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

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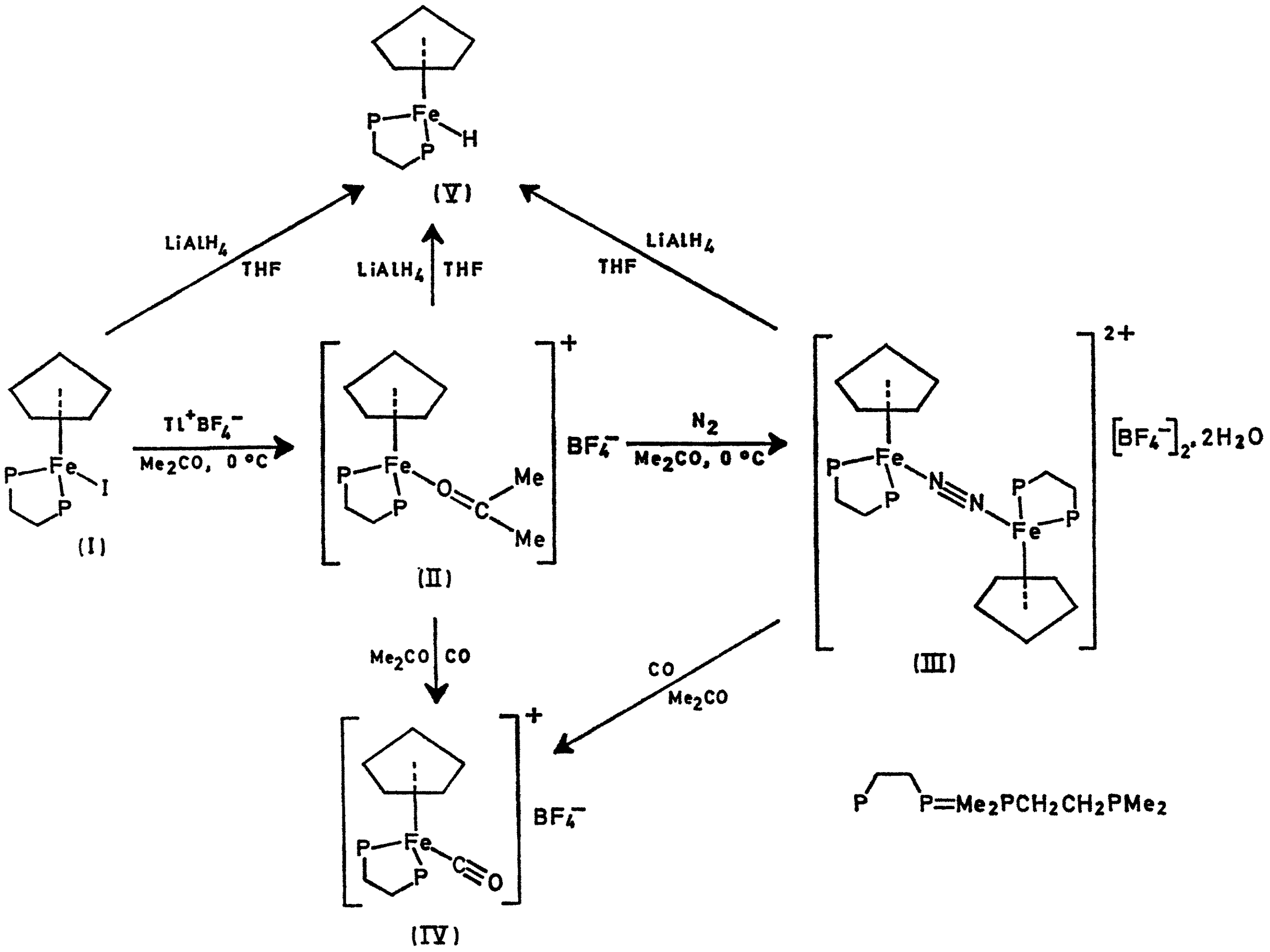
Summary Treatment of the compound π-$C_5H_5Fe(dmpe)I$ (dmpe = $Me_2PCH_2CH_2PMe_2$) in acetone with $TlBF_4$ and nitrogen gas yields the binuclear dinitrogen complex $\{[\pi\text{-}C_5H_5Fe(dmpe)]_2N_2\}^{2+}(BF_4^-)_2,2H_2O$ which readily reacts with carbon monoxide and $LiAlH_4$ giving the complexes $[\pi\text{-}C_5H_5Fe(dmpe)CO]^+BF_4^-$ and π-C_5H_5Fe(dmpe)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 π-$C_5H_5Fe(dmpe)I$ (I), prepared analogously to π-$C_5H_5Fe(Ph_2PCH_2CH_2PPh_2)I$,[1] with $TlBF_4$ at 0° C under nitrogen, yields orange crystals of stoicheiometry $\{[C_5H_5Fe(dmpe)]_2N_2\}^{2+}(BF_4)_2,2H_2O$, (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 $N{\equiv}N$ 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 π-*organometallic* dinitrogen compounds are the related compounds $[C_6H_6Mo(PPh_3)_2]_2N_2$[2] and $[(\pi\text{-}C_5H_5)_2Ti]_2N_2$.[3]

When the above reaction is carried out under argon, brown crystals of stoicheiometry $[C_5H_5Fe(dmpe)Me_2CO]^+(BF_4^-)$ (II), $\nu(C{=}O)$ (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 [π-$C_5H_5Fe(dmpe)$-$CO]^+BF_4^-$, (IV) in high yields, $\nu(C{\equiv}O)(CHCl_3)$ 1960 cm^{-1}.

The compounds [(I)—(III)] with lithium aluminium hydride in tetrahydrofuran give yellow crystals of the hydride π-$C_5H_5Fe(dmpe)H$ (V) τ(Fe–H)(C_6D_6) 25·4, ν(Fe–H)(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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[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.