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Preliminary communication

THE CONVERSION OF LIGATING DINITROGEN INTO AMINES

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SUMMARY

Treatment of organohydrazido(2–)-complexes of molybdenum and tungsten with lithium aluminium hydride gives good yields of amines. Simple acid treatment gives essentially none, and base distillation yields around 40%.

The production of ammonia and/or hydrazine from coordinated dinitrogen[1] has stimulated us to attempt the preparation of amines from complexes such as $[M(N_2)_2L_4]$ (M = Mo or W; L = tertiary phosphine or half di-tertiary phosphine). The production of amines from ill-defined nitrido-species derived directly from dinitrogen has been reported by other workers,[2,3] but no method is currently available for converting coordinated dinitrogen directly to amines.

The reaction of $[M(N_2)_2(PMe_2Ph)_4]$ with methyl bromide yields $[MBr_4(PMe_2Ph)_2] + 2N_2$, and there is no sign of alkylated nitrogen-containing products. The corresponding reaction with HBr produces ammonia.[1] We report here the production of amines from hydrazido(2–)-complexes $[MBr(N_2Me_2)(dppe)_2]^+$ and $[MBr\{N_2(CH_2)_n\}(dppe)_2]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane] which are themselves produced directly from dinitrogen complexes.[4] The results are shown in the Table.

The amines were all determined by quantitative analysis on a gas-liquid chromatograph using an organo-nitrogen selective detector. The identity of the amines was confirmed by colour tests, mass spectrometry, and comparison of retention times with those of authentic samples. Most determinations were undertaken at least twice and the values quoted are mean values within a range of a few per cent.

TABLE

(A) Amines by direct protonation

Complex	Conditions[a]	Amine	Yield (moles/mole complex)
$[WBr(N_2Me_2)(dppe)_2]$	Complex + conc. H_2SO_4 in propylene carbonate at 25°, 18h, followed by removal of solvent in vacuo at 130°C and (a) water extraction of residue or (b) base distillation of residue.	(a) $MeNH_2$ and Me_2NH (b) $MeNH_2$ and Me_2NH	0.08 and 0.19 0.08 and 0.19
$[WBr\{N_2(CH_2)_4\}(dppe)_2]Br$	Complex + conc. H_2SO_4 2h at reflux, then MeOH removed in vacuo; residue water extracted.	-	Nil
(B) Amines from reaction with $Li[AlH_4]$			
$[WBr\{N_2(CH_2)_4\}(dppe)_2]Br$	(a) $Li[AlH_4]Et_2O$ sealed at 80°C, 65h. (b) Excess of H_2SO_4. (c) Base distillation.	Pyrrolidine	0.70
$[WBr\{N_2(CH_2)_4\}(dppe)_2]Br$	(a) $Li[AlH_4]$ as above. (b) MeOH in excess.	Pyrrolidine	0.29
$[WBr\{N_2(CH_2)_4\}(dppe)_2]Br$	(a) $Li[AlH_4]$ as above. (b) MeOH in excess. (c) HBr in excess. (d) Water extraction.	Pyrrolidine	0.80
$[MoBr\{N_2(CH_2)_4\}(dppe)_2]Br$	(a) $Li[AlH_4]$ as above. (b) MeOH in excess. (c) HBr in excess. (d) Water extraction.	Pyrrolidine	0.87
$[MoBr\{N_2(CH_2)_4\}(dppe)_2]Br$	(a) $Li[AlH_4]$ as above. (b) MeOH in excess.	Pyrrolidine	0.27
$[WBr(N_2Me_2)(dppe)_2]Br$	(a) $Li[AlH_4]$ as above. (b) MeOH in excess. (c) HBr in excess. (d) Water extraction.	Me_2NH	0.95

TABLE (continued)

Complex	Conditions[a]	Amine	Yield (moles/mole complex)
(C) Amines by direct base distillation			
$[WBr(N_2Me_2)(dppe)_2]Br$	From 40% aq. KOH.	Me_2NH	0.60
$[WBr\{N_2(CH_2)_4\}(dppe)_2]Br$	From 40% aq. KOH.	Pyrrolidine	Within range 0.27-0.38 (3 experiments)
$[WBr\{N_2(CH_2)_4\}(dppe)_2]Br$	From ethanol sat. with KOH.	Pyrrolidine	Within range 0.15-0.25 (3 experiments)
$[WBr\{N_2(CH_2)_4\}(dppe)_2]Br$	From NaOEt/EtOH.	—	Nil
$[MoBr\{N_2(CH_2)_4\}(dppe)_2]Br$	From 40% aq. KOH.	Pyrrolidine	Within range 0.27-0.42 (3 experiments)
$[MoBr\{N_2(CH_2)_5\}(dppe)_2]Br$	From 40% aq. KOH.	Piperidine	0.49

[a] "MeOH in excess" means until all $Li[AlH_4]$ destroyed; "HBr in excess" means until the solution is strongly acid.

The Table shows that simple treatment of hydrazido(2-)-complexes with acid (A) is a poor way of generating amines. In fact cleavage of the nitrogen-carbon bond takes place to a considerable extent. Treatment with $Li[AlH_4]$ (B) gives amines in high yields, but the excess of $Li[AlH_4]$ forms complexes with the amine and must be destroyed (for example, by addition of methanol or acid) before attempting the work up. Base distillation (C) gives moderate yields of amine, but these reaction mixtures are not homogeneous and the yields are not as reproducible as for the other degradation procedures.

We never obtained more than a trace of ammonia in any of the reactions. The residues from the reactions of the hydrazido(2–)-complexes of tungsten with Li[AlH_4] did not contain nitrogen, and [WH_4(dppe)$_2$] (MeOH work up) or [WH_2Br_2(dppe)$_2$] (HBr work up) were isolated. The nitrogen balance and fate of the second nitrogen atom is under investigation.

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