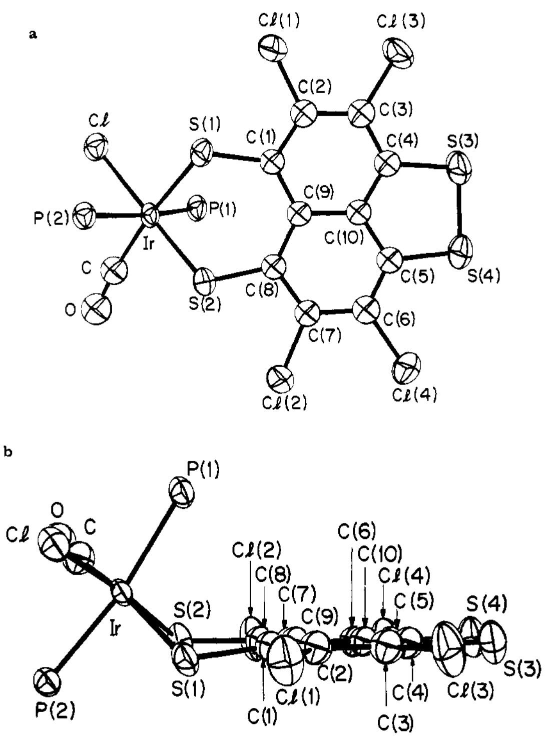


Figure 1. Stereochemistry of the $(Ph_3P)_2(CO)ClIr(C_{10}Cl_4S_4)$ molecule (ORTEP diagram; 50% probability ellipsoids): (a) view along the normal of the naphthalene plane; (b) view rotated 90° about the C9–C10 bond.

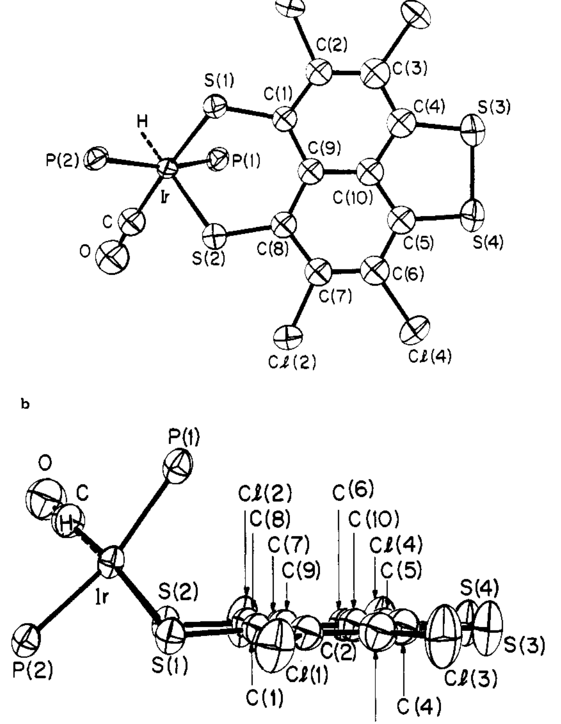


Figure 2. Stereochemistry of the $(Ph_3P)_2(CO)HIr(C_{10}Cl_4S_4)$ molecule (ORTEP diagram; 50% probability ellipsoids): (a) view along the normal of the naphthalene plane; (b) view rotated 90° about the C9–C10 bond.

---

(12) Bosman, W. P.; Van der Linden, H. G. M. *J. Chem. Soc., Chem. Commun.* **1977**, 714.

(13) The intensity I was calculated according to the expression $I = S(C - RB)$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, and B is the total background count. The standard deviation of I was calculated as $\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$, where $p = 0.05$. The data were also corrected for Lorentz and polarization effects to yield the observed structure factor $|F_o| = [I/(Lp)]^{1/2}$ and its standard deviation $\sigma(F_o) = \sigma(I)/(2|F_o|Lp)$. No extinction correction was necessary.

(14) The local Fourier program MAP originally written by Dr. J. C. Calabrese.

(15) Atomic scattering factors used for all nonhydrogen atoms are from: Hanson, H. P.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1964**, *17*, 1040.

(16) "International Tables for X-Ray Crystallography", 2nd ed.; Kynoch Press: Birmingham, England, 1968; Vol. III, pp 215–216.

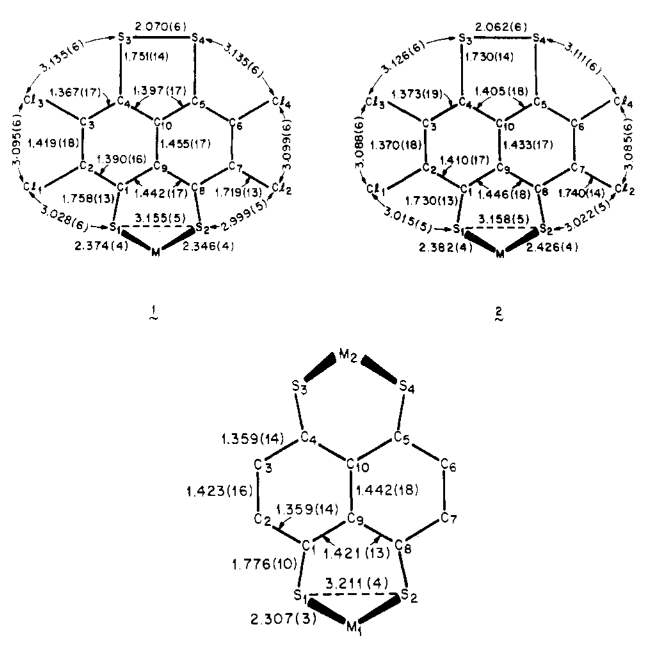
(17) All least-squares refinements were based on the minimization of $\sum w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$.

(18) $R_1 = [\sum||F_o| - |F_c||/|F_o|] \times 100$ (%) and $R_2 = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2} \times 100$ (%). See supplementary material for a listing of observed and calculated structure factors.

Table I. Summary of Crystal Data, Collection and Reduction of X-ray Data, and Solution and Refinement of Structures of $(Ph_3P)_2(CO)XIr(TCTTN)$ Where X = Cl, H (Ph = C_6H_5, TCTTN = $C_{10}Cl_4S_4$)

