Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

A convenient route to lower oxidation state complexes of molybdenum

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(Received December 11th, 1970)

We wish to report a very convenient route to complex compounds of molybdenum in oxidation states lower than four, and free from oxo- or carbonyl-ligands. In particular, the method leads to the preparation of *trans*-$[Mo(N_2)_2(diphos)_2]$[1] (diphos = $Ph_2PCH_2-CH_2PPh_2$) in 80% yield, and to a number of novel organophosphine complexes of molybdenum.

The preparations start from $[MoCl_3(THF)_3]$. This can be obtained by the zinc reduction of $MoCl_5$ in a dichloromethane and tetrahydrofuran (THF) mixture at 0°, but this preparation is unreliable owing to the presence of oxo-molybdenum species in commercial $MoCl_5$. It is better to use $[MoCl_4(EtCN)_2]$ which precipitates when $MoCl_5$ reacts with ethyl cyanide[2], leaving the oxo-complexes in solution. This reacts with THF precipitating crystalline $[MoCl_4(THF)_2]$, which, after washing free from ethyl cyanide, is reduced with granulated zinc in an equivolume mixture of dichloromethane and THF at 0° The brown solution is filtered from the zinc, reduced in volume, and $[MoCl_3(THF)_3]$ caused to crystallise by addition of THF.

The direct reaction of tertiary phosphines with $[MoCl_3(THF)_3]$ in THF yields complexes of the type $[MoCl_3(PR_3)_x(THF)_{3-x}]$ according to the size of the phosphine. For example, for PMe_2Ph, $x = 3$, and for PEt_2Ph, $x = 1$.

The reduction of $[MoCl_3(THF)_3]$ by sodium amalgam or metallic magnesium in the presence of an excess of the appropriate organophosphine in THF has provided a number of novel mononuclear molybdenum complexes according to the phosphine used. Thus PH_2Ph yields $[Mo(PH_2Ph)_6]$ under argon or dinitrogen, but PMe_2Ph yields $[Mo(PMe_2Ph)_4]$ under argon and a solution which appears to contain *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ under dinitrogen. The dinitrogen complex in the reaction solution shows strong IR bands at 1951 and 2014 cm^{-1}, closely similar to the bands in the spectrum of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$[3], but we have not yet been able to isolate a pure dinitrogen complex. Nevertheless, the same reaction with diphos yields the known *trans*-$[Mo(N_2)_2(diphos)_2]$ in 80% yield, a great improvement over the known method[1], and analogously *trans*-$[Mo(N_2)_2(Ph_2PCH{=}CHPPH_2)_2]$ is obtained in good yield from the *cis*-olefinic diphosphine. Under argon, diphos yields $[MoCl_2(diphos)_2]$. The above substances have all been characterised by analysis, magnetic moments, NMR and IR spectra. They appear to have the structures implied by the above formulations except

[Mo(PMe_2Ph)$_4$], which is monomeric and diamagnetic. It may have a formula differing by a few hydrogen atoms from that given. It is obtained in low yield and is still under investigation, as is the application of this route to the preparation of other low oxidation state complexes of molybdenum.

ACKNOWLEDGEMENT

We thank the S.R.C. for financial support and the award of a postdoctoral fellowship (to A.G.W.).

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