

### Preliminary communication

## SYNTHESIS AND CRYSTAL STRUCTURE OF *trans*-Pt[Fe(CO)<sub>3</sub>(NO)]<sub>2</sub>(NPh)<sub>2</sub>, A COMPLEX CONTAINING A LINEAR METAL CHAIN

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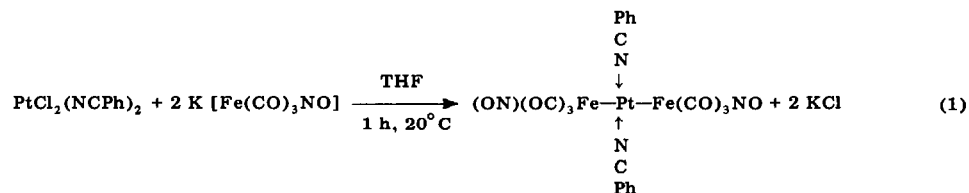
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### Summary

The complex *trans*-Pt[Fe(CO)<sub>3</sub>(NO)]<sub>2</sub>(NPh)<sub>2</sub> (1) has been prepared, and its structure has been determined by X-ray diffraction methods. It is the first example of a structurally characterized mixed trinuclear Pt–Fe complex in which a linear metal chain is present (Pt–Fe 2.657(2) Å).

Heteropolynuclear complexes in which the metal atoms are connected to each other only through metal–metal bonds form an interesting class of organometallic molecules [1]. We recently reported the syntheses and properties of heterotrinuclear chain complexes of the type *trans*-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-(OC)<sub>3</sub>M'–M(NCPh)<sub>2</sub>–M'(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>) (M = Pd, Pt; M' = Cr, Mo, W) [2] and of *trans*-(OC)<sub>5</sub>Mn–Pt(CO)<sub>2</sub>–Mn(CO)<sub>5</sub> [3]. The trinuclear benzonitrile complexes were shown to be excellent precursors for the high yield synthesis of tetranuclear planar, triangulated mixed-metal palladium and platinum clusters [2], the reaction involving in a key step the replacement of the labile PhCN ligand by a tertiary phosphine. In order to extend this class of molecules we have now prepared the title complex by the following reaction:



After completion of the reaction (IR monitoring), the THF solution was evaporated to dryness and the residue washed with pentane, which removed a small amount of  $\text{Fe}(\text{NO})_2(\text{CO})_2$ . Extraction of the residue with toluene gave a deep red solution, which was filtered and concentrated to small volume. Addition of pentane and cooling ( $-20^\circ\text{C}$ ) afforded complex 1 as deep red-brown crystals suitable for X-ray studies (80% yield). The product was identified by C, H, and N analysis and IR spectroscopy: (THF)  $\nu(\text{CO})$  2030sh, 2001vs, 1940s,br,  $\nu(\text{NO})$  1728vs; (KBr)  $\nu(\text{CO})$ : 2020sh, 1992s, 1952sh, 1918vs,  $\nu(\text{NO})$  1732sh, 1700vs  $\text{cm}^{-1}$ . The  $^{195}\text{Pt}$  resonance was found at  $-1374$  ppm (in THF/ $\text{C}_6\text{D}_6$ ,  $\Delta\nu_{1/2} \approx 600$  Hz, ext. ref.  $0.3\text{ M K}_2\text{PtCl}_4/\text{D}_2\text{O}$ ). Complex 1 must be kept under  $\text{N}_2$  in the dark at low temperature ( $-20^\circ\text{C}$ ). The structure of 1 has been fully elucidated by means of an X-ray diffraction analysis\*.

*Crystal data:*  $\text{C}_{20}\text{H}_{10}\text{Fe}_2\text{N}_4\text{O}_8\text{Pt}$ ,  $M$  741.10, monoclinic, space group  $P2_1/c$ ,  $a$  10.458(2),  $b$  13.732(5),  $c$  8.305(2) Å,  $\beta$  94.00(2)°,  $V$  1189.8(6) Å<sup>3</sup>,  $Z = 2$ ,  $D_c$  2.069  $\text{g cm}^{-3}$ ,  $F(000)$  704,  $\mu(\text{Mo-K}\alpha)$  71.81  $\text{cm}^{-1}$ .

The intensities of 2988 independent reflections were collected on a Siemens AED diffractometer (with  $\theta$  in the range  $3-28^\circ$ ); niobium-filtered Mo- $K_\alpha$  radiation and the  $\theta/2\theta$  scan technique were used. Intensities were corrected for absorption (maximum and minimum transmission factor values: 1.5943 and 0.6139). The structure was solved by Fourier methods and refined by full-matrix least-squares (with anisotropic thermal parameters for all the non-hydrogen atoms) on the basis of 1792 observed reflections (having  $I \geq 2\sigma(I)$ ) to an  $R$  value of 0.063\*.

The structure of 1 is shown in Fig. 1 together with the most significant bond distances and angles. The complex is centro-symmetric with the platinum atom lying on a crystallographic centre of symmetry, and so the Fe—Pt—Fe metal chain is perfectly linear. The Pt—Fe bonds, 2.657(2) Å, are longer than those in  $\text{PtFe}_2(\text{CO})_8(\text{PET}_3)_2$ , 2.640(1) [4],  $\text{PtFe}_2(\text{CO})_9(\text{PPh}_3)$ , 2.530(5) and 2.597(5) Å [5], in  $\text{Pt}_2\text{Fe}(\text{CO})_5[\text{P}(\text{OPh})_3]_3$ , 2.550(5) and 2.583(6) Å [6], and in  $\text{PtFe}_2(\text{CO})_8(\text{COD})$  (COD = cycloocta-1,5-diene), 2.553(3) and 2.561(3) [7], in which the metal atoms were at the vertices of  $\text{PtFe}_2$  or  $\text{FePt}_2$  triangular clusters.