	$(Ph_3P)_2(CO)ClIr(TCTTN)$	$(Ph_3P)_2(CO)HIr(TCTTN)$
A. Crystal Data		
cryst color	red	red
cryst shape	prism	parallelepiped
cryst dimens, mm^3	0.15 × 0.15 × 0.03	0.1 × 0.15 × 0.20
cell parameters (errors)		
a, Å	12.434 (4)	12.102 (4)
b, Å	20.312 (7)	19.911 (7)
c, Å	10.888 (4)	10.853 (7)
α, deg	104.05 (3)	101.26 (4)
β, deg	97.98 (3)	96.79 (4)
γ, deg	75.48 (3)	80.41 (3)
cell vol, Å^3	2573	2519
Z	2	2
Laue symmetry	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
systematic absences	none	none
equiv positions	$\pm(x, y, z)$	$\pm(x, y, z)$
B. Collection and Reduction of X-ray Diffraction Data		
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (graphite monochromated)	Mo Kα	Mo Kα
wavelength, Å	0.7107	0.7107
temp, °C	23 ± 1	23 ± 1
crystal-to-detector dist, cm	21	21
counter aperture width, mm	2.0	2.0
incident-beam collimator diameter, mm	0.7	0.7
takeoff angle, deg	2.8	2.8
scan technique	$\omega-\theta$	$\theta-2\theta$
scan rate (limits), deg/min	2–20 (in ω)	4–40
scan range, deg, in 2θ	±1.0	±0.7
bkgd:scan time ratio	0.5	0.5
no./freq of std reflcn	3/100	3/100
2θ limits, deg	0–42	0–45
cutoff of obsd data	$2\sigma(I)$	$2\sigma(I)$
unique data	5496	6555
octants	$h,\pm k,\pm l$	$h,\pm k,\pm l$
max decay (linear)	2%	0%
abs corr		
method	ψ scans	ψ scans
rel range of transmission	0.686–1.000	0.696–1.000
intens $(I)^{13}$	$I = S(C - RB)$	
std dev $(\sigma(I))^{13}$	$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$	
p	0.05	0.05
C. Solution and Refinement		
technique of soln (MAP)[14]	heavy atom	
method of refinement (ORFLS2)[17]	full-matrix least squares	
std dev (ORFEE3)[19]	full variance–covariance	
isotropic convergence[18]	$R_1 = 12.2\%$ $R_2 = 13.7\%$	$R_1 = 12.3\%$ $R_2 = 14.5\%$
isotropic–anisotropic convergence[18]	$R_1 = 6.4\%$ $R_2 = 5.7\%$	$R_1 = 6.8\%$ $R_2 = 7.3\%$
max shifts (Δ/σ)	0.1 (*x*, *y*, *z*) 0.5 (*B*)	0.2 (*x*, *y*, *z*) 0.8 (*B*)
error of fit	1.26	1.63
data/parameter	4002/397	5109/388
scattering factors, f_0	ref 15	
anomalous dispersion correction[16]		
Δ*f*′ (real)	−1.7 (Ir), 0.1 (Cl, S, P)	
Δ*f*″ (imag)	9.2 (Ir), 0.2 (Cl, S, P)	
max residual intens of final diff map, e/Å^3	0.9 (mostly H's)	1.0 (mostly H's)

estimated from the full variance–covariance matrix (ORFEE3 program),[19] are listed in Table II. Other crystallographic details are summarized in Table IC. Interatomic distances and bond angles are tabulated in Tables III and IV, respectively. The dihedral angles between selected least-squares planes are listed in Table V. The anisotropic thermal parameters (Table VI), C–C and solvent distances (Table VII), C–C–C and solvent angles (Table VIII), and the least-squares planes (Table IX) are included in the supplementary material.



1

2

3

Figure 3. Comparison of important structural parameters of $(Ph_3P)_2(CO)XIr(C_{10}Cl_4S_4)$ where X = Cl (**1**), H (**2**) with those of $(Ph_3P)_4Pt_2(C_{10}H_4S_4)$ (**3**).

Results and Discussion

General Description of the Structures. The crystal structures of $(Ph_3P)_2(CO)XIr(TCTTN)\cdot C_6H_6\cdot CH_3CN$ where X = Cl (**1**) and H (**2**) are composed of discrete molecules separated by van der Waals distances. There are two formula units, related by the crystallographic inversion symmetry *i* of the centrosymmetric space group $P\bar{1}$ [C_i^1; No. 2].

The molecular structures of $(Ph_3P)_2(CO)X(TCTTN)$ where X = Cl and H are portrayed in Figure 1a,b and 2a,b, respectively, in two different views (ORTEP2 program).[20] Each of these molecules involves an octahedrally coordinated iridium atom attached to the TCTTN ligand via cleavage of one of the two sulfur–sulfur bonds. The iridium atom is octahedrally coordinated to two triphenylphosphines in an "axial" trans configuration with the "equatorial" positions occupied by two cis sulfur atoms from the TCTTN ligand, one carbonyl ligand, and one chloride (**1**) or hydride (**2**) ligand. As in the case of $(Ph_3P)_4Pt_2(TTN)$, the equatorial $IrS_2(CO)X$ plane is not coplanar with the TCTTN plane. As we shall see later, this important structural feature seems to be characteristic of all metal tetrathiolenes.

Crystals of **1** and **2** are isomorphous with similar cell parameters. The average bond lengths of **1** and **2** are compared in Figure 3 along with $(Ph_3P)_4Pt_2(TTN)$ (**3**).[3] With the exception of the Ir–S2 distance in **2**, which is trans to ligand X, the ligand disposition and the molecular parameters are also

---

(19) ORFEE3 by W. R. Busing, K. O. Martin, and H. A. Levy with modifications by G. M. Brown, C. K. Johnson, and W. E. Thiessen, Oak Ridge National Laboratory, Oak Ridge, TN, 1971.

(20) ORTEP2: Johnson, C. K. *J. Appl. Crystallogr.* **1973**, *6*, 318.

