Synthesis of 5-Amino-4-cyanopyrazole from 1,1-Dicyanoalkenes and Elemental Dinitrogen using a Tungsten Complex

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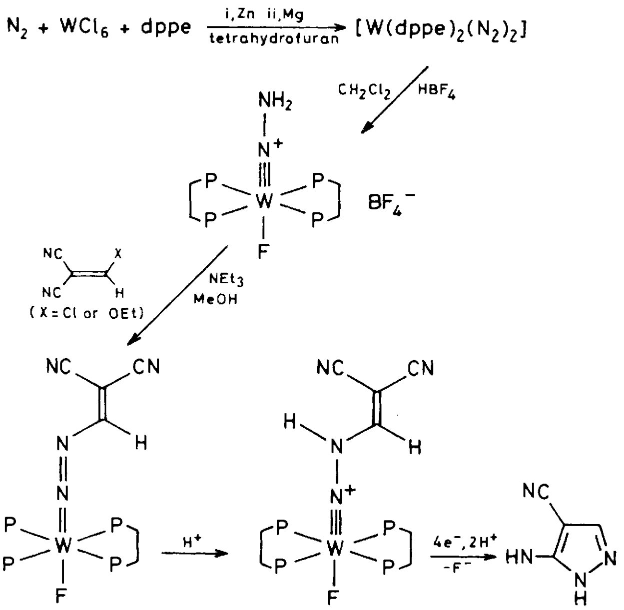
Electrochemical reduction of the dinitrogen-derived dicyanovinyl hydrazido(2−) complex $[\mathrm{WF(dppe)_2N\overline{NH(C}H{=}CCN_2)}]^+[\mathrm{BF_4}]^-$ [dppe = bis(diphenylphosphino)ethane] in tetrahydrofuran yields 5-amino-4-cyanopyrazole in up to 50% yield; when carried out under N_2, the metal-containing product of reduction is $[\mathrm{WF(dppe)_2N_2H_2}]^+[\mathrm{BF_4}]^-$, but under CO the dicarbonyl complex $\mathrm{W(dppe)_2(CO)_2}$ is formed.

In a recent communication[1] we described a series of cyanovinyl diazenido(1−) complexes, *e.g.* (**1**), which were prepared by condensation of cyanoalkenes with tungsten hydrazido(2−) complexes[2] derived from elemental dinitrogen. We now report that electrochemical cleavage of the metal–nitrogen bond in a protonated derivative of one of the former complexes gives 5-amino-4-cyanopyrazole in up to 50% yield. The complete reaction sequence, starting from dinitrogen, is shown in Scheme 1.

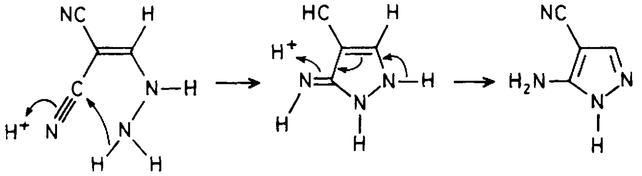
Cleavage of the metal–ligand bond was achieved by controlled potential electrolysis (c.p.e.) in tetrahydrofuran, at a potential 100 mV more negative than the peak reduction potential of the metal complex, using a mercury pool cathode and 0.1 M $[\mathrm{NBu^n_4}]^+\mathrm{BF_4}^-$ as the supporting electrolyte. Under a dinitrogen or carbon monoxide atmosphere, the total charge passed during electrolysis at −0.42 V (*vs.* Ag/AgCl electrode) corresponded to a 4-electron reduction, as has been reported for the c.p.e. of certain dialkyl hydrazido(2−) complexes under similar conditions.[3] The latter reductions yield simple dialkyl hydrazines as major organic products, but in our system the organonitrogen ligand is liberated as the heterocyclic compound 5-amino-4-cyanopyrazole[4] which we presume forms by cyclisation of a dicyanovinyl hydrazine (Scheme 2). The pyrazole (*ca.* 40% yield) was determined by g.l.c. (2½% OV 17 on Chromosorb G) and its identity was confirmed by cyclic voltammetry (c.v.) of the catholyte, and by comparison of c.v. and mass spectra of the isolated material with those of an authentic sample.

When the reduction was performed under carbon monoxide, the metal-containing product was the tungsten(0) complex $\mathrm{W(dppe)_2(CO)_2}$ [dppe = bis(diphenylphosphino)ethane], in agreement with a 4-electron reduction, but under an atmos-



(1)

Scheme 1



Scheme 2

phere of dinitrogen the hydrazido(2−) complex [WF(dppe)$_2$N$_2$H$_2$]$^+$BF$_4$$^-$ was formed by uptake of dinitrogen and subsequent protonation. This observation encouraged us to try to develop a cyclic system (Scheme 3) whereby sequential addition of alkene, base, and acid to a solution of the hydrazido(2−) complex was followed by c.p.e. under dinitrogen to liberate aminocyanopyrazole and regenerate the starting complex for a further cycle. Although the yield of pyrazole did indeed increase (from 40% to 50% based on tungsten) on a second cycle, the third and fourth cycles produced little improvement in yield, possibly as a result of the sensitivity of the hydrazido(2−) complex to degradation by mercury(II) salts[5] which may be generated in this system.

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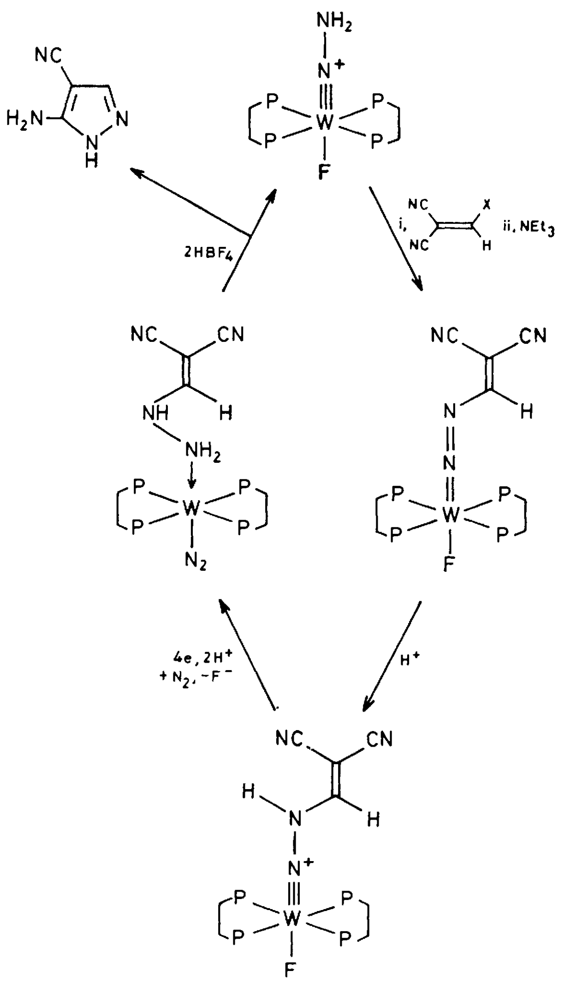

Scheme 3

References

1 H. M. Colquhoun, A. E. Crease, S. A. Taylor, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 736.
2 J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1974, 2074.
3 C. J. Pickett and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 1981, 1033.
4 R. K. Robins, *J. Am. Chem. Soc.*, 1956, **78**, 784.
5 S. A. Taylor, Ph.D. Thesis, Trent Polytechnic, 1982.