

## Preliminary communication

**A comment on the formation of N–C bonds via reactions of anionic dinitrogen complexes with organic halides: X-ray crystallographic structure of *trans*-[W(CN)(NNCHOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(dppe)<sub>2</sub>]**

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Received 20 December 1995

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**Abstract**

Reaction of *trans*-[W(N<sub>2</sub>)(CN)(dppe)<sub>2</sub>]<sup>−</sup> with Me<sub>3</sub>SiCH<sub>2</sub>I in tetrahydrofuran gives a tetrahydrofuryldiazenide product, *trans*-[W(CN)(NNCHOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(dppe)<sub>2</sub>], the formation of which confirms that N–C bond formation involving reactions between anionic dinitrogen complexes and organic halides can occur by a single electron transfer/radical coupling mechanism. The structure of the diazenide was established crystallographically.

**Keywords:** Dinitrogen complexes; Tungsten; Silicon; Crystal structure; Diazenides

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It has been reported recently [1] that certain  $\eta^6$ -metallo-haloarenes react with electron-rich anionic dinitrogen complexes [2] *trans*-[WX(N<sub>2</sub>)(dppe)<sub>2</sub>]<sup>−</sup> (dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>; X = NCS or F) to give aryl-diazenides. It was proposed that N–C bond formation occurred via nucleophilic attack of the terminal N atom on the activated aryl halide i.e. an S<sub>N</sub>Ar mechanism. Some of the activated aryl halides were found to react with the anionic dinitrogen complexes by an alternative pathway, single electron transfer, and failed to give diazenide products. From this it was inferred that rapid formation by electron transfer of W<sup>I</sup>-N<sub>2</sub> intermediates precluded N–C bond formation.

This contrasts with earlier studies [2,3] on the alkylation of anionic dinitrogen complexes which proposed a single electron transfer/radical coupling mechanism to account for both N–C or C–C bond formation reactions. For example, (i) *trans*-[Mo(N<sub>2</sub>)(X)(dppe)<sub>2</sub>]<sup>−</sup> (X = CN or NCS) reacts with BuI to give *trans*-[Mo(N<sub>2</sub>Bu)(X)(dppe)<sub>2</sub>], the reaction is first order in complex and in alkyl halide and proceeds with retention of the *trans* ligand [2]; (ii) *trans* [M(N<sub>2</sub>)(CN)(dppe)<sub>2</sub>]<sup>−</sup> (M = Mo or W) gives thermally unstable *trans*-

[M(N<sub>2</sub>)(CN)(dppe)<sub>2</sub>] and dibenzyl upon reaction with PhCH<sub>2</sub>Cl in tetrahydrofuran (thf), *trans*-[MCl(CN)(dppe)<sub>2</sub>] being the final stable metal product [3]. The kinetics and nature of the products of these reactions were rationalised by invoking a common initial single electron transfer step which gives a metallo-radical and a carbon radical. The reactive butyl radical attacks *trans*-[M(N<sub>2</sub>)(X)(dppe)<sub>2</sub>] to give the diazenide, whereas the less reactive benzyl radical dimerises to give dibenzyl. Such pathways have a parallel in the reactions of alkyl or benzyl halides with *trans*-[M(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>]. These have been shown unequivocally to involve co-generation of metallo-radicals and carbon radicals; this occurs by dissociation of one N<sub>2</sub> ligand and thence homolytic RX cleavage at the exposed metal site [4]. Nevertheless, an alternative interpretation is possible: benzyl chloride reacts by a single electron transfer but butyl iodide undergoes S<sub>N</sub>2 substitution to form the diazenide, i.e. the formation of dibenzyl does not necessarily signal an electron transfer/radical coupling pathway in the N–C bond forming reactions of other organic halides [1].

We now present evidence which shows that anionic dinitrogen complexes can form N–C bonds with alkyl halides via an electron transfer/radical mechanism. Me<sub>3</sub>SiCH<sub>2</sub>I reacts with *trans*-[W(CN)(N<sub>2</sub>)(dppe)<sub>2</sub>]<sup>−</sup>

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**A** in thf to give the tetrahydrofuranyldiazenide derivative **B**, Eq. (1). Recrystallisation of the product from  $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ , gave *trans*- $[\text{W}(\text{CN})(\text{NNCHOCH}_2\text{CH}_2\text{CH}_2)(\text{dppe})_2]$  as orange needles in 41% yield. Analytical and spectroscopic data are consistent with the formulation and the structure of **B** was unambiguously established by X-ray crystallography [5].

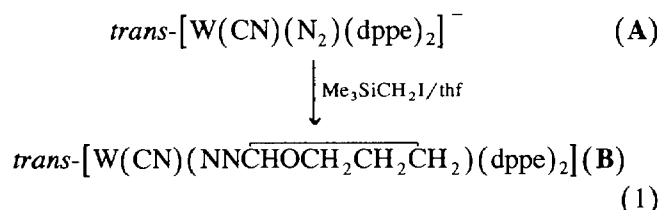


Fig. 1 shows a view of **B**: bond angles  $\text{C}(51)\text{-N}(51)\text{-N}(5) = 119.2(12)^\circ$  and  $\text{W}\text{-N}(5)\text{-N}(51) = 168.5(11)^\circ$  are typical of singly bent diazenido-complexes and the  $\text{W}\text{-N}(5)$  and  $\text{N}(5)\text{-N}(51)$  bond lengths of 1.846(12) Å and 1.281(17) Å respectively are unexceptional [6,7].

