Stoicheiometric, Homogeneous Oxidation of Amines to Aldehydes or Ketones using Bis-π-cyclopentadienyl Molybdenum Derivatives: Ketimine Molybdenum Complexes

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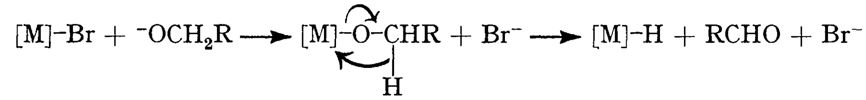
The reactions between the dimethyl sulphide complex $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF_6^-$ and some amines $RR'CHNH_2$ under a variety of conditions have been studied. Aqueous amines $RR'CHNH_2$, RR' = H_2, MeH, Me_2, HPr^n, or MeEt, which have a β-C–H system, undergo oxidation giving the hydridoamines $[(\pi\text{-}C_5H_5)_2Mo(NH_2CHRR')H]^+PF_6^-$ and the corresponding aldehydes or ketones RR'CO. Under anhydrous conditions the complexes $[(\pi\text{-}C_5H_5)_2Mo(NH_2CHRR')Br]^+PF_6^-$ or $[(\pi\text{-}C_5H_5)_2Mo(NH_2CHRR')_2]^{2+}[PF_6^-]_2$ may be formed. The diammine $[(\pi\text{-}C_5H_5)_2Mo(NH_3)_2]^{2+}[PF_6^-]_2$ has been prepared. The dimethyl sulphide complex in acetone reacts with ammonia giving the ketimine $[(\pi\text{-}C_5H_5)_2Mo(NH{=}CMeR)NH_3]^{2+}[PF_6^-]_2$, R = Me; the analogue where R = Et has also been prepared. The mechanism of the amine oxidation is discussed. Further new complexes are described which include $[(\pi\text{-}C_5H_5)_2W(NH_2Me)H]^+PF_6^-$, $[(\pi\text{-}C_5H_5)_2Mo(PMeH_2)H]^+PF_6^-$, and $[(\pi\text{-}C_5H_5)_2Mo(PMeH_2)Br]^+PF_6^-$.

It is well established that certain transition metal halide complexes react with alcohols in base causing formation of the corresponding metal hydride and oxidation of the alcohol to an aldehyde or ketone,[1] *e.g.*



$$[M]\text{-Br} + {}^-OCH_2R \longrightarrow [M]\text{-}O\text{-}\underset{H}{CHR} + Br^- \longrightarrow [M]\text{-}H + RCHO + Br^-$$

The analogous reaction using amines instead of alcohols has not been described. During our study of electron-rich molybdenum and tungsten systems based on the bis-(π-cyclopentadienyl)metal derivatives we have found that amines undergo similar oxidation reactions under mild conditions forming the corresponding aldehyde or ketone and a metal hydride. This work is described below and a preliminary communication has been presented.[2]

Chemical Studies.—Treatment of the previously described cation $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF_6^-$ (I)[3] with some aqueous solutions of primary amines $RR'CHNH_2$, where RR' = H_2, MeH,Me_2,HPr^n, or MeEt at 60° for 6 h gives orange compounds in good yields which the data given in the Table and the experimental section show to be the hydridoamine derivatives $[(\pi\text{-}C_5H_5)_2Mo(NH_2CHRR')H]^+PF_6^-$ (II). The tungsten analogue $[(\pi\text{-}C_5H_5)_2W(NH_2Me)H]^+PF_6^-$ (III) is similarly prepared but the reaction proceeds more slowly. The complexes (II) and (III) are only slowly oxidised by air, even in solution, and they are soluble in the more polar solvents such as acetone and dimethyl sulphoxide, as would be expected. Several of the complexes (II) have been shown to react readily with bromoform giving the bromo derivatives $[(\pi\text{-}C_5H_5)_2Mo(NH_2CHRR')Br]^+PF_6^-$ (IV) where RR' = H_2,MeH,Me_2, Pr^iH, or MeEt. These green compounds appear to be stable in air indefinitely. Preliminary studies on amine displacement reactions of the complexes (II) show that the amine group may be readily displaced by carbon monoxide or triphenylphosphine giving the previously described[3,4] hydrido cations $[(\pi\text{-}C_5H_5)_2Mo(L)H]^+PF_6^-$ (V; L = CO or PPh_3). This reaction provides a convenient route to the hydridocarbonyl (V; L = CO). Analogous displacement by ethylene was not observed under mild conditions (1 atmos).

Examination of aqueous mother liquors remaining after formation of the hydridoamines (II) showed them to contain the aldehydes or ketones corresponding to the initial amine, namely RR'CO. The aldehydes or ketones were identified following their isolation as the phenylhydrazone derivatives and comparison of the mass spectra with those of authentic samples.

Therefore, the overall reaction between the complex (I) and primary amines may be written as:

$$[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF_6^- + 2RR'CHNH_2 + H_2O \longrightarrow [(\pi\text{-}C_5H_5)_2Mo(NH_2CHRR')H]^+PF_6^- + RR'C{=}O + NH_4^+ + Me_2S + Br^- \quad (1)$$

It seemed reasonable that the initial step in the reaction (1) would be displacement of the dimethyl sulphide ligand giving the already mentioned bromoamine $[(\pi\text{-}C_5H_5)_2Mo(NH_2CHRR')Br]^+PF_6^-$ (IV).

