

**Synthesis and Molecular Geometry of Novel Di- and Tri-nuclear Iron Complexes Resulting from the Interaction of  $[\text{Fe}_2(\text{CO})_9]$  with  $\text{R}-\text{N}=\text{S}=\text{N}-\text{R}$  ( $\text{R} = t\text{-butyl}$  or  $p\text{-tolyl}$ ); X-Ray Crystal Structures of  $[\text{Fe}_2(\text{CO})_6\{\text{RNC}(\text{O})\text{S}\}]$  and  $[\text{Fe}_3(\text{CO})_9(\text{RNS})\text{S}]$**

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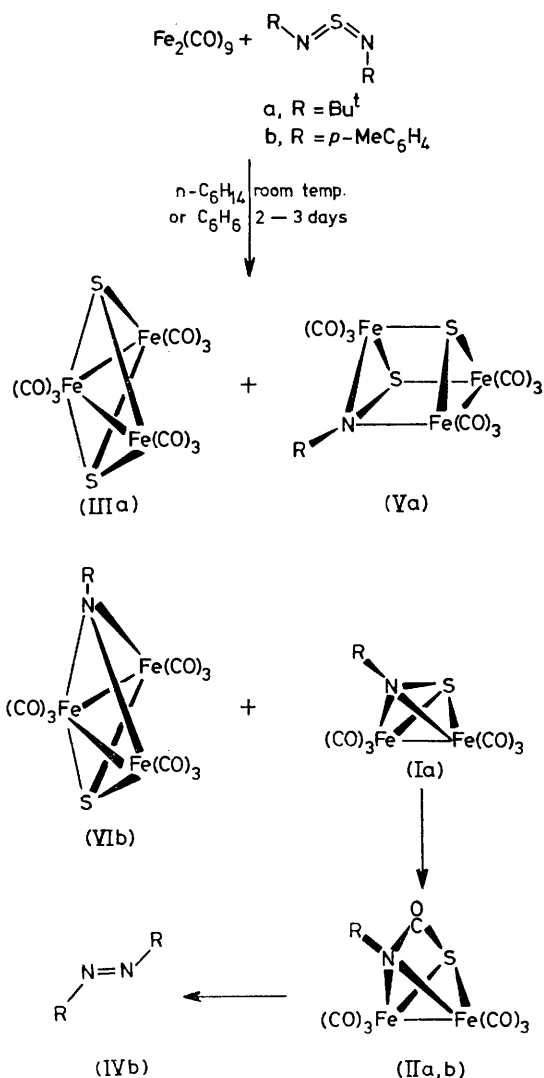
**Summary** The reaction of  $[\text{Fe}_2(\text{CO})_9]$  with  $\text{RNSNR}$  ( $\text{R} = \text{Bu}^t$  or  $p\text{-tolyl}$ ) leads to a breakdown of the di-imidosulphur ligand resulting in the formation of  $[\text{Fe}_2(\text{CO})_6(\text{RNS})]$  ( $\text{R} = \text{Bu}^t$ ),  $[\text{Fe}_3(\text{CO})_9\text{S}_2]$ ,  $[\text{Fe}_3(\text{CO})_9(\text{RNS})\text{S}]$  ( $\text{R} = p\text{-tolyl}$ ), and  $[\text{Fe}_2(\text{CO})_6\{\text{RNC}(\text{O})\text{S}\}]$  ( $\text{R} = p\text{-tolyl}$  or  $\text{Bu}^t$ ) which involves the as yet unknown insertion of CO into a N-S bond, and  $[\text{Fe}_3(\text{CO})_9(\text{RNS})\text{S}]$  ( $\text{R} = \text{Bu}^t$ ) which has the novel prismane type structure.

CO-ORDINATION of  $\text{NN}'$ -diaryldi-imidosulphur compounds to  $\text{Pt}^0$  leads to  $\pi$ -bonded complexes which rearrange to  $\text{Pt}^{\text{II}}$  complexes by a process involving N=S-bond breaking, N-C-bond formation, and hydrogen migration.<sup>1</sup> During an investigation of the factors determining the cause of this rearrangement, reactions of  $\text{RNSNR}$  molecules with polynuclear metal carbonyls have been studied.

We report here the reactions of  $\text{RNSNR}$  ( $\text{R} = \text{Bu}^t$  or  $p\text{-tolyl}$ ) with  $[\text{Fe}_2(\text{CO})_9]$  which result in the formation of some novel di- and tri-nuclear iron-carbonyl derivatives. The respective reaction mixtures were chromatographed on a silica gel column using *n*-hexane as eluent. After concentration and cooling, crystals were obtained which were purified by sublimation in yields varying from 1 to 10%. The products, shown in the Scheme, were identified by elemental analyses, <sup>1</sup>H n.m.r., mass, i.r., and Raman spectroscopy, while the structure of the complexes  $[\text{Fe}_2(\text{CO})_6\{\text{RNC}(\text{O})\text{S}\}]$ , (IIb), and  $[\text{Fe}_3(\text{CO})_9(\text{RNS})\text{S}]$ , (Va), were characterized by single crystal X-ray diffraction.