The formation of the solvent derived product **B** is indicative of an electron transfer/radical mechanism. Thus, single electron transfer leads to the generation of the radical  $\text{Me}_3\text{SiCH}_2$ , abstraction an  $\alpha$  H atom from thf by this radical, and thence N–C coupling of the daughter tetrahydrofuranyl radical with the conjugate  $\text{W}^{\text{I}}$  intermediate  $\text{trans-}[\text{W}(\text{N}_2)(\text{CN})(\text{dppe})_2]$  yields **B**, Scheme 1. Similar products arising from the generation of thf daughter radicals have also been isolated from reactions of  $\text{trans-}[\text{M}(\text{N}_2)_2(\text{dppe})_2]$  with alkyl halides [4,7]: **B** provides the first structurally authenticated representative of this type of compound.

In conclusion, it is evident that anionic dinitrogen complexes can react with organic halides to form N–C bonds by at least two pathways, viz, single electron transfer/radical or nucleophilic substitution. The forma-

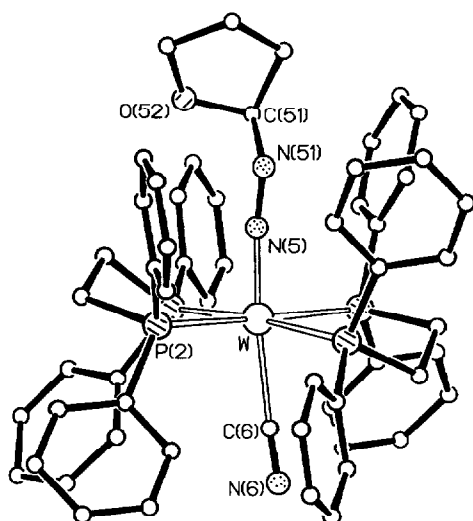
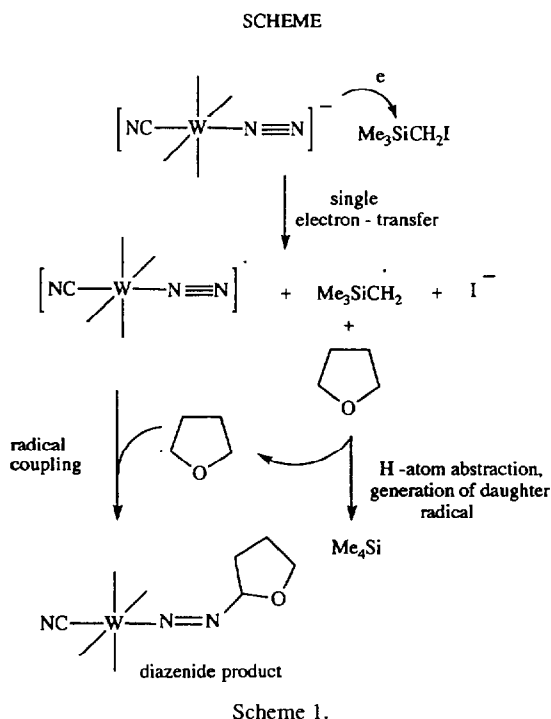


Fig. 1. Shows a view of **B**.



tion of a  $\text{M}^{\text{I}}$  dinitrogen intermediate does not necessarily preclude N–C bond formation but, in the case of the radical pathway, is of course, a prerequisite.

## Acknowledgements

We thank the EC for providing funds to support Dr. Hapipah Mohd Ali.

## References and notes

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- [5] Crystal structure analysis of *trans*- $[\text{W}(\text{CN})(\text{NNCHOCH}_2\text{CH}_2\text{CH}_2)(\text{dppe})_2]$ .  $\text{Et}_2\text{O}$ . Crystal data:  $\text{C}_{57}\text{H}_{55}\text{N}_3\text{-OP}_4\text{W}_4\text{C}_4\text{H}_{10}\text{O}$ ,  $M = 1180.0$ . Tetragonal, space group  $\text{P4}_2/\text{n}$  (no. 86, origin on an inversion centre),  $a = 29.444(2)$ ,  $c = 12.944(1)$  Å,  $U = 11221.7$  Å<sup>3</sup>.  $Z = 8$ ,  $D_c = 1.397$  g cm<sup>-3</sup>,  $F(000) = 4816$ ,  $\mu(\text{Mo-K}\alpha) = 22.6$  cm<sup>-1</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.71069$  Å. Very thin, long, orange needles which deteriorate slowly in air. After photographic examination, crystal mounted on CAD4 diffractometer for accurate cell dimensions and intensity measurements ( $\theta_{\text{max}} = 20^\circ$ ). Intensities corrected for Lorentz polarisation and absorption effects. 5220 Unique reflections (3199 with  $I > 2\sigma_I$ ) entered into SHELX system for structure determination (heavy atom method) and refinement (large-block-matrix least-squares methods) to  $R = 0.067$  and  $R_g = 0.049$  (G.M. Sheldrick,

SHELX—Program for crystal structure analysis, University of Cambridge, 1976; also extended version, SHELXN, 1977) for 3838 reflections ( $I > \sigma_I$ ) weighted  $w = (\sigma_F^2 + 0.000063F^2)^{-1}$ . All non-hydrogen atoms in W complex refined anisotropically; H atoms included in idealised positions. Solvent molecule disordered, not fully resolved. Tables of atom coordinates, thermal

parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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