Accordingly, the reaction between the complex (I) and anhydrous amines was studied. With anhydrous methylamine in dry acetone the complex (I) yields the complex (IV; RR' = H_2) in good yield. However, if a trace of water is present then the exclusive product of the reaction was the salt $[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)_2]^{2+}[PF_6^-]_2$ (VI). It was also found that treatment of the complex (I) with aqueous methylamine at room temperature for 6 h does not give the hydridoamine, which is formed at 60°, and the salt (VI) is isolated. Treatment of the complex (I) with anhydrous methylamine in dry tetrahydrofuran gives a mixture of the complexes (IV) and (VI; RR' = H_2). In similar studies the

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[1] M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 115.

[2] F. W. S. Benfield and M. L. H. Green, *Chem. Comm.*, 1971, 1274.

[3] R. H. Crabtree, A. R. Dias, M. L. H. Green, and P. J. Knowles, *J. Chem. Soc.* (*A*), 1971, 1350.

[4] F. W. S. Benfield, B. R. Francis, and M. L. H. Green, *J. Organometallic Chem.*, 1972, **44**, C13.

anhydrous amines $RR'CHNH_2$, $RR' = EtH$ or Pr^nH, were reacted with the complex (I) giving the corresponding salts $[(\pi\text{-}C_5H_5)_2Mo(NH_2CHRR')_2]^{2+}[PF_6^-]_2$ (VI; $RR' = EtH$ or Pr^nH). It may be noted that none of the reactions which were carried out under effectively anhydrous condition yielded the hydridoamines (II).

The products of incomplete reaction between the complex (I) and aqueous methylamine were investigated and, following separation of the partially formed hydridomethylamine (II; $RR' = H_2$), the red mother liquor was slowly concentrated under reduced pressure, yielding red crystals. The data in the Table and, especially, a crystal structure determination [5] showed the compound to be the hydroxoamine $[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)OH]^+PF_6^-$ (VII). This compound reacts rapidly with an excess of aqueous methylamine giving the hydridomethylamine (II; $RR' = H_2$). It may also be noted that the oxo-compound $(\pi\text{-}C_5H_5)_2MoO$ with aqueous methylamine also gives the hydridomethylamine (II) in good yield.

