Journal of Organometallic Chemistry, 170 (1979) C6—C8
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE INFLUENCE OF LIGAND ENVIRONMENT ON THE PROTONATION REACTIONS OF HYDRAZIDO(2–) COMPLEXES OF MOLYBDENUM AND TUNGSTEN: X-RAY STRUCTURES OF $[M(8\text{-quin})(NNH_2)(PMe_2Ph)_3]I$ (M = Mo OR W; 8-quin = QUINOLIN-8-OLATE)

JOSEPH CHATT, MARTIN E. FAKLEY, RAYMOND L. RICHARDS*,
A.R.C. Unit of Nitrogen Fixation, University of Sussex, BN1 9RQ (Great Britain)
IAN R. HANSON and DAVID L. HUGHES*
Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts. AL5 2 JQ (Great Britain)

(Received February 19th, 1979)

Summary

The complexes $[MX_2(NNH_2)(PMe_2Ph)_3]$ (M = Mo or W; X = Cl, Br or I) give ammonia with H_2SO_4/MeOH, the yield depending upon X. Ammonia is also obtained from $[Mo(8\text{-quin})(NNH_2)(PMe_2Ph)_3]I$ (M = Mo, 8-quin = quinolin-8-olate) but the tungsten analogue gives hydrazine only. Crystal structures of the 8-quin molybdenum and tungsten complexes are reported.

In the reactions of the complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (A, M = Mo or W) with sulphuric acid, which give ammonia and hydrazine, the product ratio depends upon both the metal and the solvent [1,2]. Thus in methanol, ammonia (1.98 mol/W atom; 0.7 mol/Mo atom) is the only product from (A, M = Mo or W), but in a variety of other solvents, although (A, M = Mo) gives only ammonia, (A, M = W) gives up to 0.32 moles of hydrazine (in *N*-methyl pyrrolidone) [1,2].

In view of this solvent effect, which might involve coordination of solvent to the metal at some stage, we have investigated the further protonation of the complexes $[MX_2(NNH_2)(PMe_2Ph)_3]$ (B, X = Cl, Br or I) and $[M(8\text{-quin})(NNH_2)(PMe_2Ph)_3]I$ (C, 8-quin = quinolin-8-olate). They contain the hydrazido(2–) ligand, a stable stage of reduction of dinitrogen at these metal sites [2], in a range of ligand environments. They react with H_2SO_4 in MeOH under standard conditions giving the nitrogenous products as listed in Table 1. As was observed for the dinitrogen complexes (A), the nature of the nitrogen hydride product depends upon the metal, since hydrazine is only observed from tungsten complexes. There are also marked ligand effects. Thus the yield of ammonia from complexes (B) increases on passing from X = Cl to X = I. A more dramatic effect

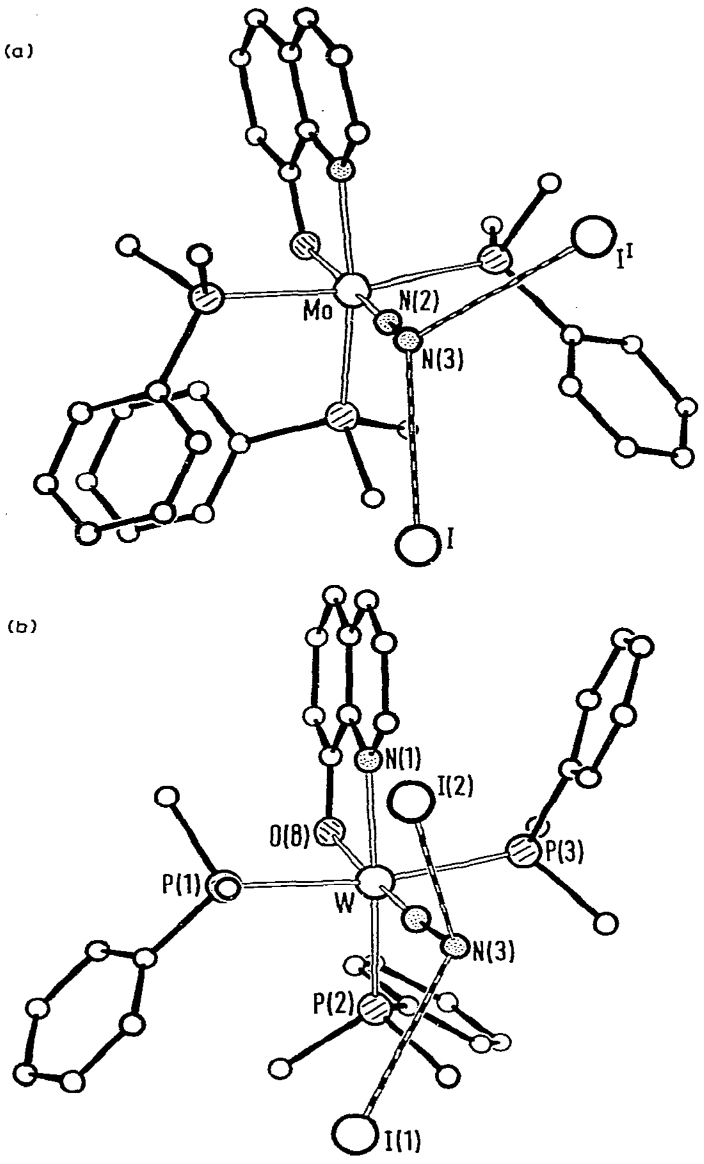

Fig. 1. X-ray structure of [M(8-quin)(NNH$_2$)(PMe$_2$Ph)$_3$]I (M = Mo or W).