The Scheme reveals that the degradation of  $\text{RNSNR}$  molecules by  $[\text{Fe}_2(\text{CO})_9]$  follows pathways different from that observed in the reaction with  $\text{Pt}^0$ .<sup>1</sup> Compound (IIb) consists of an  $\text{RNC}(\text{O})\text{S}$  fragment, acting as a six-electron donor, bound to a dinuclear  $[\text{Fe}_2(\text{CO})_6]$  entity.

**Crystal data** (IIb): monoclinic,  $a = 7.301(1)$ ,  $b = 29.845(2)$ ,  $c = 7.960(1)$  Å,  $\beta = 90.20(1)^\circ$ ,  $Z = 4$ , space group  $P2_1/n$ , 974 independent reflections, measured on a Nonius CAD 4 Diffractometer, were considered to be observed [ $I > 2\sigma(I)$ ]; the final  $R$  factor is 0.071; Fe-Fe = 2.431(4), Fe-N = 2.02(1), Fe-S = 2.270(5) and 2.279(5) Å. Compound (Va) consists of an RNS fragment, acting as a six-electron donor, and a S atom, acting as a four-electron donor, whereas each group bridges three iron atoms. This results in a skeleton, formed by the three iron, two sulphur, and one nitrogen atoms, having a prismane structure, which is to our knowledge unprecedented in cluster chemistry. **Crystal data** for (Va): monoclinic,  $a = 11.039(1)$ ,  $b = 11.525(1)$ ,  $c = 15.996(1)$  Å,  $\beta = 96.241(6)^\circ$ ,  $Z = 4$ ,



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space group  $P2_1/n$ , 1637 independent reflections, measured on a Nonius CAD 4 diffractometer, were considered to be observed [ $I > 2.5\sigma(I)$ ]; the final  $R$  factor is 0.067; Fe-Fe = 2.1614(4), Fe-N = 2.08(1) and 2.09(1), and Fe-S = 2.228(5)—2.314(6) Å.†

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

The structure of (VIb) is analogous to  $[\text{Fe}_3(\text{CO})_9(\text{RN})_2]^{2+}$  and  $[\text{Fe}_3(\text{CO})_9\text{S}_2]^{3+}$  and consists of a bent  $(\text{OC})_3\text{Fe}-\text{Fe}(\text{CO})_3-\text{Fe}(\text{CO})_3$  skeleton which is triply bridged by a nitrene, RN, and an S atom. In this complex the RN group and S atom are acting as a four-electron donor. An alternative structure comprises a  $[\text{Fe}_3(\text{CO})_9]$  unit containing three Fe-Fe bonds which are bridged by an RNS fragment. It should be noted that Otsuka *et al.* isolated from the reaction of  $[\text{Fe}(\text{CO})_5]$  and  $\text{Bu}^t\text{NSNBu}^t$  a complex for which structure (Ia) was proposed.<sup>4</sup>

The presence of a single Fe-Fe bond in these complexes is confirmed by the occurrence of a  $\nu(\text{Fe}-\text{Fe})$  in the Raman spectra at *ca.* 200  $\text{cm}^{-1}$ .

The course of the reactions between RNSNR and  $[\text{Fe}_2(\text{CO})_9]$  depends strongly on the nature of R. The reaction with  $\text{R} = \text{Bu}^t$  affords (Ia) as the main product while only traces of (IIa) could be detected in the reaction mixture. From the reaction of  $[\text{Fe}_2(\text{CO})_9]$  with (*p*-tolyl)NSN(*p*-tolyl) (IIb) instead of (Ib) was isolated. Although information about the sequence of these reactions is lacking at this moment it seems plausible that the formation of (II) is a result of CO insertion into the NS bond of (I). A related

process involving insertion of CO into an NN bond has been observed in  $[\text{Fe}_2(\text{CO})_6(\text{RNNR})]$  which rearranges in solution to  $[\text{Fe}_2(\text{CO})_6\{\text{RNC}(\text{O})\text{NR}\}]$ .<sup>2</sup> The formation of azotoluene (IV) is most probably caused by decomposition of (IIb), because it is formed when (IIb) is heated in the solid state. This reaction, which seems to be exclusive for  $\text{R} = p\text{-tolyl}$ , necessarily involves elimination of a nitrene which dimerizes to give an azo-compound. This may explain why a nitrene stabilized complex (VI) is isolated only for  $\text{R} = p\text{-tolyl}$ . The formation of the two other trimetallic cluster compounds, (III) and (V), also depends on the nature of R and are only obtained when  $\text{R} = \text{Bu}^t$ . These results show clearly that S, RN, RNS, and RNC(O)S fragments resulting from degradation of  $\text{R}-\text{N}=\text{S}=\text{N}-\text{R}$  by metal carbonyls can be captured resulting in novel and interesting compounds which may provide insight into the pathways of such degradation processes.

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<sup>4</sup> S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, 1968, **7**, 1833.