Analytical and i.r. data

	Compound	Colour	Analytical data (%)			Selected i.r. data [a]
			C	H	N	
1	$[(\pi\text{-}C_5H_5)_2W(NH_2Me)H]^+PF_6^-$	Deep orange	26·0 (26·7)	3·2 (3·6)	2·1 (2·8)	3340m,[b] 3320m,[b] 3115m,[c] 1940w,[d] 1610s [e]
2	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)H]^+PF_6^-$	Orange	32·7 (32·8)	4·1 (4·0)	3·4 (3·5)	3350m,[a,b] 3320m,[a,b], 3120w,[a,c] 1890w,[a,d,f] 1610s [a,e,g]
3	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Et)H]^+PF_6^-$	Orange	34·3 (34·5)	4·4 (4·4)	3·6 (3·4)	3335s,[a,b] 3300m,[a,b], 3120m,[a,c] 1830m,[a,d] 1603s [a,e,h]
4	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Pr^i)H]^+PF_6^-$	Orange	36·0 (36·2)	4·8 (4·7)	3·0 (3·3)	3330m,[a,b] 3290m,[a,b], 3130m,[a,c] 1830m,[a,d] 1592s [a,e,i]
5	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Bu^n)H]^+PF_6^-$	Orange	37·7 (37·8)	5·2 (5·0)	3·4 (3·2)	3340m,[b] 3300m,[b] 3120m,[c] 1850m,[d] 1600s [e]
6	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Bu^s)H]^+PF_6^-$	Orange	37·6 (37·8)	4·9 (5·0)	3·0 (3·2)	3320ms,[b] 3280ms,[b] 3120w,[c] 1830m,[d] 1580s [e]
7	$[(\pi\text{-}C_5H_5)_2Mo(NH_2C_6H_{11})H]^+PF_6^-$	Orange	40·6 (40·7)	5·0 (5·1)	2·9 (3·0)	3330ms,[b] 3300ms,[b] 3140w,[c] 1840m,[d] 1600s [e]
8	$[(\pi\text{-}C_5H_5)_2Mo(NHC_5H_{10})H]^+PF_6^-$	Orange	39·4 (39·4)	4·9 (4·8)	2·9 (3·1)	3290s,[b] 3140s,[b] 1850s,[c] 1650br [e]
9	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)Br]^+PF_6^-$	Green	27·7 (27·4)	3·0 (3·1)	2·8 (2·9)	3220m,[b] 3240,[b] 3140m,[c] 1600m [b]
10	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Et)Br]^+PF_6^-$	Green	29·1 (29·0)	3·5 (3·5)	2·6 (2·8)	3300s,[b] 3230s,[b] 3155s,[c] 1590s [b]
11	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Pr^i)Br]^+PF_6^-$	Green	30·5 (30·6)	3·8 (3·7)	2·8 (2·7)	3300m,[b] 3210m,[b] 3140m,[c] 1585m [e]
12	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Bu^n)Br]^+PF_6^-$	Green	32·0 (32·2)	4·2 (4·0)	2·5 (2·6)	3280s,[b] 3140s,[b] 3120s,[c] 1590s [e]
13	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Ph)Br]^+PF_6^-$	Green	35·3 (35·4)	3·3 (3·3)	2·5 (2·4)	3295w,[b] 3225w,[b] 3130w,[c] 1700w, 1600s [e]
14	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)OH]^+PF_6^-$	Red	31·4 (31·5)	3·7 (3·9)	3·6 (3·4)	3620s [j or b] 3330,[b or j] 3220w,[b] 3130s,[b] 3090s,[c] 1615s,[k or e] 1585sh [e or k]
15	$[(\pi\text{-}C_5H_5)_2Mo(NH{=}CMe_2)NH_3]^{2+}[PF_6^-]_2$	Deep red	26·6 (26·5)	3·6 (3·5)	4·8 (5·0) [l]	3370s,[a,b] 3310s,[a,b], 3240w,[a,b], 3140m,[c] 1640s,[a,e and m,n] 1340s [o,p]
16	$[(\pi\text{-}C_5H_5)_2Mo(NH{=}CMeEt)NH_3]^{2+}[PF_6^-]_2$	Deep red	27·5 (27·8)	3·4 (3·7)	4·5 (4·7)	3370s,[b] 3300s,[b] 3240s,[b] 3140m,[c] 1640s,[e and m] 1340s [o]
17	$[(\pi\text{-}C_5H_5)_2Mo(NH_3)_2]^{2+}[PF_6^-]_2$	Red-purple	21·6 (21·8)	2·8 (2·9)	4·9 (5·1)	3380m,[a,b] 3320s,[a,b] 3230sh,[a,b] 3150m,[c], 1635m,[d,e], 1325,[a,o] 1305 [a,o,q]
18	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)_2]^{2+}[PF_6^-]_2$	Red-brown	24·7 (24·9)	3·7 (3·5)	4·8 (4·8)	3650m,[b] 3580m,[b] 3320m,[b] 3260w,[b] 3220w,[b] 3170w [b]
19	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Et)_2]^{2+}[PF_6^-][Br]$	Buff	31·5 (31·2)	4·8 (4·5)	5·3 (5·2)	3640s,[b] 3570m,[b] 3305s,[b] 3260w,[b] 3205m,[b] 3160m,[b] 3130s,[c] 1630s
20	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Bu^n)_2]^{2+}[PF_6^-]_2$	Light brown	33·4 (32·8)	5·2 (4·9)	4·0 (4·4)	3315s,[b] 3290s,[b] 3220w,[b] 3120m,[c] 1620m [e]
21	$[(\pi\text{-}C_5H_5)_2Mo(NH_2CH_2Ph)_2]^{2+}[PF_6^-]_2$	Light brown	39·3 (39·5)	4·0 (3·9)	4·1 (3·8)	3310m[b] 3280m,[b] 3120m,[c] 1615s [c]
22	$[(\pi\text{-}C_5H_5)_2Mo(PMe_2Ph)_2]^{2+}[PF_6^-]_2$	Lemon-yellow	39·3 (39·4)	4·1 (4·1)		3150m [c]
23	$[(\pi\text{-}C_5H_5)_2Mo(PMeH_2)H]^+PF_6^-$	Orange-yellow	32·0 (31·4)	4·0 (3·8)		3130m,[c] 1330w,[r] 1850w [d]
24	$[(\pi\text{-}C_5H_5)_2Mo(PMeH_2)Br]^+PF_6^-$	Purple	26·2 (26·4)	3·1 (3·0)		3140m,[c] 2390w [r]

[a] Bands which are absent or much reduced in intensity in samples which have been recrystallised from $[^2H_6]Me_2CO\text{–}D_2O$ mixture. [b] N–H Str., or N–D str. [c] C–H Str. of $\pi\text{-}C_5H_5$. [d] Mo–H Str., or Mo–D Str. [e] N–H Def., or N–D def. [f] Mo–D Str. not detected and presumed to be obscured. [g] New bands in the deuterium exchanged sample occur at 2500,[b] 2450,[b] 1200.[e] [h] New bands in the deuterium exchanged sample occur at 2480,[b] 2430,[b] 1315,[d] 1190.[e] [i] New bands in the deuterium exchanged sample occur at 2483,[b] 2421,[b] 1315,[d] 1180.[e] [j] O–H Str. [k] O–H Def. [l] Analyses: Mo, 16·2 (16·0); P, 10·6 (10·5); F, 38·6 (38·5) %. [m] C≡N Str. [n] This band becomes narrower in the deuterium exchanged sample which supports the assignment, [e] and [n]. [o] NH_3 Sym. def. (or ND_3). [p] New bands in the deuterium exchanged sample occur at 2505,[b] 2405,[b] 2360.[b] [q] New bands in the deuterium exchanged sample occur at 2520,[b] 2460,[b] 2300,[b] 1200,[e] 1025,[o] 1010 [o] [r] P–H Str.

The reduction of metal halides to metal hydrides using alcohol and base is thought to proceed *via* a β-elimination step. Assuming the analogy between the alcohol and amine oxidations then the hydridoamine ought not to be formed when the amine has no β-hydrogen. In support of this argument it has been shown that treatment of the complex (I) with aniline or with anhydrous ammonia in methyl phenyl ketone gives the salts $[(\pi\text{-}C_5H_5)_2MoL_2]^{2+}[PF_6^-]_2$, (VIII; $L = PhNH_2$ or NH_3 respectively). However, the presence of a β-hydrogen does not necessarily give rise to hydridoamines since the compound (I) with aqueous benzylamine or aqueous cyclohexylamine gives the salts (VIII; $L = PhCH_2NH_2$ or $C_6H_{11}NH_2$).