Table II. Positional and Thermal Parameters with Esd's

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
A. $(Ph_3P)_2(CO)ClIr(C_{10}Cl_4S_4)$									
Ir	0.01273 (5)	0.20701 (3)	0.16737 (6)	*a*	C22	−0.2746 (13)	0.1584 (7)	0.3729 (14)	4.5 (4)
Cl	0.0471 (3)	0.0879 (2)	0.1962 (4)	*a*	C23	−0.2585 (11)	0.3054 (6)	0.2806 (13)	3.2 (3)
Cl1	0.1121 (3)	0.2557 (2)	0.6508 (4)	*a*	C24	−0.2901 (12)	0.3462 (7)	0.1901 (14)	4.2 (3)
Cl2	−0.1401 (4)	0.4588 (2)	0.0946 (4)	*a*	C25	−0.3633 (14)	0.4145 (8)	0.2243 (16)	5.5 (4)
Cl3	−0.0140 (4)	0.3847 (2)	0.8341 (4)	*a*	C26	−0.3988 (14)	0.4362 (8)	0.3453 (16)	5.2 (4)
Cl4	−0.2422 (4)	0.5832 (2)	0.3044 (4)	*a*	C27	−0.3668 (14)	0.3973 (8)	0.4350 (16)	5.5 (4)
S1	0.1056 (3)	0.2455 (2)	0.3679 (4)	*a*	C28	−0.2933 (12)	0.3287 (7)	0.4060 (13)	3.8 (3)
S2	−0.0071 (3)	0.3219 (2)	0.1467 (4)	*a*	C29	0.1969 (11)	0.1240 (6)	−0.0739 (12)	3.1 (3)
S3	−0.1508 (4)	0.5151 (2)	0.7309 (4)	*a*	C30	0.2509 (12)	0.1383 (7)	−0.1645 (13)	3.8 (3)
S4	−0.2164 (4)	0.5680 (2)	0.5873 (4)	*a*	C31	0.2444 (12)	0.0995 (7)	−0.2921 (14)	4.2 (3)
P1	−0.1699 (3)	0.2179 (2)	0.2342 (4)	*a*	C32	0.1890 (13)	0.0457 (7)	−0.3229 (14)	4.5 (4)
P2	0.1965 (3)	0.1747 (2)	0.0917 (4)	*a*	C33	0.1360 (13)	0.0309 (8)	−0.2321 (15)	5.1 (4)
O	−0.0885 (8)	0.1887 (5)	−0.1026 (9)	*a*	C34	0.1411 (12)	0.0705 (7)	−0.1051 (14)	3.9 (3)
C	−0.0495 (11)	0.1905 (7)	0.0004 (14)	*a*	C35	0.3066 (11)	0.1191 (6)	0.1753 (13)	3.2 (3)
C1	0.0208 (10)	0.3197 (6)	0.4582 (12)	*a*	C36	0.4097 (12)	0.0926 (7)	0.1135 (13)	3.7 (3)
C2	0.0273 (11)	0.3238 (7)	0.5883 (12)	*a*	C37	0.5039 (13)	0.0540 (7)	0.1755 (14)	4.6 (4)
C3	−0.0242 (11)	0.3821 (7)	0.6762 (12)	*a*	C38	0.4937 (13)	0.0415 (7)	0.2917 (15)	4.7 (4)
C4	−0.0852 (11)	0.4391 (7)	0.6295 (12)	*a*	C39	0.3937 (14)	0.0661 (8)	0.3536 (15)	5.4 (4)
C5	−0.1540 (11)	0.5015 (6)	0.4655 (13)	*a*	C40	0.2984 (12)	0.1061 (7)	0.2925 (13)	3.7 (3)
C6	−0.1656 (12)	0.5068 (7)	0.3429 (14)	*a*	C41	0.2563 (11)	0.2480 (6)	0.0939 (12)	3.0 (3)
C7	−0.1177 (11)	0.4477 (6)	0.2488 (12)	*a*	C42	0.2121 (12)	0.2897 (7)	0.0037 (13)	3.8 (3)
C8	−0.0591 (11)	0.3849 (6)	0.2781 (12)	*a*	C43	0.2594 (13)	0.3468 (7)	0.0086 (14)	4.5 (4)
C9	−0.0441 (10)	0.3788 (6)	0.4082 (12)	*a*	C44	0.3440 (13)	0.3629 (8)	0.1008 (15)	5.0 (4)
C10	−0.0949 (11)	0.4391 (7)	0.5015 (12)	*a*	C45	0.3854 (13)	0.3234 (7)	0.1931 (14)	4.5 (3)
C11	−0.2566 (12)	0.1763 (7)	0.1048 (13)	3.6 (3)	C46	0.3413 (12)	0.2647 (7)	0.1894 (13)	3.9 (3)
C12	−0.2101 (14)	0.1083 (8)	0.0383 (16)	5.4 (3)	C54	0.4253 (19)	0.2182 (12)	0.6071 (22)	9.0 (6)
C13	−0.2745 (14)	0.0756 (8)	−0.0657 (15)	5.1 (3)	C47	−0.4779 (18)	0.4043 (12)	−0.1285 (20)	8.6 (6)
C14	−0.3847 (13)	0.1089 (8)	−0.0988 (15)	4.9 (4)	C48	−0.4021 (21)	0.4321 (11)	−0.1676 (21)	9.0 (6)
C15	−0.4312 (14)	0.1742 (8)	−0.0300 (16)	5.3 (4)	C52	−0.4587 (19)	0.3331 (12)	−0.1430 (21)	9.2 (6)
C16	−0.3662 (12)	0.2076 (7)	0.0739 (14)	4.1 (3)	C50	−0.2841 (18)	0.3190 (12)	−0.2251 (20)	8.7 (6)
C17	−0.1749 (11)	0.1777 (6)	0.3662 (13)	3.2 (3)	C51	−0.3574 (20)	0.2864 (11)	−0.1905 (21)	9.2 (6)
C18	−0.0888 (13)	0.1696 (7)	0.4565 (14)	4.6 (4)	N	0.4372 (19)	0.1782 (12)	0.6650 (22)	9.5 (6)
C19	−0.0969 (14)	0.1448 (8)	0.5669 (15)	5.4 (4)	C49	−0.3048 (20)	0.3889 (13)	−0.2188 (22)	9.8 (6)
C20	−0.1975 (14)	0.1263 (8)	0.5743 (15)	5.3 (4)	C53	0.4278 (20)	0.2663 (12)	0.5260 (22)	10.1 (7)
C21	−0.2856 (14)	0.1335 (8)	0.4788 (15)	5.1 (4)					
B. $(Ph_3P)_2(CO)HIr(C_{10}Cl_4S_4)$									
Ir	−0.03001 (5)	0.21938 (3)	0.17843 (5)	*a*	C43	0.2482 (15)	0.3352 (9)	−0.0194 (17)	6.1 (4)
Cl1	0.0858 (4)	0.2556 (2)	0.6552 (3)	*a*	C11	−0.2969 (11)	0.1811 (7)	0.1294 (12)	3.5 (3)
Cl2	−0.1438 (4)	0.4751 (2)	0.1111 (4)	*a*	C24	−0.3103 (13)	0.3550 (8)	0.2116 (15)	4.9 (3)
Cl2	−0.0327 (4)	0.3771 (2)	0.8387 (4)	*a*	C33	0.0557 (12)	0.0261 (8)	−0.1843 (14)	4.4 (3)
Cl4	−0.2441 (4)	0.5892 (2)	0.3206 (4)	*a*	C18	−0.1192 (13)	0.1704 (8)	0.4683 (15)	4.7 (3)
S1	0.0758 (3)	0.2508 (2)	0.3747 (3)	*a*	C37	0.4327 (13)	0.0625 (8)	0.2453 (15)	4.9 (3)
S2	−0.0173 (3)	0.3372 (2)	0.1598 (3)	*a*	C42	0.1948 (12)	0.2791 (7)	−0.0167 (14)	4.4 (3)
S3	−0.1595 (4)	0.5086 (2)	0.7384 (4)	*a*	C15	−0.4636 (13)	0.1767 (8)	−0.0170 (15)	5.1 (4)
S4	−0.2184 (4)	0.5653 (2)	0.5980 (4)	*a*	C36	0.3559 (12)	0.1080 (7)	0.1771 (13)	3.8 (3)
P1	−0.2068 (3)	0.2267 (2)	0.2543 (3)	*a*	C31	0.2123 (15)	0.0668 (9)	−0.2483 (16)	5.9 (4)
P2	0.1473 (3)	0.1779 (2)	0.1060 (3)	*a*	C21	−0.3235 (15)	0.1277 (9)	0.5003 (17)	6.3 (4)
O	−0.1430 (9)	0.2020 (6)	−0.0877 (9)	*a*	C14	−0.4289 (14)	0.1091 (8)	−0.0652 (16)	5.4 (4)
C	−0.1007 (11)	0.2051 (7)	0.0120 (13)	*a*	C22	−0.3135 (14)	0.1593 (9)	0.3968 (16)	5.7 (4)
C1	0.0019 (11)	0.3231 (6)	0.4625 (11)	*a*	C45	0.3548 (13)	0.3267 (8)	0.1793 (15)	4.9 (3)
C2	0.0071 (12)	0.3250 (7)	0.5934 (12)	*a*	C13	−0.3271 (15)	0.0750 (9)	−0.0117 (16)	6.0 (4)
C3	−0.0408 (13)	0.3788 (8)	0.6786 (13)	*a*	C23	−0.2918 (12)	0.3115 (7)	0.3025 (14)	4.1 (3)
C4	−0.0991 (13)	0.4364 (7)	0.6389 (13)	*a*	C28	−0.3372 (14)	0.3298 (9)	0.4171 (16)	5.8 (4)
C5	−0.1617 (12)	0.5021 (7)	0.4799 (13)	*a*	C30	0.2149 (12)	0.1169 (7)	−0.1346 (14)	4.5 (3)
C6	−0.1694 (12)	0.5121 (7)	0.3562 (14)	*a*	C12	−0.2600 (14)	0.1117 (9)	0.0900 (16)	5.4 (4)
C7	−0.1259 (12)	0.4596 (6)	0.2651 (13)	*a*	C44	0.3273 (14)	0.3583 (9)	0.0759 (17)	5.9 (4)
C8	−0.0710 (11)	0.3941 (6)	0.2870 (12)	*a*	C27	−0.4063 (17)	0.3945 (10)	0.4469 (19)	7.5 (5)
C9	−0.0572 (11)	0.3837 (7)	0.4170 (12)	*a*	C20	−0.2294 (15)	0.1184 (8)	0.5894 (16)	5.7 (4)
C10	−0.1058 (12)	0.4394 (7)	0.5086 (12)	*a*	C32	0.1302 (15)	0.0250 (9)	−0.2698 (17)	6.1 (4)
C29	0.1397 (11)	0.1192 (7)	−0.0462 (12)	3.5 (3)	C19	−0.1279 (15)	0.1399 (9)	0.5734 (16)	6.1 (4)
C17	−0.2107 (12)	0.1813 (7)	0.3837 (13)	3.7 (3)	C26	−0.4269 (16)	0.4355 (10)	0.3552 (19)	6.9 (5)
C35	0.2413 (11)	0.1237 (6)	0.2029 (12)	3.1 (3)	C54	0.3945 (18)	0.1891 (11)	0.6108 (20)	7.7 (5)
C41	0.2239 (11)	0.2445 (6)	0.0894 (12)	3.3 (3)	C53	0.3782 (18)	0.2382 (11)	0.5284 (21)	8.5 (6)
C34	0.0614 (12)	0.0735 (7)	−0.0693 (13)	3.8 (3)	N	0.4098 (18)	0.1448 (11)	0.6684 (20)	11.0 (6)
C16	−0.3982 (12)	0.2139 (7)	0.0769 (13)	4.1 (3)	C47	0.5070 (30)	0.3999 (20)	0.8708 (32)	14.1 (10)
C40	0.2037 (12)	0.0966 (7)	0.2955 (13)	4.5 (3)	C48	0.5868 (35)	0.4274 (18)	0.8630 (33)	14.1 (10)
C46	0.3041 (12)	0.2692 (7)	0.1867 (14)	4.3 (3)	C51	0.6098 (36)	0.2857 (18)	0.7874 (33)	14.7 (11)
C39	0.2811 (14)	0.0519 (8)	0.3649 (15)	5.2 (4)	C50	0.6917 (35)	0.3158 (25)	0.7656 (38)	17.1 (13)
C25	−0.3836 (15)	0.4207 (9)	0.2424 (17)	6.0 (4)	C52	0.5114 (39)	0.3233 (28)	0.8308 (42)	19.6 (15)
C38	0.3933 (15)	0.0374 (9)	0.3372 (16)	5.8 (4)	C49	0.6713 (47)	0.3874 (33)	0.8090 (52)	22.7 (20)

