

Electrochemical Carbon–Carbon Coupling of Diazomethane Ligands

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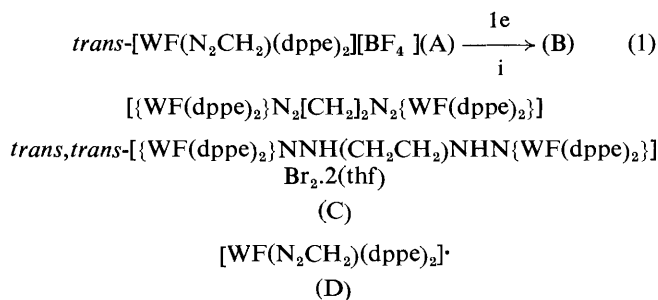
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Carbon–carbon bond formation *via* electrochemical coupling of diazoalkane ligands has been investigated; one-electron reduction of *trans*-[WF(N₂CH₂)L₂]⁺ in a MeCN electrolyte at a Hg pool cathode affords [L₂FW{N₂CH₂CH₂N₂}WFL₂] in moderate yield (L = Ph₂PCH₂CH₂PPh₂).

We report the first example of carbon–carbon bond formation *via* intermolecular coupling of diazomethane ligands. Electrochemical oxidation or reduction of transition metal complexes can lead to the formation of reactive intermediates which undergo ligand-centred chemistry and recently several interesting examples of such electrode reactions have been described.^{1–3} We find that the electrochemical activation of a diazomethane complex allows the convenient synthesis of a compound containing the hitherto unreported NNCH₂CH₂NN bridging ligand.

Controlled-potential reduction of *trans*-[WF(N₂CH₂)(dppe)₂][BF₄], (A), dppe = Ph₂PCH₂CH₂PPh₂, affords the ditungsten complex [{WF(dppe)₂}N₂[CH₂]₂N₂{WF(dppe)₂}], (B), in an overall one-electron process, equation (1). The electrosynthesis of (B) is particularly facile as the *product* is deposited from the MeCN catholyte during the reduction as a bright-yellow powder (isolated yield 55%).

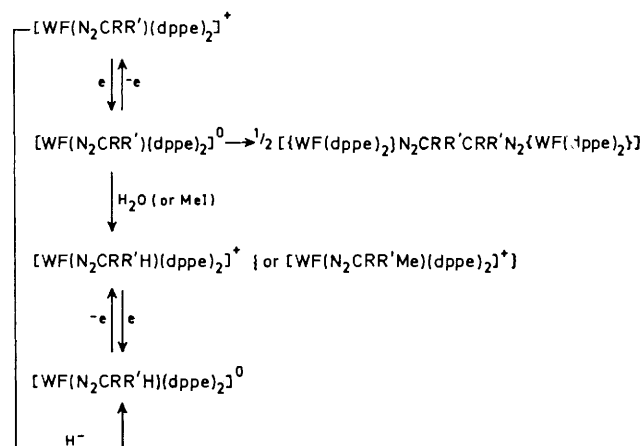


i, –1.8 V vs. saturated calomel electrode, Hg pool, MeCN–0.2M-[NBu₄][BF₄], room temp.

The elemental analysis of (B) is consistent with its formulation as a diazenido-complex. Although (B) is too insoluble in organic solvents for adequate characterisation by n.m.r. spectroscopy, it is readily converted into a soluble hydrazido-(2–)-derivative. Thus, a suspension of (B) in tetrahydrofuran (thf) reacts with anhydrous HBr at room temperature to give

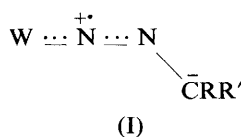
trans,trans-[WF(dppe)₂]₂NNH(CH₂CH₂)NHN{WF(dppe)₂}]Br₂·2(thf), (C), as an analytically pure buff-coloured solid. The ¹H n.m.r. spectrum of (C) in CD₂Cl₂ shows a multiplet of 4 protons, which we assign to the bridging NCH₂CH₂N group, in addition to resonances characteristic of NH, C₆H₅, PCH₂, and thf protons, which integrate in the correct intensity ratio. The ³¹P n.m.r. spectrum of (C) in CD₂Cl₂ shows a simple doublet of equal-intensity peaks indicative of P–F coupling, |J(PF)| 43.0 Hz, and of a *trans*-geometry at each of the W centres. The molar conductivity of a 0.304 mM solution of (C) in MeOH was 148 ohm⁻¹ mol⁻¹ cm² at 24 °C.

The cyclic voltammetry of (A) in MeCN–0.2M-[NBu₄][BF₄] shows that the primary electrochemical process is a diffusion-controlled one-electron reduction which remains irreversible even at 100 V s⁻¹, at –75 °C. Although we cannot directly detect the formation of the metallo-radical [WF(N₂CH₂)(dppe)₂][•], (D), we believe it to be an intermediate in the formation of (B) for the following reasons. Formal substitution of the H atoms in the diazomethane ligand of (A) by methyl or ferrocenyl gives complexes which undergo electrochemically reversible one-electron reduction to more-or-less stable analogues of (D). Other workers have shown that one-electron reduction of related aryldiazoalkane complexes give e.s.r. active complexes and suggest that the unpaired electron density is distributed over the two N atoms of the ligand.⁴ The formation of (B) plausibly occurs *via* radical–radical coupling or by radical–cation coupling followed by further electron-transfer.⁵ In principle, such mechanisms can be distinguished by cyclic voltammetric studies of the dependence E_p or E_{p/2} potentials upon scan rate and concentration;⁶ in practice, we find that deposition of insoluble (B) at the electrode surface precludes meaningful interpretation of such data. The radical–cation coupling reaction would represent an electrophilic attack by (A) upon (D). That such species are susceptible to attack by electrophiles is supported by our observations that in the presence of H₂O or MeI, complexes *trans*-[WF(N₂CRR')(dppe)₂][BF₄] undergo an overall two-electron reduction to give mononuclear diazenido-products *via* an e.c.e. mechanism, Scheme 1. The *parent* diazoalkane



Scheme 1

complexes are susceptible to attack by H^- or LiMe reagents,⁷ Scheme 1; thus electrochemical activation switches the character of the NNCRR' ligand from that of an electrophile to that of a nucleophile at the carbon centre. On the basis of these findings and the reported e.p.r. data⁴ we suggest that the reactivity of the reduced diazoalkane ligands may be attributed to a carbanionic contribution to their electronic structure (I).



We have shown that certain organodiazenido- and organohydrazido(2-)-ligands derived from co-ordinated N_2 can be chemically or electrochemically converted into free ammonia, amines, or hydrazines;⁸⁻¹⁰ complex (A), and the related diazoalkane complexes described above, are prepared from *trans*- $[\text{W}(\text{N}_2)_2(\text{dppe})_2]$, thus reaction (1) suggests a possible route from N_2 to 1,2-di(amino)ethanes or 1,2-di(hydrazido)-ethanes.

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