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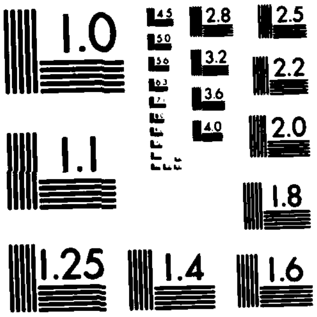

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Molecular Polyhydrides of the type MH_xL_y ($L = PR_3$) are examined in connection with the problem of hydrogen storage. Several preparative routes and hydrogen release reactions are studied.

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Final Report

We set out to discover whether polyhydride complexes of the type MH_xL_y could be used for hydrogen storage, an approach that has not been tried to date. If this were possible, the complex could be supported on a polymer resin to give a material with a very high storable H/weight ratio.

Advances in the area

During the current grant period we have been able to study several aspects of the problem: 1) improved syntheses of metal polyhydrides; 2) the preparative and mechanistic details of the uptake and release of H_2 by these complexes; 3) unexpected deactivation reactions which can take place; and 4) weakly binding ligands capable of competitively displacing H_2 from polyhydrides.

Improved syntheses of polyhydrides

The review[1] by Borisov including the recent extensive Russian work illustrates the fact that many polyhydrides are still obtained by rather crude methods. We set out to improve this situation and were able to employ a number of reagents that have proved useful in organic chemistry. These organic-soluble hydride donors such as $LiBR_3H$ and $NaAlH_2(OCH_2OR)_2$ give much higher yields of product on appropriate work-up.[2] In the cases shown in Table 1, a comparison is made between the yields obtained with $NaBH_4$ and $LiBEt_3H$.

Table I. Comparison of Yields (%) from $NaBH_4$ and $LiEt_3BH$

compd	$NaBH_4$	$LiEt_3BH$
$MoH_4(PMePh_2)_4$	45	67
$MoH_4(dppe)_2$	15	50
$WH_4(PMePh_2)_4$	4	70
$WH_4(PEtPh_2)_4$	2.5	49

On applying these new techniques to the case of $MoCl_4L_2$ (L = PCy_3, PCy_3Ph, $PPr^i{}_3$, and $PPr^i{}_2Ph$) and in particular using $NaH_2Al(OCH_2CH_2OCH_3)_2$ in thf at -78°, we were able to synthesise the new complexes MoH_6L_3, the first examples of nine-coordinate molybdenum.[3]

These have not yet been isolated because of their very great solubility and thermal sensitivity. Identification was accomplished using the powerful technique of selective H-decoupling of the ^{31}P spectra of the complexes. In this way the phosphine ligand protons can be decoupled and the effect of the hydrides directly bonded to the metal can be observed. We found that the ^{31}P NMR resonances of all our polyhydrides of known formulation gave an (n+1)-membered multiplet, where n is the number of H ligands. The new complexes gave clear septets, helping to confirm their formulation.[3]

Hydrogen Release Reactions

We have examined the protonation, heat and photolysis. Of the three, protonation has given the most interesting results and we will briefly review these here. We have protonated six representative polyhydrides in various solvents and find[4] that hydrogen release is complete (Os) or nearly so (Mo, W, Re, Ir). We used the NMR techniques, mentioned above, to help identify the products. In each case, a solvent molecule S acts as as ligand to fill the vacant sites generated. In the case where S is acetonitrile,

$$WH_6L_3 \longrightarrow WH_2S_3L_3{}^{2+}$$

$$MoH_4L_4 \longrightarrow MoH_2S_3L_3{}^{2+}$$

$$ReH_5L_3 \longrightarrow ReHS_3L_3{}^{2+}$$

$$ReH_7L_2 \longrightarrow ReHS_3L_2{}^{2+}$$

$$OsH_4L_4 \longrightarrow OsS_3L_3{}^{2+}$$

$$IrH_5L_2 \longrightarrow IrH_2S_2L_2{}^{+}$$

the complexes formed do not take up H_2 even in the presence of a base. In the case of the more weakly binding solvents S = Me_2CO or MeOH, we now know that reversal with base is possible under H_2 (1 atm.), at least in the case we have examined most carefully (Ir). We therefore wished to used the same technique with the inexpensive metals Mo and W, but came across a most unexpected transformation, discussed in the next section.

These reactions were mechanistically interesting in that certain of the metals possess lone pairs and can protonate initially to give $MH_{n+1}L_m^+$, for which evidence has been obtained in some cases.[5] In other cases, the metals do not possess lone pairs, and initial protonation of the M-H bond itself may well take place to give a species containing an $M{-}{-}H{-}{-}H^+$ system. A similar species may be involved in H_2 addition to metals.[6]

Unexpected Deactivation Products

Wilkinson et al[5a] reported that MoH_4L_4 (L = $PMePh_2$) reacts with HBF_4 in thf to give $MoH_3L_3^+$. We found this surprising, since the proposed complex has only 12 valence electrons and would be expected to be highly reactive. As mentioned above, we wished to try to protonate Mo and W polyhydrides to give reversible H_2 release. We found that instead Wilkinsons reported complex was formed. We were not satisfied with the proposed formulation and carried out an X-ray crystallographic study in collaboration with Professor W. Holt (Oklahoma State). Our findings illustrated in Fig. 1 are most unexpected. In spite of the presence of H_2O, the molybdenum very rapidly abstracted F^- from the BF_4^- counter-ion to form a triply fluoride-bridged complex even though BF_4 is normally considered a non-coordinating anion. Further study has shown that $HSbF_6$ and HPF_6 do not lead to F^- transfer and we are following up this work at the moment.