[a] The anisotropic thermal parameters are listed in Table VI, supplementary material.

Table III. Interatomic Distances (Å) with Esd's for $(Ph_3P)_2(CO)XIr(TCTTN)$ Where X = Cl, H

	X = Cl	X = H		X = Cl	X = H
		A. Ir Coordination			
Ir–X	2.438 (4)		Ir–S1	2.374 (4)	2.382 (4)
Ir–P1	2.421 (4)	2.354 (4)	Ir–S2	2.346 (4)	2.426 (4)
Ir–P2	2.417 (4)	2.336 (4)	C–O	1.155 (15)	1.136 (14)
Ir–C	1.860 (15)	1.895 (13)			
		B. TCTTN			
S1···S2	3.155 (5)	3.158 (5)	S3–S4	2.070 (6)	2.062 (6)
S1–C1	1.767 (12)	1.737 (13)	Cl1–C2	1.736 (13)	1.747 (13)
S2–C8	1.748 (13)	1.723 (13)	Cl2–C7	1.724 (13)	1.741 (14)
S3–C4	1.748 (13)	1.731 (14)	Cl3–C3	1.695 (13)	1.735 (14)
S4–C5	1.754 (14)	1.729 (14)	Cl4–C6	1.719 (14)	1.735 (13)
C1–C2	1.391 (16)	1.409 (17)	C7–C8	1.388 (16)	1.411 (17)
C2–C3	1.403 (17)	1.367 (18)	C6–C7	1.434 (18)	1.372 (18)
C3–C4	1.384 (17)	1.360 (19)	C5–C6	1.350 (17)	1.386 (19)
C4–C10	1.382 (16)	1.420 (18)	C10–C5	1.411 (17)	1.390 (18)
C1–C9	1.450 (16)	1.439 (17)	C9–C8	1.434 (17)	1.452 (18)
C9–C10	1.455 (17)	1.433 (17)			
		C. PPh_3			
P1–C11	1.822 (14)	1.830 (13)	P2–C29	1.847 (13)	1.830 (14)
P1–C17	1.831 (13)	1.822 (14)	P2–C35	1.831 (13)	1.822 (13)
P1–C23	1.834 (13)	1.840 (15)	P2–C41	1.817 (13)	1.787 (13)

quite similar for **1** and **2**. The remarkable structural invariance is also apparent from Figures 1–3. We shall now discuss salient structural features of these and related compounds.

The Ir Coordination. For the sake of convenience, we shall designate the two phosphine ligands as occupying the "axial" positions and the remaining four ligands, two sulfurs, one carbonyl, and one chloride (**1**) or hydride (**2**), as forming an "equatorial" plane.

The two Ir–S distances in the chloride (**1**) are quite similar (2.374 (4) and 2.346 (4) Å). On the other hand, the two Ir–S distances in the hydride (**2**) are significantly different; the Ir–S2 distance of 2.426 (4) Å, which is trans to the hydride ligand (presumed to occupy to missing coordination site), is significantly longer than the Ir–S1 distance of 2.382 (4) Å, which is trans to the carbonyl ligand. This is apparently due to the larger trans influence of the hydride vs. the chloride. The same phenomenon is also observed in $[(MeO)_3P(CO)HIr(S\text{-}t\text{-}Bu)]_2$[21] where the Ir–S bond trans to the hydride ligand is 0.077 Å (2.445 (5) vs. 2.368 (4) Å) longer than that trans to the carbonyl ligand. The average Ir–S distance of 2.404 Å in **2** is also larger than the corresponding value of 2.360 Å in **1**. These values, however, are in line with the average Ir–S distances of 2.407 and 2.356 Å reported for $[(MeO)_3P(CO)HIr(S\text{-}t\text{-}Bu)]_2$[21] and $(Ph_3P)_2(CO)_2Br_2Ir_2(TTN)$,[4] respectively.

