

**Preliminary communication**

**Iridium initiated C–C-coupling of malonodinitrile  
 with carbon disulfide: synthesis and crystal structure  
 of  $[\text{H}_2\text{Ir}(\text{PPhMe}_2)_4]^+ [\text{HS}(\text{S})\text{CC}(\text{CN})_2]^-$**

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**Abstract**

Carbon disulfide reacts with malonodinitrile in the presence of  $\text{HIr}(\text{PPhMe}_2)_4$  to give  $[\text{H}_2\text{Ir}(\text{PPhMe}_2)_4]^+ [\text{HS}(\text{S})\text{CC}(\text{CN})_2]^-$  (1). The structure revealed by an X-ray diffraction study is consistent with the presence of S–H ··· S bonding.

The coordination chemistry of  $\text{CS}_2$  has been studied extensively since the discovery of the first transition metal- $\text{CS}_2$  complexes in 1966 [1]. Many carbon disulfide metal complexes and a number of insertion and disproportionation reactions have been described [2–4]. Complexes of  $\text{CS}_2$  with transition metals are more stable than complexes with its analogue  $\text{CO}_2$ , and they are of interest as models for bonding and reactions of both of these small molecules, especially in view of the important activation of carbon dioxide. Recently, we reported the C–C coupling of carbon dioxide with malonodinitrile in the presence of various rhodium and iridium complexes [5,6] (eq. 1).



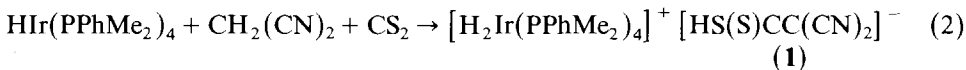
(L =  $\text{PMe}_3$ ,  $n = 4$ ; L =  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ,  $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ ,  $n = 2$ ;

X = Cl, H; M = Ir, Rh)

Use of  $\text{CS}_2$  in this reaction is of interest because the coupling of  $\text{CS}_2$  with active methylene compounds provides a potential pathway to S-containing heterocycles [7,8]. At present inorganic or organic bases are used to prepare the carbanions from the C–H acidic compounds needed for the synthesis of heterocycles. Use of

transition metal complexes instead of conventional bases could lead to a change in regio-selectivity in this type of reaction.

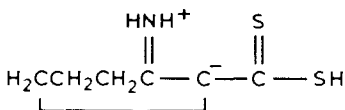
The iridium complex  $\text{HIr}(\text{PPhMe}_2)_4$  reacts with malonodinitrile and  $\text{CS}_2$  to give  $[\text{H}_2\text{Ir}(\text{PPhMe}_2)_2]^+ [\text{HS}(\text{S})\text{CC}(\text{CN})_2]^-$  (**1**) (eq. 2).



Complex **1** has been completely characterized by elemental analysis and spectroscopical data. The IR spectrum of **1** shows the  $\nu(\text{SH})$  band at  $2403 \text{ cm}^{-1}$ . Because of exchange reactions no signal is observed for the S–H proton in the  $^1\text{H}$  NMR spectrum. In order to permit a comparison of the structure of **1** with that of the previously prepared  $[\text{H}_2\text{Ir}(\text{PMe}_3)_2]^+ [\text{HO}(\text{O})\text{CC}(\text{CN})_2]^-$  (**2**) [5], an X-ray diffraction study of **1** has been performed [9] \*.

As can be seen from Fig. 1, the coordination of four phosphorus and two hydrogen ligands around the iridium atom is best described as distorted octahedral; the Ir–P distances are between 230.9(1) and 235.8(1) pm and the two hydrogens are in a *cis*-disposition. The coordination sphere in the cation is quite similar to that in the previously described  $[\text{H}_2\text{Ir}(\text{PMe}_3)_2]^+ [\text{HO}(\text{O})\text{CC}(\text{CN})_2]^-$  (**2**) and  $[\text{H}_2\text{Ir}(\text{PMe}_3)_2]^+ [\text{CH}(\text{CN})_2]^-$  (**3**) [6].

The dicyano-dithio-acetic acid anion shows almost the same arrangement as that in compounds **2** and **3**. Carbon atom C(3) has a planar environment, the sum of the three bond angles around this atom being  $360.0(3)^\circ$ . This implies that the negative charge in the anion resides mainly on this carbon atom. As in compounds **2** and **3**, two anions are connected via a centre of symmetry to dimeric units. The intermolecular distance between the two sulfur atoms S(1)–S(2)' is 376.8 pm, and is similar to the value of 379.0(1) found for the S–H · · S bridged diphenyl dithiophosphinic acid  $(\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{SH}$  [10]. Miyamae et al. [11] reported the same atomic arrangement, with the negative charge on the  $\beta$ -carbon atom in 2-iminocyclopentane-dithioic acid **4**.