Further support for a β-elimination reaction arose

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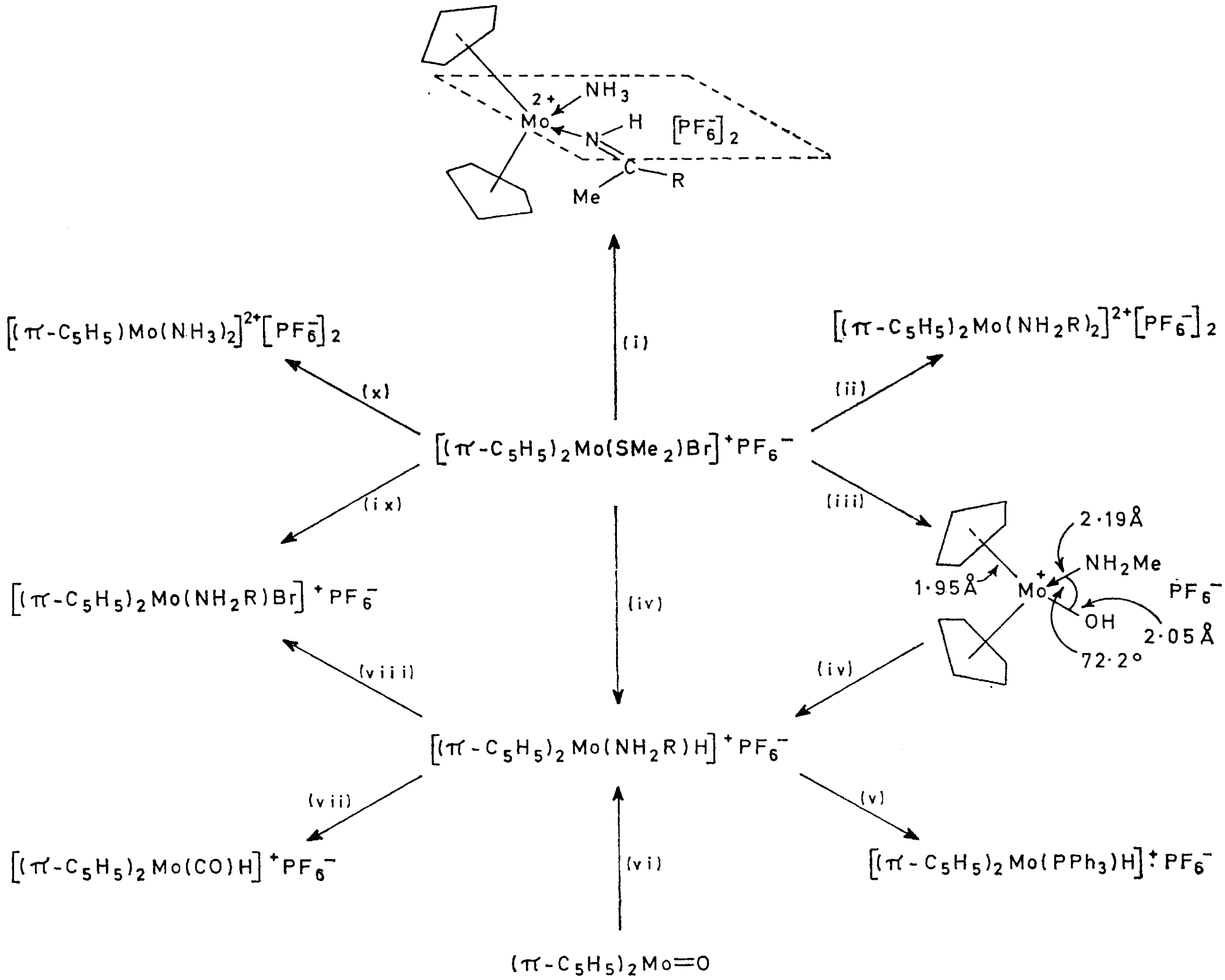
[5] C. K. Prout and S. Cameron, *Acta Cryst.*, submitted for publication.

accidentally during an attempt to prepare the bis-ammine $[(\pi\text{-}C_5H_5)_2Mo(NH_3)_2]^{2+}[PF_6^-]_2$ (IX) by treatment of the complex (I) in acetone with ammonia gas. Deep red crystals separated from the reaction mixture which the data in the Table and the ^1H n.m.r. spectrum in the Experimental section show to be the ketimine $[(\pi\text{-}C_5H_5)_2Mo(NH{=}CMeR)NH_3]^{2+}[PF_6^-]_2$ (X; R = Me). Rather surprisingly, this complex may be recrystallised from boiling water and no marked hydrolysis of the ketimine ligand occurs. The ethyl analogue of (X) was prepared using methyl ethyl ketone instead of acetone.



