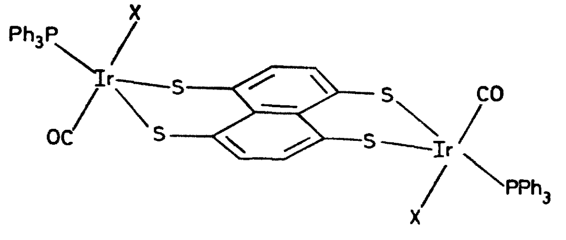
Metal–Tetrathiolene Chemistry: the First Disulphur Bridge in the Novel Di-iridium Cluster $(Ph_3P)_2(CO)_2Br_2Ir_2(C_{10}H_4S_4)$. *X*-Ray Crystal Structure

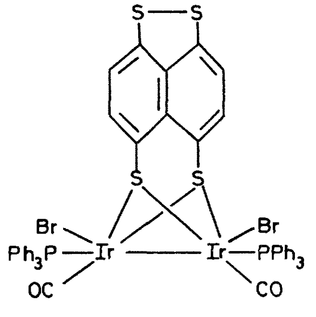
By Boon-Keng Teo* and P. A. Snyder-Robinson
(*Bell Laboratories, Murray Hill, New Jersey* 07974)

Summary The first di(μ-S)-bridge between two metal atoms has been observed in the tetrathionaphthalene (naptho[1,8-*cd*]dithiole-4,5-dithiolato) complex $(Ph_3P)_2(CO)_2Br_2Ir_2(C_{10}H_4S_4)$ and rationalized in terms of electronic effects which prevail over the steric constraints.

Recently we reported[1-3] the preparations and characterizations of two series of dimetallic tetrathiolene complexes $(Ph_3P)_4Pt_2L^2$ [L = $C_{10}H_4S_4$ (ttn), $C_{10}Cl_4S_4$ (tcttn), or $C_{18}H_8S_4$ (ttt)] and $(Ph_3P)_2(CO)_2X_2Ir_2$ (ttn)[3] (X = Cl, Br, or I). The stereochemistry of the diplatinum series was established by a structural study on $(Ph_3P)_4Pt_2$ (ttn) which revealed two $(Ph_3P)_2Pt$ species bridged by the bis-bidentate μ-(ttn) ligand.[2a] Since both series were prepared *via* oxidative cleavage of the S–S bond(s), it was expected that the di-iridium complexes will adopt a similar structure (**1**) with two five-co-ordinated iridium atoms bridged by the ttn ligand. To our surprise, $(Ph_3P)_2(CO)_2Br_2Ir_2$(ttn) adopts the unexpected molecular structure (**2**) which we have established by *X*-ray crystallography.



(**1**)



(**2**)

The orange-red title compound was prepared from *trans*-$Ir(PPh_3)_2(CO)Br$ and ttn (2:1) in benzene.[3] The red plate-like crystals of $(Ph_3P)_2(CO)_2Br_2Ir_2(ttn)\cdot 2(DMF)$, obtained from *NN*′-dimethylformamide (DMF)–MeCN, crystallize in the monoclinic cell with space group $P2_1/c$, a = 16·153(3), b = 18·398(6), c = 20·239(5) Å, β = 113·52(2)°, U = 5516 Å^3, Z = 4. *X*-Ray data with $0° < 2\theta < 44°$ were collected with an Enraf Nonius CAD4 diffractometer† using Mo-K_α radiation. The structure was solved by the heavy atom method and refined to R_1 = 4·4 and R_2 = 5·2%‡ for 3748 observed data with $F_o^2 > 3\sigma(F_o^2)$.