The Ir–C distances of 1.860 (15) and 1.895 (13) Å and the C–O distances of 1.155 (15) and 1.136 (14) Å in the chloride (**1**) and the hydride (**2**), respectively, appear to be normal and comparable to the corresponding values of 1.84 (2), 1.87 (2) Å and 1.16 (2), 1.14 (2) Å observed in $(Ph_3P)_2(CO)_2Br_2Ir_2(TTN)$. The correlation of long Ir–C with short C–O distances in these systems is in harmony with the conventional metal–carbonyl back-bonding model. The Ir–C–O angles of 171.5 (28)° in **1** and 172.7 (23)° in **2** deviate somewhat from the expected linearity.

The two Ir–P distances appear to be equivalent in both molecules. The average value of 2.419 Å in **1**, however, is significantly larger than that of 2.345 Å in **2**. One possible explanation of the longer Ir–P distances in **1** vs. those in **2** is the steric hindrance between P···Cl contacts (though other factors cannot be ruled out). The P1–Ir–P2 angles of 170.1 (1)° in **1** and 163.1 (1)° in **2** deviates significantly from linearity, with P1 tilting away from the TCTTN ligand due to steric hindrance as is evident from Figures 1b and 2b. Further evidence for such steric avoidance comes from the average P–Ir–S angles: P1–Ir–S angles of 99.1 and 101.5° in **1** and **2**, respectively, are larger than P2–Ir–S angles of 87.7 and 88.0°, which are close to the expected value of 90°.

Judged from the Ir–S, Ir–C, and Ir–P distances, respectively, the degree of metal-to-ligand back-bonding exhibits the following trend: Ir→TCTTN, **1** > **2**; Ir→CO, **1** > **2**; $Ir \rightarrow PPh_3$, **2** > **1**.

The "Half-Coordinated" TCTTN Ligand. The $C_{10}Cl_4S_4$ (TCTTN) ligand coordinates to the iridium atom via cleavage of one of the two sulfur–sulfur bonds, resulting in a nonbonding S1···S2 distance of 3.155 (5) Å in the chloride (**1**) and 3.158 (5) Å in the hydride (**2**) complexes. The S3–S4 bond remains more or less intact at 2.070 (6) Å in **1** and 2.062 (6) Å in **2**. The half-coordinated TCTTN retains an essentially planar configuration in both molecules.

The most important finding of the present study is the observation that the intact S3–S4 bond is somewhat shorter than the S–S bonds in free ligand, as shown in Figure 3. This is consistent with the hypothesis that *the second S–S bond is strengthened and, therefore, "deactivated" somewhat toward further oxidative-addition reaction, upon cleavage of the first S–S bond via metal coordination.* Since the structure of TCTTN has not yet been determined, a detailed comparison will be made between the "half-coordinated" TCTTN in **1** and **2** with free $C_{10}H_4S_4$ (TTN) and its cation,[22] as well as with $(Ph_3P)_4Pt_2(TTN)$[3] in which both sulfur–sulfur bonds have been cleaved upon coordinating to two $(Ph_3P)_2Pt$ moieties. We shall first examine the S–S bonds in TTN and TTN^+ and then the S–S and S···S distances in the title compounds.

The S–S distances in TTN, TTN^+, **1**, and **2** are 2.097 (1), 2.085 (3), 2.070 (6), and 2.062 (6) Å, respectively. All these values are consistent with single S–S bond distances observed in diaryl disulfides. For example, the S–S single bond distances in PhS–SPh,[23] S_8,[24] and chloro(dipyrimidin-2-yl disulfide)copper(I) hydrate[25] are 2.03 (1), 2.060 (3), and 2.113 (1) Å, respectively. Also, the S–S distance in 3,5-dimethyl-1,2-dithiolium[26] and 3,5-diphenyl-1,2-dithiolium[27] cations are 2.019 (2) and 2.010 (2) Å, respectively. For comparison, the S–S bond distances in the $Ir(dppe)_2S_2^+$ cation[28] and in the $[Mo_2(S_2)_6]^{2-}$ dianion[29a] (the latter has four terminal and two bridging "side-on" S_2 ligands) are 2.066 (6) and 2.035 (6)–2.063 (6) Å, respectively. These values are substantially larger than that of 1.889 Å in free S_2[30] (presumed to be a double bond), close to that of 2.12 Å in Na_2S_2[31] (presumed to be a single bond) and significantly smaller than that of 2.25–2.50 Å observed in 2,5- and 2,4-disubstituted thiothiophthene shown in I and II, respectively, which are presumed to have a partial S–S bond with bond order $^1/_2$ due to

---

(21) Bonnet, J. J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *J. Am. Chem. Soc.* **1979**, *101*, 5940.

(22) Riga, J.; Verbist, J. J.; Wudl, F.; Kruger, A. *J. Chem. Phys.* **1978**, *69*, 3221.

(23) Lee, J. D.; Bryant, M. W. B. *Acta Crystallogr., Sect. B* **1969**, *B25*, 2094.

(24) Caron, A.; Donohue, J. *Acta Crystallogr.* **1965**, *18*, 562.

(25) Simmons, C. J.; Lundeen, M.; Seff, K. *J. Chem. Soc., Chem. Commun.* **1979**, 595.

(26) (a) Mason, R.; McKenzie, E. D.; Robertson, G. B.; Rusholme, G. A. *Chem. Commun.* **1968**, 1673. (b) Freeman, H. C.; Milburn, G. H. W.; Nockolds, C. E.; Mason, R.; Robertson, G. B.; Rusholme, G. A. *Acta Crystallogr., Sect. B* **1974**, *B30*, 886.

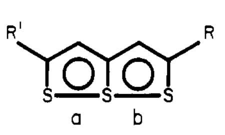
(27) Mason, R.; Robertson, G. B.; Rusholme, G. A. *Acta Crystallogr., Sect. B* **1974**, *B30*, 894.

(28) Bonds, W. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 3413.

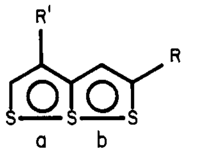
(29) (a) Müller, A.; Nolte, W. O.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 279. (b) Müller, A.; Nolte, W. O.; Krebs, B. *Inorg. Chem.* **1980**, *19*, 2835.

(30) Herzberg, G. "Molecular Spectra and Molecular Structure"; Van Nostrand: Princeton, NJ, 1950; Vol. I, p 566.

(31) Föppl, V. H.; Busmann, E.; Frorath, F. K. *Z. Anorg. Allg. Chem.* **1962**, *314*, 12.



I



II

zero-bond resonances. In the latter case, both symmetrical (I) and asymmetrical (II)

$$\mathrm{S}\overset{a}{-}\mathrm{S}\overset{b}{-}\mathrm{S}$$

linkages have been observed. For symmetrical ones, $a \approx b \approx$ 2.30–2.36 Å (R,R' = H,[32] Me,[33] Ph[34]) whereas, for asymmetrical ones, $a \approx 2.25$ Å and $b \approx 2.45$–2.50 Å (R = Ph, R' = H,[35] Ph[36]).

For S–S single bonds in acyclic and saturated cyclic disulfides, a relationship between S–S distances and C–S–S–C tension angles has been observed by Hordvik.[37] It was found that the longest S–S bonds occur when the electron repulsion between the sulfur lone pairs is at a maximum, when the torsion angle C–S–S–C is 0 or 180°. For our systems the torsion angle of close to 0° may be responsible for the somewhat longer sulfur–sulfur single-bond distances, as in free TTN.[22] We note that Shefter[38] and Seff and coworkers[39] also found a correlation between the S–S bond length and the X–C–S–S torsion angle where X = C, N.