SCHEME 1 (i) NH_3 gas, RCOMe; (ii) RNH_2 anhydrous; (iii) $MeNH_2$ aqueous 1 h; (iv) $MeNH_2$ in water, 6 h; (v) PPh_3; (vi) $MeNH_2$ in water, reflux; (vii) CO, 1 atmos.; (viii) $CHBr_3$; (ix) $MeNH_2$ in dry acetone; (x) NH_3 in MeCOPh

The ^1H n.m.r. spectrum of the complex (X; R = Me) shows that although the $\pi\text{-}C_5H_5$ groups give only a single band the two Me groups of the ketimine ligand are not equivalent. This may be understood in terms of a planar MoN_2C_3 system as represented in Scheme 1, where the ketimine is *N*-bonded to the metal. If the ketimine ligand in complex (IX; R = Et) was π-bonded to the metal, in the manner of π-propene, then at least two $\pi\text{-}C_5H_5$ resonances would again be expected. In fact, the $\pi\text{-}C_5H_5$ bands occur as a single resonance which is more consistent with there being present one isomer, with a structure of the type shown in Scheme 1.*

Since internal oxidative addition of C–H groups in transition metal–PCH_3 systems has been demonstrated we treated the complex (I) with methylphosphine to see whether a reaction analogous to that of methylamine occurred. This, however, was not the case and the sole isolated product from (I) and $MePH_2$ was the bromo derivative $[(\pi\text{-}C_5H_5)_2Mo(PMeH_2)Br]^+PF_6^-$ (XI). In order to ascertain whether the hydrido complex $[(\pi\text{-}C_5H_5)_2Mo(PMeH_2)H]^+PF_6^-$ (XII) would be isolable the complex (XI) was treated with sodium borohydride. The resulting air-sensitive yellow product was shown by the data to be the expected hydridomethylphosphine (XI).

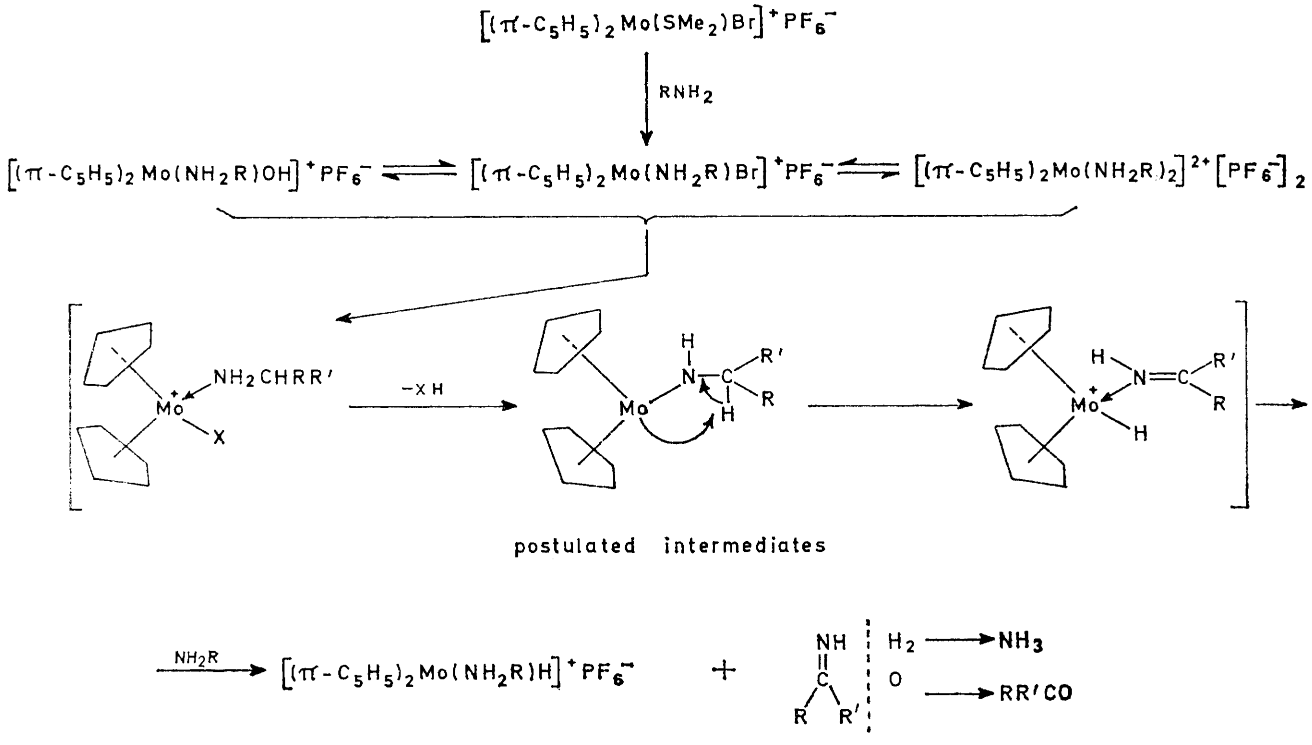
* *Note added in proof:* This structure has been confirmed by *X*-ray diffraction studies (C. K. Prout, personal communication).

DISCUSSION

In the light of the above observations and bearing in mind the mechanism of formation of transition metal hydrides from alcohols,[1] the mechanism in Scheme 2 for the amine oxidation reaction may be put forward. In particular, the isolation of the ketimines (X) supports a general mechanism along these lines shown in Scheme 2.

