

Formation of a Cationic Binuclear Iron–Dinitrogen Compound from Molecular Nitrogen

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Summary Treatment of the compound $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{dmpe})\text{I}$ ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) in acetone with TiBF_4 and nitrogen gas yields the binuclear dinitrogen complex $\{[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{dmpe})]_2\text{N}_2\}^{2+}(\text{BF}_4^-)_2 \cdot 2\text{H}_2\text{O}$ which readily reacts with carbon monoxide and LiAlH_4 giving the complexes $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{dmpe})\text{CO}]^+\text{BF}_4^-$ and $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{dmpe})\text{H}$, respectively.

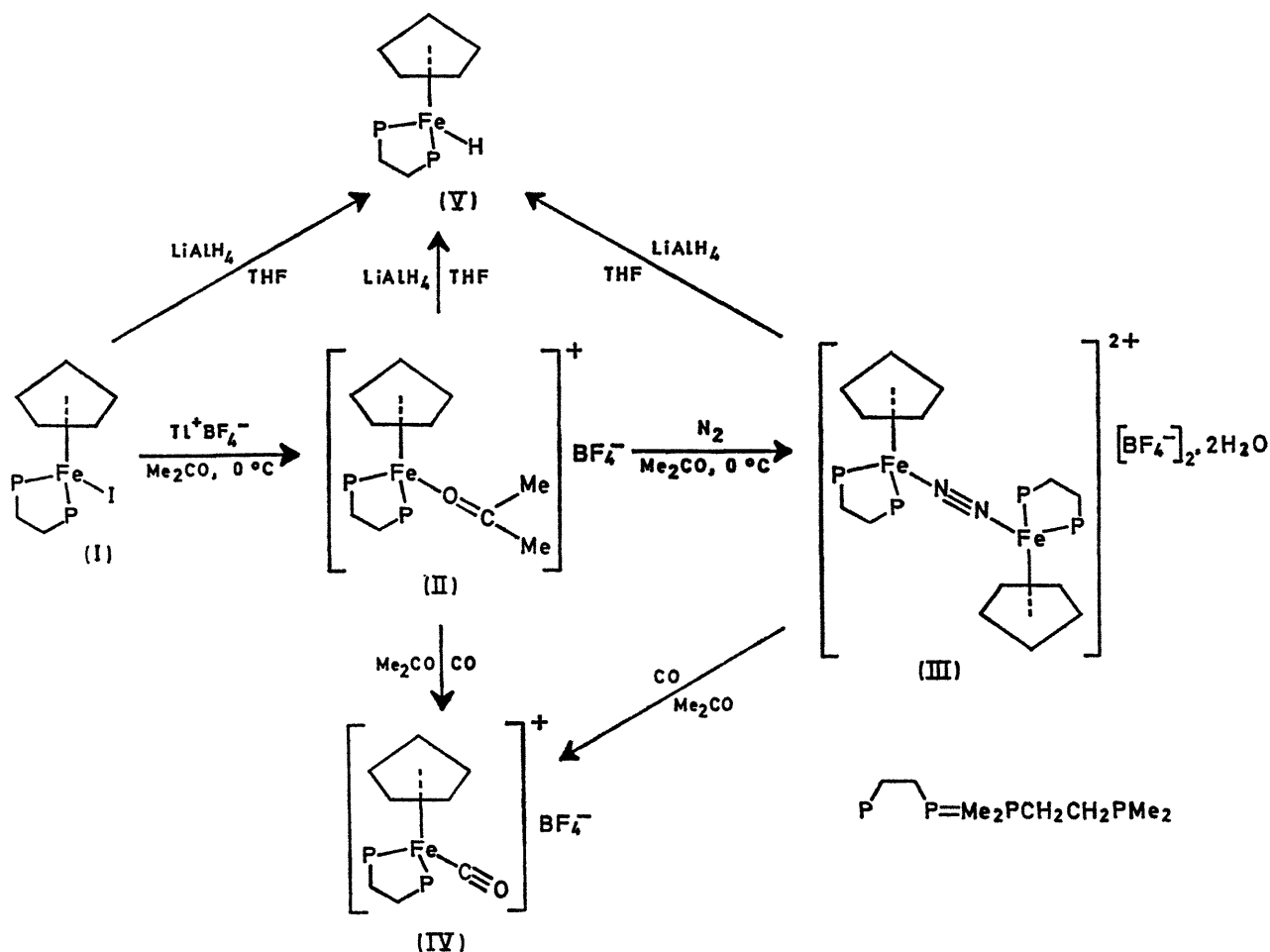
THE biological fixation of molecular nitrogen may well involve a di-iron–dinitrogen system, the isolation of such a system for the first time is described here.

Treatment of an acetone solution of the compound $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{dmpe})\text{I}$ (I), prepared analogously to $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{I}$,¹ with TiBF_4 at 0° C under nitrogen, yields orange crystals of stoicheiometry $\{[\text{C}_5\text{H}_5\text{Fe}(\text{dmpe})]_2\text{-}$

$\text{N}_2\}^{2+}(\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$, (III). Conductivity measurements in acetone are consistent with formulation as a 2 : 1 electrolyte. The compound does not show an absorption near 2000 cm^{-1} in the i.r., however, the Raman spectrum of the solid shows a very intense band at 2054 cm^{-1} assignable to a symmetric $\text{N}\equiv\text{N}$ stretching frequency. Therefore the centrosymmetric structure (III), shown in the Scheme, is proposed for the cation.

Apart from compound (III) the only other well characterized $\pi\text{-organometallic}$ dinitrogen compounds are the related compounds $[\text{C}_6\text{H}_6\text{Mo}(\text{PPh}_3)_2]_2\text{N}_2^{2+}$ and $[(\pi\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2$.³

When the above reaction is carried out under argon, brown crystals of stoicheiometry $[\text{C}_5\text{H}_5\text{Fe}(\text{dmpe})\text{Me}_2\text{CO}]^+(\text{BF}_4^-)$ (II), $\nu(\text{C}=\text{O})$ (Nujol) 1650 cm^{-1} , are obtained. Acetone solutions of compound (II) react readily with nitrogen gas at 0°C giving compound (III).



SCHEME

Both (II) and (III) in acetone react rapidly with carbon monoxide to give pale yellow crystals of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{dmpe})\text{-CO}]^+\text{BF}_4^-$, (IV) in high yields, $\nu(\text{C}\equiv\text{O})(\text{CHCl}_3)$ 1960 cm^{-1} .

The compounds [(I)—(III)] with lithium aluminium hydride in tetrahydrofuran give yellow crystals of the hydride $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{dmpe})\text{H}$ (V) $\tau(\text{Fe-H})(\text{C}_6\text{D}_6)$ 25.4 , ν -

$(\text{Fe-H})(\text{Nujol})$ 1830 cm^{-1} , m/e 272. No ammonia was detected in the products of the above reduction of (III).

All of the above complexes have been characterized by analysis, i.r., and conductivity measurements.

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¹ M. L. H. Green, and R. N. Whiteley, *J. Chem. Soc. (A)*, 1971, 1943.

² M. L. H. Green and W. E. Silverthorn, *Chem. Comm.*, 1971, 557.

³ R. H. Marvich and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1971, **93**, 2046.