(4)

\* Crystal data for **1**,  $\text{C}_{36}\text{H}_4\text{IrN}_2\text{P}_4\text{S}_2$ ,  $M = 888.0$ , triclinic space group  $P\bar{1}$  (It.Nr.:2),  $a$  1103.9(2),  $b$  1326.0(3),  $c$  1455.2(2) pm,  $\alpha$  88.86(1) $^\circ$ ,  $\beta$  78.58(1) $^\circ$ ,  $\gamma$  74.84(1) $^\circ$ ,  $Z = 2$ ,  $V$   $2014 \times 10^6 \text{ pm}^3$ ,  $d(\text{calc})$  1.464  $\text{g cm}^{-3}$ ,  $\mu$  35.8  $\text{cm}^{-1}$  (Mo- $K_\alpha$ ), 6250 independent reflections  $I \geq 1\sigma(I)$ ,  $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0| = 0.022$ ,  $R_w = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w|F_0|^2]^{1/2} = 0.017$ ,  $\text{GOF} = [\Sigma w(F_0 - F_c)^2 / (\text{NO-NV})]^{1/2} = 1.642$ ,  $w = 1/\sigma^2(F_0)$ . 594 parameters full matrix refined. Data were collected an ENRAF–NONIUS CAD4 diffractometer in the range  $2.0^\circ < 2\theta < 25.0^\circ$  ( $+h; \pm k; \pm l$ ). The structure was solved with Patterson and difference Fourier methods, atomic scattering factors including anomalous dispersion, all non-hydrogen atoms anisotropic thermal parameters, hydrogens located and refined with individual isotropic thermal parameters. Further details can be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (Germany), by quoting the depository number CSD 52773, the names of the authors, and the journal citation.

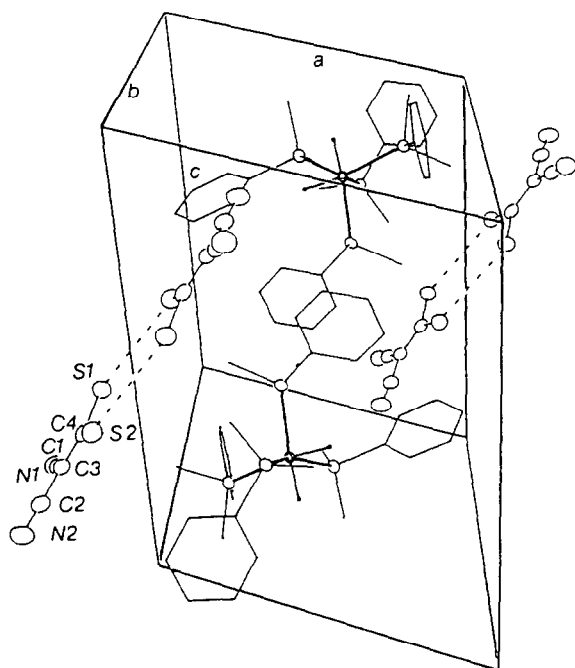
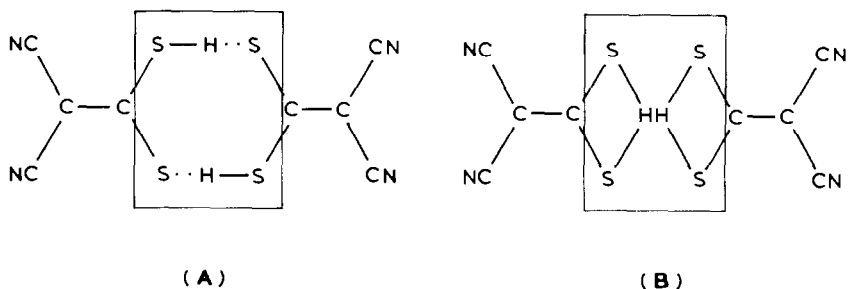


Fig. 1. The molecular structure of  $[\text{H}_2\text{Ir}(\text{PPhMe}_2)_4]^+ [\text{HS}(\text{S})\text{CC}(\text{CN})_2]^-$  (**1**).

Comparison of the C–S distances of C(4)–S(1) 176.7(4) pm and C(4)=S(2) 169.5(4) pm in compound **1** with some previously reported (**4**, C=S 169.0(3), C–S 176.2(3) [11];  $\text{CH}_3\text{C}(\text{S})\text{SFe}(\text{CO})_3$  [12], C–S 170 pm, C=S 164 pm;  $\text{CH}_3\text{SH}$  [13], C–S 181.9 pm;  $\text{H}_2\text{C}=\text{S}$  [14], 161 pm) show the  $\text{CS}_2$ -unit to be asymmetrical like the  $\text{CO}_2$ -unit in complex **2** (C=O, 125.7(9) pm; C–O, 131.7(9) pm). The S–S distances do not allow unequivocal distinction between structures **A** and **B**.



However, by comparison with the  $\text{CO}_2$ -analogue, structure **A** is favoured. Especially noteworthy is that one hydrogen from malonodinitrile has migrated to a sulfur atom.

## Literature

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