EXPERIMENTAL

All preparations and manipulations were carried out in the absence of oxygen. Light petroleum had b.p. 30—40°. I.r. spectra were determined using a Perkin-Elmer 457 instrument in mulls and calibrated with polystyrene film. ^1H N.m.r. spectra were determined at 60 MHz in a Japan Electron Optics Laboratory instrument or at 100 MHz on a Perkin-Elmer instrument. The compound $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF_6^-$ was prepared as previously described.[3]



SCHEME 2

Preparations of the Hydridoamines $[(\pi\text{-}C_5H_5)_2Mo(NHCHRR')H]^+PF_6^-$.—A typical reaction is described. The compound $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF_6^-$ (1 g, 2·0 mmol) was stirred with an excess of aqueous methylamine (30%, 10 ml, 100 mmol) at 60° for 6 h. The initially green solution turned orange. After cooling to room temperature the solution was concentrated under reduced pressure giving orange crystals, which were separated and washed with water (3 × 2 ml). The washings were combined with the mother liquor and the mixture further investigated as described below. The crystals were dried *in vacuo*, then extracted with acetone (15 ml), and the solution was filtered. Saturated aqueous ammonium hexafluorophosphate (1 ml) and water (3 ml) were added to the clear orange filtrate. Slow concentration of the solution under reduced pressure gave orange crystals which were separated, washed with water (3 × 2 ml) and dried *in vacuo* giving the hydridoamine $[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)H]^+PF_6^-$. Recrystallisation was from acetone–ether. Essentially similar reactions were found using the amines $RR'CHNH_2$ where RR' = MeH, Pr^nH, Me_2, or MeEt. The combined liquors, obtained as described above, were acidified with sulphuric acid to pH 2—4. The solution was distilled and the distillate was collected in a cooled solution of Brady's reagent giving yellow-orange precipitates. These were collected and washed with ethanol and then recrystallised from hot ethanol and dried. The 2,4-dinitrophenylhydrazone derivatives were identified by comparison of the mass spectra with those of separately prepared authentic samples. The amines $RR'CHNH_2$ listed above gave the corresponding alkehyde or ketone MeCHO, Pr^nCHO, Me_2CO, or MeEtCO respectively.

Bromomethylaminobis(π-cyclopentadienyl)molybdenum Hexafluorophosphate.—The hydride $[(\pi\text{-}C_5H_5)_2Mo(MeNH_2)H]^+PF_6^-$ (0·5 g) in acetone (25 ml) was treated with bromoform (0·5 ml) at room temperature for 20 min. The initially orange solution turned green. The solvent was removed *in vacuo* and the green residue was extracted with acetone (25 ml) the solution was filtered and an excess of aqueous ammonium hexafluorophosphate was added. The solvent was removed slowly under reduced pressure giving dark green crystals which were collected, washed with water (3 × 2 ml), and dried *in vacuo*. Finally, they were recrystallised from acetone–ethanol or acetone–ether, and dried giving the pure product, yield *ca.* 90%.

The corresponding bromo derivatives $[(\pi\text{-}C_5H_5)_2Mo(NH_2R)Br]^+PF_6^-$, R = Et, Pr^i, or Bu^n were similarly prepared in *ca.* 90% yield.

Hydroxomethylaminebis(π-cyclopentadienyl)molybdenum Hexafluorophosphate.—The compound $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF_6^-$ (3 g) was treated with an excess of aqueous methylamine at 60° for 1 h. The resulting deep red solution was cooled giving orange crystals of the hydridomethylamine $[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)H]^+PF_6^-$ which were separated by filtration. The deep red filtrate was concentrated under vacuum giving deep red crystals. These were collected, washed with a little cold water, and dried *in vacuo* giving the pure hydroxo-compound.

Reaction of $[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)OH]^+PF_6^-$ *with Aqueous Methylamine.*—The complex $[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)OH]^+PF_6^-$ (0·25 g) in aqueous methylamine was warmed at 60° for 4 h. An orange solution formed and this was cooled to room temperature and solvent was slowly removed under reduced pressure. Orange crystals separated and they were recrystallised from acetone–water. After being washed with water and dried *in vacuo* they were identified by their i.r. spectrum as the hydridomethylamine $[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)H]^+PF_6^-$, *ca.* 60% yield.

Reactions between the Compound $(\pi\text{-}C_5H_5)_2MoO$ *and Aqueous Methylamine.*—The compound $(\pi\text{-}C_5H_5)_2MoO$ (0·23 g) in tetrahydrofuran (5 ml) was treated with aqueous methylamine (10 ml, 30%). The mixture was heated gradually to 90° and maintained at that temperature for 6 h. The orange-red reaction mixture was cooled to room temperature and then concentrated under reduced pressure. Orange crystals separated which were collected, washed with water, recrystallised from acetone–water and dried *in vacuo*. The i.r. spectrum showed the product to be the hydridomethylamine $[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)H]^+PF_6^-$, yield *ca.* 60%.

Reactions of Hydridomethylaminobis(π-cyclopentadienyl)molybdenum Hexafluorophosphate.—(a) *With carbon monoxide.* The hydride $[(\pi\text{-}C_5H_5)_2Mo(MeNH_2)H]^+PF_6^-$ (0·5 g) in acetone (25 ml) at 50° was treated with carbon monoxide for 20 min. The initial orange solution became yellow. After 30 min the solution was cooled to room temperature and solvent was removed under reduced pressure giving a brown-yellow residue. This was extracted with acetone (25 ml) and filtered. Water (5 ml) was added to the yellow filtrate and the solution was concentrated under reduced pressure giving yellow crystals. These were washed with water and dried *in vacuo* giving the pure carbonyl derivatives $[(\pi\text{-}C_5H_5)_2Mo(CO)H]^+PF_6^-$, yield, *ca.* 60%.