Crystal data: (C, M = Mo): $C_{33}H_{41}IN_3OP_3Mo$, M = 811.5, Monoclinic, space group $P2_1/c$, a 15.749(1), b 13.012(1), c 17.776(1) Å, β 103.377(5)°. U 3544 Å^3, Z = 4, $F(000)$ = 1632. μ(Mo-K_α) 13.85 cm^{-1}. D_m 1.51 (flotation), D_c 1.52 g cm^{-3}. 3629 reflections with $I > 2\sigma(I)$, θ_{max} 22°; final R = 0.038, R' = 0.037 with $w = c$ (constant). (C, M = W): $C_{33}H_{41}IN_3OP_3W$, ½(C_9H_7NO), M = 972.0, Orthorhombic, space group $Pbcn$, a 18.889(2), b 23.013(2), c 18.106(2) Å. U 7870 Å^3, Z = 8, $F(000)$ = 3824. μ(Mo-K_α) 39.3 cm^{-1}. D_m 1.64 (flotation), D_c 1.64 g cm^{-3}. 2206 reflections with $I \gg 2\sigma(I)$, θ_{max} 17.5°; final R = 0.034, R' = 0.034 with $w = c$. A molecule of quinolin-8-ol was found disordered about a two-fold symmetry axis.

Structural data: (C, M = Mo): Mo—N(2) 1.743(4), N(2)—N(3) 1.347(7), N(3)—I 3.689, N(3)—I^{I} 3.637 Å. ∠ Mo—N(2)—N(3) 172.3(5)°. (C, M = W): W—N(2) 1.753(10), N(2)—N(3) 1.360(17), N(3)—I(1) 3.716, N(3)—I(2) 3.604 Å. ∠ W—N(2)—N(3) 174.7(9)°.

For both structures, cell dimensions and diffraction intensities were measured on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α radiation; one hydrazido hydrogen was located in a Fourier difference map, the position of the other was calculated, and both were included in the refinement.

Hydrogen bonds are shown as dashed lines.

occurs in complexes (C, M = W) which contain the quinolin-8-olate ligand [3]. They give hydrazine as the only nitrogen hydride product, whereas (C, M = Mo) gives only ammonia.

We have determined the X-ray structures of (C, M = Mo and W) (Fig. 1) to see if the M=N—NH_2 unit shows any marked structural difference for (C, M = W) compared to its analogues. These structures show that the coordination environment is the same for both Mo and W with oxygen *trans* to the N—NH_2 group. The bond lengths of the M=N—NH_2 system are, in both cases, not significantly different from those observed in related hydrazido(2–) complexes [4].

In each structure, there is strong hydrogen bonding from the NH_2 group to two anions. Slight differences in the hydrogen bonding schemes and the variations in the phosphine group orientation lead to different molecular packing arrangements in the crystals of C (M = Mo) and C (M = W), but these factors are unlikely to be significant in influencing the product of protonation reactions in solution*.

TABLE 1

REACTION OF HYDRAZIDO(2–) COMPLEXES WITH H_2SO_4/MeOH[a]

Complex	NH_3[b]	N_2H_4[b]	N_2[b,c]
$[WCl_2(NNH_2)(PMe_2Ph)_3]$	1.26(4)	0.12(4)	n.m.
$[WBr_2(NNH_2)(PMe_2Ph)_3]$	1.58(3)	0.05(2)	n.m.
$[WI_2(NNH_2)(PMe_2Ph)_3]$	1.88(2)	0.04(2)	n.m.
$[MoCl_2(NNH_2)(PMe_2Ph)_3]$	0.61(4)	0.0	0.44
$[MoBr_2(NNH_2)(PMe_2Ph)_3]$	0.98(6)	0.0	0.38
$[MoI_2(NNH_2)(PMe_2Ph)_3]$	0.99(7)	0.0	0.40
$[W(8\text{-quin})(NNH_2)(PMe_2Ph)_3]I$	0.0	0.39	0.45[c]
$[Mo(8\text{-quin})(NNH_2)(PMe_2Ph)_3]I$	0.55	0.0	0.17

[a] Approx. 0.1 mmol complex treated with approx. 2 mmol H_2SO_4 in 40 ml MeOH. NH_3 and N_2H_4 determined after distillation from an excess of KOH by colour tests, as in ref. 1. [b] Mol/atom metal. [c] Evolved at base distillation step.

The difference in reaction therefore appears to lie in the electronic state of the highly conjugated M=N—NH_2 system in its various ligand environments and possibly also the relative robustness of the tungsten as compared with the analogous molybdenum complexes. Further experiments are in progress to extend their range.

References

1 J. Chatt, A.J. Pearman and R.L. Richards, J. Chem. Soc. Dalton, (1977) 1852.
2 M. Hidai, Y. Mizobe, T. Takahashi and Y. Uchida, Chem. Lett., (1978) 1187.
3 J. Chatt, A.J. Pearman and R.L. Richards, J. Chem. Soc. Dalton, (1978) 1766.
4 J. Chatt, J.R. Dilworth and R.L. Richards, Chem. Rev., (1978) 589 and ref. therein.

---

*The bromide analogue of the molybdenum complex, whose X-ray crystal structure has also been determined, shows the NH_2 group very similarly hydrogen bonded to two anions; the extended hydrogen bonding scheme, however, differs markedly from that of the iodide complexes.