In going from TTN to TTN$^+$, one observes a small but significant shortening of the S–S bonds, from 2.097 (1) to 2.085 (3) Å. This is in accord with our molecular orbital (MO) calculation on TTN that the two highest occupied MOs (HOMOs) $b_{2g}(\pi^*)$ and $a_u(\pi^*)$, portrayed in Figure 5 of ref 5, are highly antibonding between the sulfur atoms. (Qualitatively, one can visualize the five-membered heterocyclic C_3S_2 as a seven-π-electron ring such that one- or two-electron oxidation produces the mono- or dication with one or two six-π-electron "Hückel-like" $C_3S_2^+$ rings, one on each side of the molecule. It must be emphasized, however, that in TTN$^+$ the π-electron density remains delocalized such that the cation conforms to the idealized D_{2h} geometry.) Consistent with the notion that the HOMOs are highly sulfur in character, Geiger[40] found that in TTT$^+$, most of the spin density resides in the C–S–S–C bridges (EPR evidence).

In going from TTN to the title compound, one observes a small but significant shortening of ca. 0.03 Å in the intact S–S bond (corresponding to 6 times the standard deviation).[22] At the first glance, this is a surprising result because, upon metal coordination, the "half-coordinated" TCTTN ligand is, formally, reduced and one expects a weakening and hence a lengthening of the remaining S–S bond. A possible explanation is provided in our previous MO calculations.[5] Using Figure 5 of ref 5, we find that, upon coordination to two metal atoms, one on each side, the S–S σ-antibonding orbitals $b_{3u}(\sigma^*)$ and $b_{1g}(\sigma^*)$ interact with the metal orbitals (to form metal–sulfur bonds) and are stabilized energetically and fully occupied, giving rise to, formally, TTN^{4-}. Concomitantly, $a_u(\pi^*)$ and $b_{2g}(\pi^*)$ are stabilized while $b_{3g}(\pi)$ is destabilized (all due to the drastic increase in S–S distance), leaving $a_u(\pi^*)$ and $b_{3g}(\pi^*)$ as the two highest occupied orbitals. For the title compounds, $b_{1g}(\sigma^*)$ and $b_{3u}(\sigma^*)$ hybridize to give two orbitals, one S1–S2 antibonding $b_2(\sigma^*)$ and the other S3–S4 antibonding $b_2'(\sigma^*)$. Upon metal coordination at the S1–S2 site, $b_2(\sigma^*)$ is stabilized and fully occupied, corresponding to (TTN)$^{2-}$. Similar argument applies to $a_u(\pi^*)$ and $b_{2g}(\pi^*)$, giving rise to $a_2(\pi^*)$ and $a_2'(\pi^*)$, which are S1–S2 and S3–S4 π antibonding, respectively. If these orbital partitionings are complete, the two S–S bonds will act independently. In reality, under the idealized C_{2v} (considering only the TTN ligand) geometry, the two $b_2(\sigma^*)$ and, likewise, the two $a_2(\pi^*)$ orbitals of same symmetry can mix. The net result is, in qualitative terms, a "flow" of S–S antibonding electron density from S3–S4 to S1$\cdots$S2 via the naphthalene ring, thereby strengthening the S3–S4 bond in comparison with the free ligand. This strengthening is also observed in the infrared spectra of the title and related compounds. For example, the weak S–S asymmetric stretching frequency is increased from 667 (m) cm^{-1} in free TCTTN to that of 678 (sh) cm^{-1} in **1** and **2**. For comparison, ν_{S-S} of 530 cm^{-1} was observed in $[Mo_2(S_2)_6]^{2-}$, which has four terminal and two bridging "side-on" S_2 ligands.[29a] Similarly, ν_{S-S} values of 511 (m) and 545 (m) cm^{-1} were observed in $[Mo_3S(S_2)_6]^{2-}$, which contains three terminal and three bridging "side-on" S_2 units.[41] In $[Mo_4(NO)_4S_{13}]^{4-}$, which has both "end-on" and "side-on" disulfides, ν_{S-S} values of 533 (w) and 548 (w) cm^{-1} have been reported.[42]

The nonbonding S1$\cdots$S2 distances of 3.16 Å in the title compounds are among the shortest known for five- or six-membered heterocyclic rings, normally $\gtrsim$3.2 Å. They are even shorter than that of 3.211 (4) Å observed in $(Ph_3P)_4Pt_2$(TTN).[3] These values are to be compared with the sum of the van der Waals radii of two sulfur atoms, which is 3.70 Å.[43] As in this latter compound, steric constraints imposed by the chlorine atoms (Cl1 and Cl2) are believed to be the reason for the short S$\cdots$S nonbonding contacts. The average S$\cdots$Cl contacts are 3.014 (6) and 3.019 (5) Å in **1** and **2**, respectively. The sum of the van der Waals radii for S$\cdots$Cl contacts is 3.65 Å.[43]

As shown in Figure 3, the average C–S distances of 1.755 (14) and 1.730 (14) Å in **1** and **2**, respectively, are similar to the corresponding values of 1.766 (3) and 1.745 (9) Å in TTN and TTN$^+$.[22] No significant difference in C–S distances was observed in either **1** or **2** for the two sides of the molecule (viz., with and without an S–S bond).

A correlation between C–S and S–S bond lengths in aliphatic and aromatic disulfides was observed by Riga et al.[22] It was found that the S–S bond is long (2.05–2.10 Å) for cyclic and linear aromatic disulfides and short (2.00–2.04 Å) for aliphatic and aryl aliphatic disulfides. In contrast, the corresponding C–S bonds are short (1.73–1.78 Å) and long (1.81–1.88 Å), respectively. Clearly, both **1** and **2**, as well as TTN$^{0,+}$, fall in the former category.

While the naphthalene ring dimensions appear to be normal, several interesting observations can be made from Figure 3. First, the central C9–C10 bond seems to shorten somewhat (by about 0.06 Å) upon oxidation for the tetrathiolene ligands from a value similar to that in naphthalene (1.410 Å).[44] If we make the reasonable assumption (cf. ref 5) that, upon metal coordination as in **1** and **2**, the naphthalene ring is partially reduced, then one should expect an increase in the C9–C10 distance. Indeed the C9–C10 distances in **1**, **2**, and $(Ph_3P)_4Pt_2$(TTN) are 1.455 (17), 1.433 (17), and 1.442 (18)

---

(32) Hansen, L.; Hordvik, A. *Acta Chem. Scand.* **1970**, *24*, 2246.

(33) (a) Mammi, M.; Bardi, R.; Garbuglio, C.; Bezzi, S. *Acta Crystallogr.* **1960**, *13*, 1048. (b) Leung, F.; Nyburg, S. C. *Chem. Commun.* **1969**, 137.

(34) Hordvik, A. *Acta Chem. Scand.* **1968**, *22*, 2397.

(35) Bezzi, S. *Gazz. Chim. Ital.* **1960**, *92*, 859.

(36) Hordvik, A.; Sletten, E.; Sletten, J. *Acta Chem. Scand.* **1966**, *20*, 2001; **1969**, *23*, 1852.

(37) Hordvik, A. *Acta Chem. Scand.* **1966**, *20*, 1885.

(38) Shefter, E. *J. Chem. Soc. B* **1970**, 903.