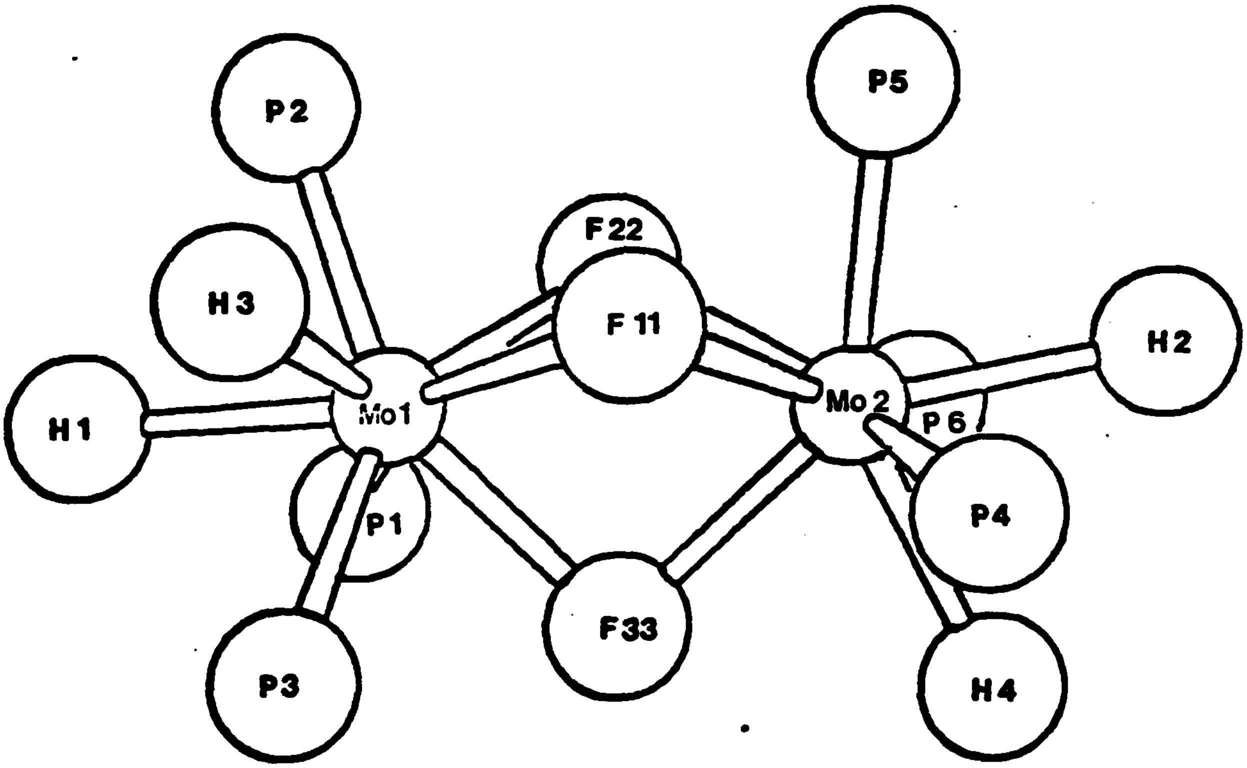

Figure 1. The structure of $[((PMe_2Ph)_3H_2Mo)_2(\mu\text{-}F)_3]BF_4$. The organic groups bound to P are omitted for clarity.

No triple fluoride bridges has previously been observed and this was thought to be due to a supposed requirement for pi-bonding in a linear M-F-M array. We have proposed that 18-electron M-F-M bridges will be bent.

A further feature of interest is the fact that the complex contains the hardest (F) and softest (H) ligands on the same metal, and that the H's are terminal not bridging as might have been expected.

Finally the complex is the first example of a bidodecahedral geometry. We have been able to understand the geometry of the complex in terms of the sharing equilateral faces between two staggered dodecahedral Mo fragments. This has cast light on the formation of multinuclear complexes in high coordination number polyhedra, about which almost nothing had been known. The full details of this work including a discussion of the dynamic and chemical behavior of the complex will appear in a paper in J. Amer. Chem. Soc.[7]

We previously showed that iridium polyhydrides tend to be deactivated for reversible H_2 addition by formation of H-bridged clusters.[8] The work described above shows that in Mo and W chemistry, other processes occur.

Weakly Binding "Solvent Ligands"

In order to stablise hydrides against deactivation to give multinuclear species, we have found that weakly coordinating solvents are useful. In the iridium series[9] these solvents are H_2O, MeOH, Me_2CO, and MeCN. Of these, MeCN binds too strongly to allow subsequent substitution (e.g., by H_2), so we have turned to the weaker-binding S ligands H_2O, MeOH and Me_2CO. Solvents-complexes of these have very unusual properties, which we have reported in a number of papers.[9,10,11] In connection with the present work we were concerned with the unusual ligands RI,[10] and RCO_2Et which had previously not been known to complex to metals. We have made the first examples and have unambiguously characterised one example by X-ray crystallography.[10] These ligands are sufficiently strongly binding to prevent deactivation but labile enough to allow substitution.

Conclusion

We have met several important goals in our research plan. We have developed new methods of polyhydride synthesis and H_2 release. We have identified several deactivation reactions that we will have to guard against but have developed proposed strategies to solve these remaining problems (see renewal proposal recently submitted).

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G- G.G. Hlatky and R.H. Crabtree, Polyhydride Complexes, Coord. Chem. Revs., in preparation.

Degrees awarded to contributors to the Project

G.G. Hlatky, Ph.D. 1983

M.F. Mellea, Ph.D., 1984

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