Reaction of Ligating Dinitrogen and Tetrahydrofuran to form Tetrahydropyridazido-complexes

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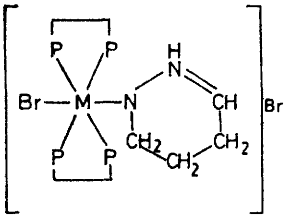
Summary In the presence of methyl bromide visible irradiation causes the reaction of tetrahydrofuran with the complexes $[M(N_2)_2(dpe)_2]$ (M = W or Mo; dpe = $Ph_2PCH_2CH_2PPh_2$) to form tetrahydropyridazido-complexes $[MBr(N_2C_4H_7)(dpe)_2]$ and their hydrobromide salts $[MBr(N_2C_4H_8)(dpe)_2]Br$; in this reaction the ligating dinitrogen appears to have replaced oxygen directly in the tetrahydrofuran ring.

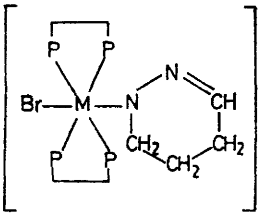
We have shown[1] that alkyl bromides in benzene react with the complexes $[M(N_2)_2(dpe)_2]$ [M = W or Mo; dpe = 1,2-bis(diphenylphosphino)ethane] on irradiation with visible light to form alkylazo-complexes of the type $[MBr(N_2R)(dpe)_2]$ (R = Me, Et, or Bu^t).

When the reactions are attempted in tetrahydrofuran (thf) as solvent the alkylazo-complexes are generally contaminated with another substance which, when R = Me, is the major product. This is isolated after addition of one mole of HBr, as a green substance when M = W or dark brown when M = Mo. It is independent of the alkyl halide used, but is not produced in its absence. The two substances (M = W or M = Mo) are 1 : 1 electrolytes and give analytical data consistent with the structure (A). Treatment of (A) with base yields orange-yellow non-ionic substances which give analytical data consistent with structure (B).

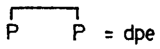
Apart from analysis and conductivity, these formulations rest on the following data. (i) The mass spectrum of compound (B; M=W) has a cluster of peaks in the range *m/e* 1138—1148, with the most intense peak at *m/e* = 1143 ± 1. There are no higher peaks. The formula weight of (B; M = W) is 1143. (ii) In the ^1H n.m.r. spectrum of (A; M = W) in $CDCl_3$ solution in the presence of D_2O there is a triplet (α) at τ 4·28 assignable to a C-*H*, a triplet (β) at τ 6·58 assignable to CH_2, and what appears to be a quartet (γ) at τ 8·68, close to a triplet (δ) at τ 8·96. These are each assignable to CH_2. In dry solvents there is also a singlet at τ *ca.* 6, which we assign to a single N-*H* proton. The ^{1}H n.m.r. spectrum of (A; M = Mo) is analogous. (iii) The interconnection of the protons identified in (ii) was established by double resonance. Thus irradiation of the unique proton resonance (α) caused the collapse of resonance (δ), irradiation of resonance (β) altered the shape of (γ), irradiation of (γ) and (δ) caused the resonances of (β) and (α), respectively, to become singlets. (iv) In the ^{15}N analogue of (A) (α) becomes a doublet of triplets due to ^{15}NH coupling, $^2|J_{N-H}|$ 10 Hz. These data establish the presence of $-N{=}CH{-}CH_2-$, $-CH_2{-}CH_2-$, and NH groups, presumably joined as in structure (A) (v) The i.r. spectrum of (A; M = W) shows ν(N–H) at 3200 cm^{-1} shifting to 2170 cm^{-1} after deuteriation, a strong band at 1572 cm^{-1} (1558 cm^{-1} in the ^{15}N analogue) assigned to ν(C=N) and a weak band at 1230 cm^{-1} (1200 cm^{-1} in the ^{15}N analogue) assigned to ν(N–N). The i.r. spectra of (A; M = Mo) and of (B; M = Mo or W) are in accord with these assignments. (vi) Compound (A; M = W) is not the same as the product obtained from [W$(N_2)_2$(dpe)$_2$] and 1,4-dibromobutane, although it has the same stoicheiometric formula.[1] This latter compound contains the grouping (C).

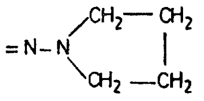


(A)



(B)





(C)

It is not clear how this complex is formed. Tetrahydrofuran is presumably the source of the hydrocarbon chain in the tetrahydropyridazine in (A) and (B). The role of the alkyl bromide (RBr) is not known but it possibly leads to the elimination of the oxygen from the tetrahydrofuran as the alcohol ROH. Tetrahydrothiophen does not react analogously to tetrahydrofuran.

The observation that ligating dinitrogen can displace oxygen from a heterocyclic ring is unique, and work is continuing to confirm the structures and elucidate the mechanism of formation of (A) and (B).

We thank the Royal Commission for the Exhibition of 1851 for an Overseas Research Scholarship (to G.A.H.), the University of Adelaide for sabbatical leave (A.A.D.), the S.R.C. for financial assistance, and Mr. Wasif Hussein for experimental assistance.

(*Received, 4th November* 1974; *Com.* 1340.)

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[1] A. A. Diamantis, J. Chatt, G. A. Heath, and G. J. Leigh, *J. Organometallic Chem.*, in the press.