(39) Higashi, L. S.; Lundeen, M.; Seff, K. *J. Am. Chem. Soc.* **1978**, *100*, 8101.

(40) Geiger, W. E., Jr. *J. Phys. Chem.* **1973**, *77*, 1862.

(41) Müller, A.; Sarkar, S.; Bhattacharyya, R. G.; Pohl, S.; Dartmann, M. *Angew Chem., Int. Ed. Engl.* **1978**, *17*, 535.

(42) Müller, A.; Eltzner, W.; Mohan, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 168.

(43) Pauling, L. "The Nature of the Chemical Bond", 3d ed.; Cornell University Press: Ithaca, NY; p 260.

Table IV. Bond Angles (deg) with Esd's for $(Ph_3P)_2(CO)XIr(TCTTN)$ Where X = Cl, H

	X = Cl	X = H		X = Cl	X = H
A. Ir Coordination					
P1-Ir-P2	170.1 (1)	163.1 (1)	S1-Ir-C	168.3 (4)	170.0 (4)
			S2-Ir-X	175.8 (1)	
P1-Ir-S1	99.3 (1)	98.6 (1)	P2-Ir-S1	84.7 (1)	83.6 (1)
P1-Ir-S2	98.9 (1)	104.4 (1)	P2-Ir-S2	90.6 (1)	92.4 (1)
P1-Ir-C	87.9 (4)	88.6 (4)	P2-Ir-C	89.8 (4)	91.6 (4)
P1-Ir-X	84.3 (1)		P2-Ir-X	86.4 (1)	
S1-Ir-S2	83.9 (1)	82.1 (1)	X-Ir-C	97.1 (4)	
S1-Ir-X	92.9 (1)		S2-Ir-C	85.9 (4)	89.3 (4)
Ir-C-O	171.7 (13)	174.5 (13)			
B. TCTTN					
Ir-S1-C1	111.2 (4)	109.3 (4)	Ir-S2-C8	113.8 (4)	110.0 (5)
S1-C1-C2	117 (1)	117 (1)	S2-C8-C7	114 (1)	117 (1)
S1-C1-C9	124 (1)	127 (1)	S2-C8-C9	127 (1)	126 (1)
S3-C4-C3	121 (1)	124 (1)	S4-C5-C6	123 (1)	122 (1)
S3-C4-C10	117 (1)	118 (1)	S4-C5-C10	116 (1)	120 (1)
S3-S4-S5	95.2 (5)	93.9 (5)	S4-S3-C4	94.9 (5)	95.5 (5)
Cl1-C2-C1	119 (1)	118 (1)	Cl3-C3-C2	123 (1)	123 (1)
Cl1-C2-C3	116 (1)	116 (1)	Cl3-C3-C4	120 (1)	117 (1)
Cl2-C7-C8	122 (1)	118 (1)	Cl4-C6-C7	122 (1)	122 (1)
Cl2-C7-C6	112 (1)	117 (1)	Cl4-C6-C5	119 (1)	118 (1)
C9-C1-C2	119 (1)	116 (1)	C9-C8-C7	119 (1)	116 (1)
C1-C2-C3	124 (1)	125 (1)	C8-C7-C6	123 (1)	125 (1)
C2-C3-C4	117 (1)	120 (1)	C7-C6-C5	119 (1)	120 (1)
C3-C4-C10	122 (1)	118 (1)	C6-C5-C10	121 (1)	118 (1)
C1-C9-C10	116 (1)	117 (1)	C4-C10-C9	122 (1)	123 (1)
C8-C9-C10	117 (1)	117 (1)	C5-C10-C9	121 (1)	124 (1)
C1-C9-C8	127 (1)	126 (1)	C4-C10-C5	117 (1)	113 (1)
C. PPh_3					
Ir-P1-C11	110.5 (5)	108.0 (4)	Ir-P2-C29	111.9 (4)	112.4 (4)
Ir-P1-C17	116.7 (5)	116.5 (5)	Ir-P2-C35	117.4 (5)	115.1 (4)
Ir-P1-C23	118.5 (4)	120.5 (5)	Ir-P2-C41	114.3 (4)	113.9 (4)
C11-P1-C17	104.1 (6)	101.8 (6)	C29-P2-C35	102.8 (6)	101.4 (6)
C11-P1-C23	102.1 (6)	104.2 (6)	C29-P2-C41	105.9 (6)	107.3 (6)
C17-P1-C23	103.0 (6)	103.8 (6)	C35-P2-C41	103.3 (6)	105.7 (6)
P1-C11-C12	118 (1)	116 (1)	P2-C29-C30	122 (1)	121 (1)
P1-C11-C16	122 (1)	123 (1)	P2-C29-C34	117 (1)	119 (1)
P1-C17-C18	122 (1)	122 (1)	P2-C35-C36	115 (1)	117 (1)
P1-C17-C22	117 (1)	118 (1)	P2-C35-C40	125 (1)	122 (1)
P1-C23-C24	118 (1)	115 (1)	P2-C41-C42	119 (1)	120 (1)
P1-C23-C28	119 (1)	122 (1)	P2-C41-C46	120 (1)	121 (1)

Table V. Dihedral Angles (deg) between Least-Squares Planes[a]

plane no.[a]	atoms	plane no.[a]	atoms
1	C1-C10	4	Ir, S1, S2, C1, C
2	S1, S2, C1, C8, C9	5	Ir, C9, C10
3	Ir, S1, S2		

	dihedral angle			dihedral angle	
planes	X = Cl	X = H	planes	X = Cl	X = H
1-2	5.2	3.0	2-4	−44.9	−50.3
1-3	−43.7	−50.2	2-5	89.2	88.5
1-4	−41.1	−47.6	3-4	2.7	2.6
1-5	85.8	87.1	3-5	89.6	90.6
2-3	−47.5	−52.8	4-5	90.4	91.3

[a] For the equations of the least-squares planes and atomic deviations from the planes, see Table IX (supplementary material).

Å, respectively. Second, the C–C distances (C1–C9 and C9–C8) within the C_3S_2 ring with no sulfur–sulfur bond seem to be somewhat longer (by ca. 0.04 Å) than the corresponding distances (C4–C10 and C10–C5) within the C_3S_2 ring with the sulfur–sulfur bond. Third, with the apparent exception of the central C9–C10 bond and, perhaps, **2**, the C–C distances within the naphthalene ring seem to follow the alternating long–short pattern of naphthalene.[44]

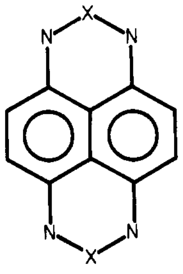
Molecular Distortion. As shown in Figures 1b and 2b, the "equatorial" plane of the coordination sphere of iridium is not coplanar with the TCTTN plane, with dihedral angles of 47.5 and 52.8° for **1** and **2**, respectively. These values are significantly larger than that of 38.9° (dihedral angle between planes II and V in ref 3) observed in $(Ph_3P)_4Pt_2(TTN)$. This structural feature, characteristic of all the tetrathiolene complexes, has been rationalized by us previously.[3] Suffice to say here that, in the absence of strong π-delocalization within the heterocyclic C_3S_2Ir ring, the sulfur ligands tend to adopt a sp^3 hybridization with average Ir–S–C angles of 112.5 (4)° for **1** and 109.7 (5)° for **2**, both being very close to the tetrahedral angle of 109.5°. This structural feature is to be contrasted with the planar structures of naphtho[1,8-*cd*:4,5-*c′d′*]bis[1,2,6]thiadiazine (III, X = S)[45a] and -selenadiazine (III, X = Se)[45b] where average X–N–C angles of 121.4° for X = S and 121.2° for X = Se, both being very close to the trigonal value of 120°, have been observed.