(b) *With triphenylphosphine.* The hydride $[(\pi\text{-}C_5H_5)_2Mo(MeNH_2)H]^+PF_6^-$ (0·1 g) in refluxing acetone (5 ml) was treated with triphenylphosphine (0·2 g) for 12 h. The initially orange solution turned yellow. The solvent was removed from the cooled reaction mixture under reduced pressure giving a yellow-orange oil. This was washed with benzene (3 × 2 ml) and the resulting yellow solid was dried *in vacuo* and recrystallised from acetone–toluene. The yellow crystals were washed with toluene and dried *in vacuo* giving the pure product $[(\pi\text{-}C_5H_5)_2Mo(PPh_3)H]^+PF_6^-$. This was identified by comparison of the i.r. spectrum with that of a fully characterised sample, yield *ca.* 60%.

Bismethylaminobis(π-cyclopentadienyl)molybdenum Bishexafluorophosphate.—(a) The compound $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF_6^-$ (1 g, 2·0 mmol) and aqueous methylamine (30%, 10 ml, 100 mmol) were stirred for 6 h. The initially green solution became brown-red. Saturated aqueous ammonium hexafluorophosphate (3 ml) was added and the solution was concentrated under reduced pressure giving red-brown crystals. These were collected, washed with water (3 × 2 ml), and recrystallised from acetone–water by slow removal of solvent under reduced pressure or from hot water, giving the pure *compound*, yield *ca.* 60%.

(b) The compound $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF_6^-$ (0·5 g; 1·0 mmol) in dry tetrahydrofuran (5 ml) at 70° was treated with dry methylamine gas for 15 min and a buff solid separated. The solvent was removed under reduced pressure and the residue was extracted with acetone and filtered giving a green filtrate and a yellow-brown residue. The solvent was removed under reduced pressure and the residue was recrystallised from acetone–water and dried *in vacuo* as the pure product $[(\pi\text{-}C_5H_5)_2Mo(MeNH_2)Br]^+PF_6^-$. The yellow-brown residue was recrystallised from hot water giving orange crystals which were dried *in vacuo* and identified from the i.r. spectrum as the compound $[(\pi\text{-}C_5H_5)_2Mo(MeNH_2)_2]^{2+}PF_6^-Br^-$.

Bisamminebis(π-cyclopentadienyl)molybdenum Bishexafluorophosphate.—The compound $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF_6^-$ (0·5 g) in methyl phenyl ketone (25 ml) at 55° was treated with anhydrous ammonia gas for 2 h. The mixture became red and a red solid separated. After cooling to room temperature the solid was separated, washed with diethyl ether (4 × 5 ml), and dried *in vacuo*. Extraction with water (20 ml) followed by addition of an excess of aqueous ammonium hexafluorophosphate gave a garnet precipitate. This was collected, washed with water, and dried *in vacuo*. The product was recrystallised from acetone–water giving red-purple crystals of the pure compound, *ca.* 35% yield.

Amminedimethylketiminebis(π-cyclopentadienyl)molybdenum Bishexafluorophosphate.—The compound $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF_6^-$ (1 g) in acetone (40 ml) was treated with ammonia gas. Bright red crystals precipitated from the initially green solution and after 40 min the reaction appeared complete. The crystals were separated from the pink mother liquor, washed with acetone (3 × 5 ml), and dried *in vacuo*. They were then dissolved in water (10 ml), the solution was filtered, and aqueous ammonium hexafluorophosphate was added to the filtrate. Rose pink crystals separated which were collected, washed with water, and finally recrystallised from boiling water giving deep red crystals which were washed and dried *in vacuo* giving the pure compound, yield, *ca.* 65%.

The analogue $[(\pi\text{-}C_5H_5)_2Mo(NH{=}CMeEt)NH_3]^{2+}[PF_6^-]_2$ was similarly prepared using methyl ethyl ketone instead of acetone, yield, *ca.* 60%.

Bromo(methylphosphine)bis(π-cyclopentadienyl)molybdenum Hexafluorophosphate.—The compound $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF_6^-$ (1·0 g, 1·8 mmol) in acetone (50 ml) was cooled (−196°) and methylphosphine (3·5 mmol) was distilled into the reaction vessel. The mixture was slowly warmed to room temperature and refluxed (6 h) using a low-temperature condenser (−78°). The solvent was removed from the resulting purple solution under reduced pressure giving a red residue which was extracted with acetone. After filtration, aqueous ammonium hexafluorophosphate was added to the filtrate. The solution was slowly concentrated under reduced pressure giving purple crystals which were collected, washed with water, and dried *in vacuo*. Recrystallisation was from acetone–ethanol giving the pure product, yield *ca.* 82%.

Hydrido(methylphosphine)bis(π-cyclopentadienyl)molybdenum Hexafluorophosphate.—The bromo-derivative $[(\pi\text{-}C_5H_5)_2Mo(PMeH_2)Br]^+PF_6^-$ (0·8 g, 1·6 mmol) in acetone (30 ml) was treated with sodium borohydride (3 mmol) and water (0·1 ml) with stirring. The initially purple solution turned yellow after 15 min and after a further 15 min the solvent was removed under reduced pressure giving a yellow residue. This was washed with water (3 × 10 ml), dried *in vacuo*, and extracted with acetone. The extract was filtered and the orange filtrate was treated with aqueous ammonium hexafluorophosphate. The solution was concentrated under reduced pressure giving orange-yellow crystals which were separated, washed with water, and dried *in vacuo*. Recrystallisation was from acetone–ethanol at −78° and the resulting orange crystals were washed with a little ethanol and dried *in vacuo* giving the pure product, yield *ca.* 60%.

