Journal of Organometallic Chemistry, 84 (1975) C11–C12

Preliminary communication

THE ALKYLATION OF LIGATING DINITROGEN TO FORM ALKYLAZO AND RELATED COMPLEXES

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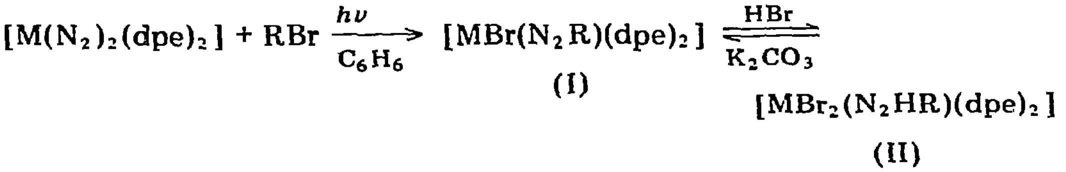
(Received October 31st, 1974)

Summary

The dinitrogen complexes $[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo or W) react with alkyl halides in benzene to form alkylazo complexes and with 1,4-dibromobutane to form complexes derived from the heterocyclic hydrazine $H_2N{-}NC_4H_8$.

Generally ligating dinitrogen in stable mononuclear dinitrogen complexes is inert to chemical attack. However, we have shown that in the complexes $[M(N_2)_2(dpe)_2]$ (M = Mo or W; dpe = 1,2-bis(diphenylphosphino)ethane) one molecule of dinitrogen is attacked by relatively mild reagents to form nitrogen derivatives. Thus organic acid halides RCOCl produce the compounds $[MCl_2(N_2COR)(dpe)_2]$ and $[MCl_2\{N_2H(COR)\}(dpe)_2]$ [1], and hydrogen halides produce compounds containing NH=NH or $=N{-}NH_2$ ligands [2]. We now find that the related reaction with alkyl bromides can be induced by irradiation from two 150 Watt tungsten filament bulbs to produce in benzene, orange-yellow alkylazo (alkyldiazenato) complexes. These are protonated to give *N*-alkyldiazene-*N′* or *N*-alkylhydrazido(2—)-*N′* complexes, but further alkylation to give *N,N*-dialkylhydrazido(2—)-*N′* complexes occurred in only two examples.

When the dinitrogen complexes in benzene containing an alkyl halide are irradiated they react as follows to form the product I (eqn. 1). This reaction has



$$[M(N_2)_2(dpe)_2] + RBr \xrightarrow[C_6H_6]{h\nu} \underset{(I)}{[MBr(N_2R)(dpe)_2]} \underset{K_2CO_3}{\overset{HBr}{\rightleftharpoons}} \underset{(II)}{[MBr_2(N_2HR)(dpe)_2]} \qquad (1)$$

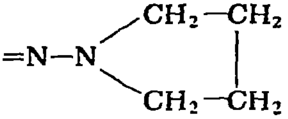
been confirmed for R = Me, Et or t-Bu when M = W, and for R = Me or Et when M = Mo. In the single case of R = Me, M = W, reaction with an excess of methyl bromide leads to a 1,1-dimethylhydrazido(2−) derivative $[WBr_2(NNMe_2)(dpe)_2]$.

Compounds I are characterised by a strong band at 1500-1520 cm^{-1}, assignable to $\nu(N{=}N)$ and compounds II, obtained from I by addition of hydrogen halide, have a broad series of bands in the region 3080-2828 cm^{-1}, which shifts to 2300-2180 cm^{-1} upon deuteriation, and which we assign to $\nu(N{-}H)$.

The alkyl protons in both kinds of complex can be identified from the ^1H NMR spectra, and ^{13}C NMR spectra can be assigned. In solution the complex II (M = W, R = Me) apparently occurs in two tautomeric forms, containing —NH=NMe and =N—NHMe, respectively, the ratio of the two forms depending upon solvent (cf. the N_2H_2 complexes [2]).

The structure of II (M = W, R = Me) has been determined [3]. It contains the system W—N—NHMe with angles W—N—N = 176° and N—N—C = 120°.

No other dialkylhydrazido derivatives could be obtained despite repeated attempts using an excess of the alkyl halides. Moreover, 1,3-dibromopropane yielded homologues of I and II in which R = $CH_2CH_2CH_2Br$. However, 1,4-dibromobutane yielded a complex analysing for $[WBr_2\{N_2(CH_2)_4\}(dpe)_2]$ which, on the basis of ^1H and ^{13}C NMR spectra, we formulate as containing the structural unit III.



(III)

We are now attempting to remove these new ligands as organo-hydrazines or -amines from their complexes.

We thank the Royal Commission for the Exhibition of 1851 for the award of an Overseas Research Scholarship (to G.A.H.), the Science Research Council for financial assistance, and Mr. Wasif Hussein for his exemplary experimental assistance.

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