To our knowledge 1 is the first example of a complex containing a structurally characterized linear Fe—Pt—Fe array.

The benzonitrile ligands are *trans* linearly bound to the platinum atom through the terminal nitrogen atoms. Whereas the phenyl groups are coplanar with the coordination plane in *trans*- $\text{PtCl}_2(\text{NCPH})_2$  [8], in complex 1 the dihedral angle between the platinum coordination plane and the phenyl ring is  $32.6(3)^\circ$ .

The coordination around the iron atom involves in addition to the Pt atom, three carbon atoms from carbonyl groups and one nitrogen atom from a nitrosyl ligand, all linear, with a geometry intermediate between trigonal bipyramidal and square pyramidal (NO apical), as indicated by the angles at the iron atom. The length of the Fe—N bond, 1.654(13) Å, agrees well with those found for totally ordered Fe—NO bonds in four-coordinate nitrosyl

\*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

iron complexes [9,10]. It is noteworthy that the approximately tetrahedral  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  anion is disordered when associated with  $\text{PPN}^+$  [9] (the NO ligand occupying each of the four tetrahedral sites with nearly the same occupancy factor) and becomes ordered after coordination to the platinum atom.

For the related isonitrile trinuclear complexes  $\text{trans-Pt}[\text{Fe}(\text{CO})_3\text{NO}]_2(\text{CNR})_2$  a local  $C_2$  symmetry about the Fe atoms was postulated, with an equatorial position for the NO ligand [11]. Furthermore, the present structure determination reveals a Pt—Fe—C(1) angle which is much smaller than the value of  $180^\circ$  which would have been expected.

The reactions of 1 with small molecules (e.g. CO, phosphines) are studied.

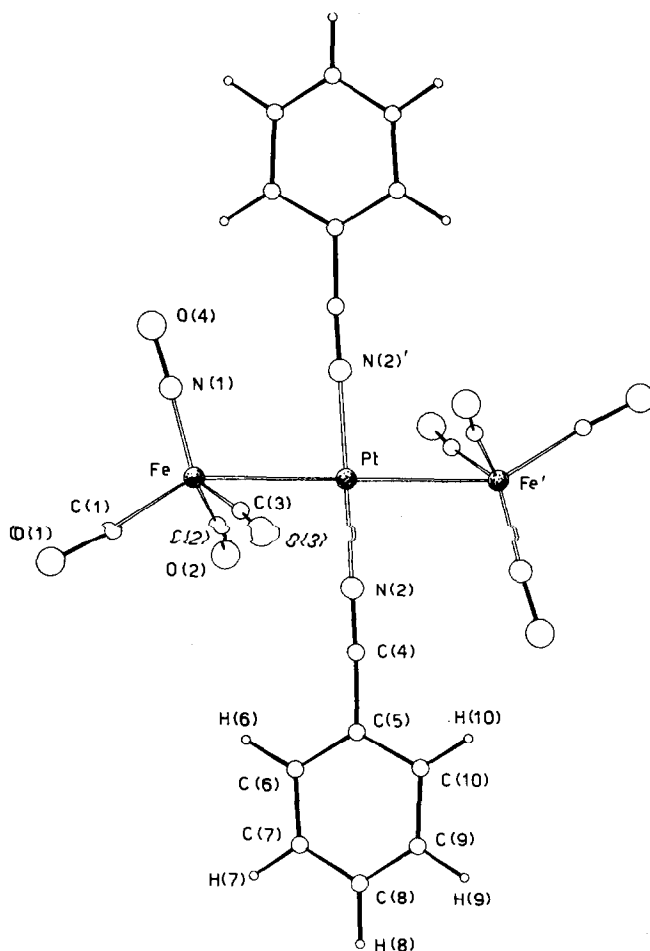


Fig. 1. View of the complex  $\text{Pt}[\text{Fe}(\text{CO})_3(\text{NO})]_2(\text{NCPh})_2$  with the atomic numbering scheme. Important bond distances (Å) and angles ( $^\circ$ ): Pt—Fe 2.657(2), Pt—N(2) 1.945(12), Fe—C(1) 1.782(17), Fe—C(2) 1.806(15), Fe—C(3) 1.820(14), Fe—N(1) 1.654(13), C(1)—O(1) 1.157(21), C(2)—O(2) 1.136(19), C(3)—O(3) 1.132(17), N(1)—O(4) 1.164(18), N(2)—C(4) 1.144(17); Fe—Pt—N(2) 93.3(4), Pt—Fe—C(1) 146.6(5), Pt—Fe—C(2) 72.7(5), Pt—Fe—C(3) 67.8(5), Pt—Fe—N(1) 103.7(4), C(1)—Fe—C(2) 93.3(7), C(1)—Fe—C(3) 94.0(7), C(2)—Fe—C(3) 117.0(7), N(1)—Fe—C(1) 109.6(6), N(1)—Fe—C(2) 117.7(7), N(1)—Fe—C(3) 118.0(7), Fe—C(1)—O(1) 175(1), Fe—C(2)—O(2) 174(1), Fe—C(3)—O(3) 171(1), Fe—N(1)—O(4) 177(1), Pt—N(2)—C(4) 180(1).

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