^{1}*H N.M.R. Data.*—Data are given as follows: compound number (see the Table); chemical shift (τ); *rel. intensity*; **multiplicity** [*J*/Hz]; assignment, *etc.*

1 4·50;[a] 6·40, *2*, **s** (br), NH_2; 7·50, *3*, **t**, [(*J*(NH_2,Me) 6·0] Me; 17·0, *1*, **s**, W–H [b]

2 4·25;[a] 6·10, *2*, **s** (br), NH_2; 7·50, *3*, **t** [*J*(H,Me) 6·7] Me; 18·9, *1*, **s**, Mo–H [c]

3 4·31;[a] 6·15, *2*, **s** (br), NH_2; 8·60, *5*, **c**, Et; 19·0, *1*, **s**, Mo–H [c]

4 4·65;[a] 6·8, *2*, **s** (br), NH_2; 7·60, *1*, **c**, CH; 8·9, *6*, **d** [*J*(MeH) 6·6] Me_2; 19·00, *1*, **s**, Mo–H [b]

5 4·67;[a] 7·0, *2*, **s** (br), NH_2; 7·5—8·9, *9*, **c**, Bu^n; 18·0, *1*, **s**, Mo–H [b]

6 4·72;[a] 6·20, *2*, **s** (br) NH_2; *9*, **c**, Bu^s; 18·0, *1*, **s**, Mo–H [b]

7 4·68;[a] 6·8, *3*, **s** (br), NH_2, CH; 8·70, *10*, **c**, $(CH_2)_5$; 19·10, *1*, **s**, Mo–H [b]

8 4·50;[a] 6·8, *1*, **s** (br), NH; 7·20, *4*, **c**, $N(CH_2)_2$; 8·70, *6*, **c**, $(CH_2)_3$, 19·10, *1*, **s**, Mo–H [b]

9 4·10;[a] 6·40, *2*, **s**, NH_2; 7·60, *3*, **t** [*J*(H,Me) 7·5] Me [b]

10 3·65;[a] 5·75, *2*, **s**, NH_2; 7·40, *2*, **c**, CH_2; 8·50, *3*, **t** [*J*(Me,CH_2) 7·5] Me [c]

11 3·90;[a] 6·50, *2*, **s**, NH_2; 7·10, *1*, **c**, CH; 8·90, *6*, **d** [*J*(H,Me) 10·0] Me [c]

12 3·65;[a] 5·75, *2*, **s**, NH_2; 7·40—8·20; *9*, **c**, Bu^n [c]

13 2·60;[a] *3*, **c**, *m*-H_2, *p*-H_2; 4·10—4·12, *12*, two lines; $(\pi\text{-}C_5H_5)_2$ *o*-H_2 [b]

15 3·72;[a] 6·2, *3—4*, **s**; NH_3 (NH?); 7·35, *3*, **s**, *cis*- or *trans*- Me; 7·78, *3*, **s**, *trans*- or *cis*- Me [c,d]

16 4·00;[a] 6·80, *4* **s** (br), NH_3 and NH; 7·50, *2*, **q** [*J*(Me,CH_2) 8·0] CH_2; 8·00, *3*, **s**, Me; 9·00, *3*, **t**, [*J*(Me,CH_2) 8·0] C–Me [b,c]

17 3·55;[a] 6·30, *6*, **s** (br), $(NH_3)_2$ [c]

18 3·55;[a] 5·77, *4*, **s** (br), NH_2; 7·87, *6*, **t** [*J*(NH_2,Me) 4·5] Me_2 [c]

19 3·90;[a] 6·0, *4*, **s** (br), NH_2; 8·1—8·9, *10*, **c**, Et_2 [c]

20 3·78;[a] 6·40, *4*, **s** (br), NH_2; 8·50, *18*, **c**, $Bu^n{}_2$ [c]

21 2·60, *10*, **c**, Ph_2; 3·60;[a] 6·10, *8*, **s** (br), $(NH_2CH_2)_2$ [b,c]

22 2·00, *10*, **c**, Ph_2; 3·80, *10*, **t** [*J*(^{31}P, $\pi\text{-}C_5H_5$) 3·7] $(\pi\text{-}C_5H_5)_2$; 7·70, *12*, **c**, Me_4 [c]

23 4·45, *10*, four lines [*J*(^{31}P,H) 4]; [*J*(H,H) 2] $(\pi\text{-}C_5H_5)_2$; 8·00, *5*, **c**, PH_2Me; 18·8, *1*; **d** [*J*(^{31}P,H) 30·0] Mo–H [c]

24 4·25, *10*, **d** [*J*(^{31}P,$\pi\text{-}C_5H_5$) 3·0] $(\pi\text{-}C_5H_5)_2$; 8·00, *5*, **c**, PH_2Me [c]

[a] As 10, **s**, $(\pi\text{-}C_5H_5)_2$. [b] In [$^2H_6$]acetone. [c] In [$^2H_6$]dimethyl sulphoxide. [d] The non-equivalence of the methyl groups arises from the planar structure (see the text).

We wish to thank the Imperial Chemical Industries for a Fellowship (to F. W. S. B.) and the Petroleum Research Fund administered by the American Chemical Society for partial support.

[3/2260 *Received, 2nd November*, 1973]