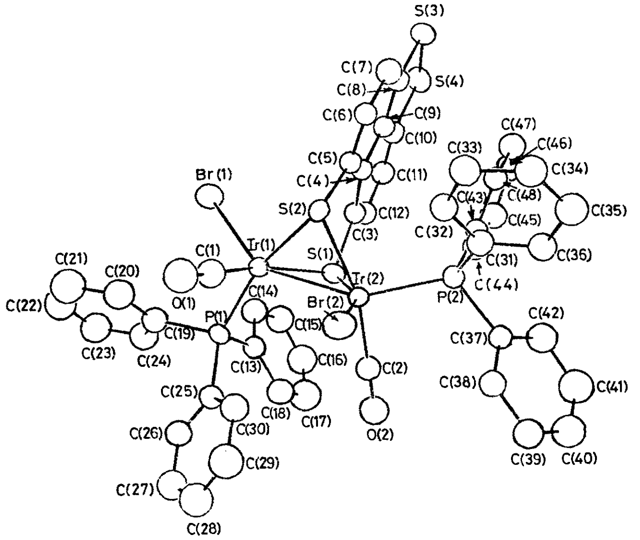


Figure. The structure of (**2**). Some important distances (Å) are: Ir(1)–Ir(2), 2·676(1); S(1) · · · S(2), 3·096; S(3)–S(4), 2·068(7); Ir(1)–Br(1), 2·565(2); Ir(2)–Br(2), 2·532(2); Ir(1)–S, 2·372(av.); Ir(2)–S, 2·340(av.); Ir(1)–P(1), 2·308(4); Ir(2)–P(2), 2·333(4); Ir(1)–C(1), 1·84(2); Ir(2)–C(2), 1·87(2); C–S, 1·766(av.); C–O, 1·15(av.).

The unusual stereochemistry of (**2**) is portrayed in the Figure. It consists of two iridium atoms bridged by two sulphur atoms [S(1) · · · S(2), 3·096 Å] from one end of the ttn ligand, leaving the other S(3)–S(4) bond [2·068(7) Å] intact. The molecule has a short Ir(1)–Ir(2) distance of 2·676(1) Å[4] with the metal–metal bond conceptually occupying the sixth co-ordination site of the highly distorted octahedral co-ordinations which include two sulphur atoms (from ttn), one carbonyl group, one Ph_3P group, and one bromine atom.§

Three approximate planes can be identified; one passes through the bridging ttn ligand while the other two pass through atoms Ir(1), Ir(2), S(1), Br(2), C(1), O(1) and Ir(1), Ir(2), S(2), P(1), C(2), O(2).

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† Molecular Structure Corporation, College Station, Texas.

‡ $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

We note that Vaska's compound reacts with RYYR (R = alkyl or aryl; Y = S or Se) in a 2:2 ratio (releasing two moles of Ph_3P) to give an edge-sharing bis-octahedral dimer, with each iridium atom being 18-electron Ir^{III}. The octahedral-like co-ordinations consist of one Ph_3P group, one CO group, one Cl atom, one terminal YR group, and two bridging YR groups.[5]

The molecule deviates from the idealized C_{2v} symmetry *via* a concerted permutation of the three terminal ligands on one iridium atom. While it may be possible to obtain other isomers *via* thermal equilibrum (as indicated by i.r. spectroscopy¶), the molecule (as well as some of its potential stereoisomers) appears to be under considerable steric strain as evidenced by the low symmetry and atomic displacements from the expected planes.

We believe that this molecule represents a rare case of electronic effect prevailing over the steric constraints; the molecule, instead of adopting a sterically more favourable $(Ph_3P)(CO)BrIrS_2C_{10}H_4S_2IrBr(CO)(PPh_3)$ structure (**1**) with both iridium atoms being five-co-ordinated 16-electron Ir^{III}, adopts an electronically more favourable $(Ph_3P)_2(CO)_2Br_2Ir_2S_2C_{10}H_4S_2$ structure (**2**) with both iridium atoms being six-co-ordinated 18-electron (rather uncommon) Ir^{II}. It is the first metal–tetrathiolene cluster in which the ttn ligand, instead of conforming to a four-electron-donating bis-bidentate (μ-ttn) bridging mode,** adopts a six-electron-donating bis-bidentate di(μ-S) bridging configuration.

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¶ Heating to reflux solutions of $(Ph_3P)_2(CO)_2X_2$ (ttn) for prolonged periods gave rise to 2—6 unresolved carbonyl bands at *ca.* 2020 cm^{-1}.

** For example, the intramolecular Pt · · · Pt distance in $(Ph_3P)_4Pt_2$ (ttn) is 9·044(4) Å (ref. 2a).

[1] B. K. Teo, 'Inorganic Compounds with Unusual Properties,' Adv. Chem. Ser., ed. R. B. King, no. 173, p. 364, 1979.
[2] (a) B. K. Teo and P. A. Snyder-Robinson, *Inorg. Chem.*, 1978, **17**, 3489; (b) *ibid.*, 1979, **18**, in the press.
[3] B. K. Teo and P. A. Snyder-Robinson, *Inorg. Chem.*, to be submitted.
[4] The average Ir–Ir bond in $Ir_4(CO)_{12}$ is 2·68(2) Å: G. R. Wilkes and L. F. Dahl, unpublished results.
[5] B. K. Teo and J. C. Calabrese, unpublished results.