As a result of the folding along the S1···S2 edge, the P1 triphenylphosphine bends away from the TCTTN ligand (steric hindrance) as evident from Figures 1b and 2b. This

---

(44) Cruickshank, D. W. J. *Acta Crystallogr.* **1957**, *10*, 504.

(45) (a) Gieren, A.; Lamm, V.; Haddon, R. C.; Kaplan, M. L. *J. Am. Chem. Soc.* **1979**, *101*, 7277. (b) *Ibid.* **1980**, *102*, 5070.



III

X = S, Se

results in the deviation of the P1–Ir–P2 angle from linearity as well as larger P1–Ir–S angles than P2–Ir–S angles (vide supra; cf. Table IV).

Other molecular planes and the dihedral angles are tabulated in Table V (see also Table IX, supplementary material).

Solvent Molecules. The solvent molecules are refined with unity weight as indicated by the density measurements. For **1**, the isotropic thermal parameter for benzene ranges from 8.6 to 9.8 Å^2 and for acetonitrile from 9.0 to 10.1 Å^2. For **2**, the coresponding values are 14.1–22.7 and 7.7–11.0 Å^2. These values are to be compared with the average value of ca. 4 Å^2 for the phenyl carbon atoms in both structures. It is apparent that both solvent molecules undergo larger thermal motions and/or they are partially lost in the data collection process. In particular, the latter is a likely cause of the high thermal parameters for the benzene molecule in **2**.

The solvent molecules are hydrogen bonded to the iridium complexes, thereby contributing to the stability of the crystal. In **1**, the methyl group of the acetonitrile (C53) makes hydrogen-bonding contacts of 3.77, 3.86, and 3.75 Å with S1, Cl1, and Cl4 while the nitrogen atom (N) makes contacts of 4.15 and 5.32 Å with Cl1 and Cl4, respectively. In **2**, the orientation of the acetonitrile molecule is rotated by 180° with respect to that in **1** (viz., interchange of C53 and N positions) such that N now makes contacts of 4.93 and 3.88 Å with S1 and Cl1 while C53 makes hydrogen-bonding contacts of 3.66, 4.19, and 4.38 Å with Cl4, S1, and Cl1, respectively. Despite the opposite orientations exhibited by the acetonitrile molecules in these crystals, the C–C and C–N bonds are determined to be 1.48 (3) and 1.11 (2) Å in **1** and 1.42 (3) and 1.16 (2) Å in **2**, respectively, in accord with the single- and triple-bond characters of these bonds.

The C–C bond lengths in the benzene molecules show a larger range of scattering than the phenyl rings in the complexes: 1.21 (4)–1.50 (5) Å vs. 1.35 (2)–1.46(2) Å in **2** but not in **1** (1.37 (3)–1.45 (3) Å vs. 1.38 (2)–1.45 (2) Å). The average values of 1.39 Å in **1** and 1.35 Å in **2** appear to be normal.

Registry No. **1**, 87763-87-9; **2**, 87763-88-0.

Supplementary Material Available: Table VI (anisotropic thermal parameters), Table VII (distances involving phenyl groups and solvent molecules), Table VIII (angles involving phenyl groups and solvent molecules), Table IX (least-squares planes and the atomic displacements), and Table X (structure factor amplitudes) (101 pages). Ordering information is given on any current masthead page.

Contribution from the Departament de Química Inorgânica and the Departament de Cristal.lografia i Mineralogia,
Universitat Autònoma de Barcelona, Bellaterra, Barcelona, Spain,
and the Departament de Cristal.lografia i Mineralogia, Universitat de Barcelona, Barcelona-7, Spain

Synthesis and Crystal and Molecular Structure of *cyclo*-Tetrakis[bis(μ-*N*-methylpiperidine-4-thiolato)nickel(II)]

W. GAETE,*[1a] J. ROS,[1a] X. SOLANS,[1b] M. FONT-ALTABA,[1b] and J. L. BRIANSÓ[1c]

Received February 2, 1983

The reaction of nickel chloride with 4-mercapto-*N*-methylpiperidine in a basic solution gives the title complex. Crystals of the compound are monoclinic, space group $P2/n$, with a = 24.345 (3) Å, b = 10.638 (2) Å, c = 12.323 (2) Å, and β = 92.34 (2)°. With Z = 2 the calculated density is 1.32 g cm^{-3} (measured density 1.33 g cm^{-3}). Solution of the structure by direct methods led to a final weighted R factor of 0.077 for 2433 independent reflections. The crystal structure of the complex consists of a cyclic tetranuclear array of nickel atoms, bridged by eight sulfur atoms. The approximate square-planar NiS$_4$ units form the faces of a skew parallelogram with the sulfur atoms located at the corners. Axial and equatorial ligands alternate around the ring. The Ni–Ni distances average 2.665 (5) Å, and the closest S–S distances average 2.868 (6) Å. The Ni–S–Ni angles are 74.3 (1)°. The steric bulk of the piperidine rings provides a reasonable rationalization for the tetrameric structure.

Introduction

As a part of our work on the coordination of γ-mercapto amines to metal ions we have recently reported some solid complexes formed by *N*-methyl-4-mercaptopiperidine.[2-5] The reaction of this ligand with NiCl$_2$ in a basic solution yields a brown precipitate whose properties suggested a cyclic polynuclear structure, similar to the cyclic hexameric mercaptides of nickel previously reported.[6-8] The molecular weight determination, however, was consistent with a tetrameric structure. To our knowledge no cyclic tetrameric mer-

---

(1) (a) Departament de Química Inorgânica, Universitat Autònoma de Barcelona. (b) Universitat de Barcelona. (c) Departament de Cristal.lografia i Mineralogia, Universitat Autònoma de Barcelona.

(2) Bayón, J. C.; Briansó, M. C.; Briansó, J. L.; González-Duarte, P. *Inorg. Chem.* **1979**, *18*, 3478.

(3) Briansó, M. C.; Briansó, J. L.; Gaete, W.; Ros, J.; Suñer, C. *J. Chem. Soc., Dalton Trans.* **1981**, 852.

(4) Bayón, J. C.; Casals, I.; Gaete, W.; González-Duarte, P.; Ros, J. *Polyhedron*, **1982**, *1*, 157.

(5) Barrera, H.; Bayón, J. C.; González-Duarte, P.; Sola, J.; Viñas, J. M.; Briansó, M. C.; Briansó, J. L.; Solans, X. *Polyhedron* **1982**, *1*, 647.

(6) Woodward, P.; Dahl, L. F.; Abel, E. W.; Crosse, B. C. *J. Am. Chem. Soc.* **1965**, *87*, 5251.

(7) Abel, E. W.; Crosse, B. C. *J. Chem. Soc. A* **1966**, 1377.

(8) Gould, R. O.; Harding, M. H. *J. Chem. Soc. A* **1970**, 875.

0020-1669/84/1323-0039$01.50/0