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REACTION OF <u>trans</u>-$Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$ WITH HYDROAROMATIC COMPOUNDS, ALCOHOLS, AND METHYL FORMATE; THE FORMATION OF CARBONYL AND HYDRIDE COMPLEXES OF MOLYBDENUM

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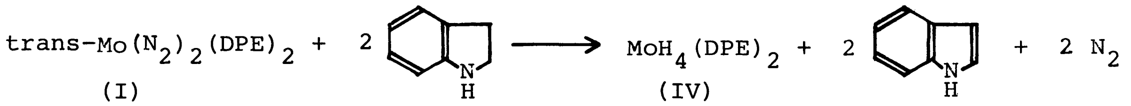
Reaction of trans-$Mo(N_2)_2(DPE)_2$ ($DPE=Ph_2PCH_2CH_2PPh_2$) with tetrahydrofuran, MeOH, EtOH, and HCOOMe gives the molybdenum carbonyls, trans-$Mo(CO)(N_2)(DPE)_2$ and cis-$Mo(CO)_2(DPE)_2$; in the case of tetrahydrofuran the hydride $MoH_4(DPE)_2$ is also formed. The hydride is selectively obtained from pyrrolidine, indoline, and 2-propanol.

As part of our exploration of the chemistry of the molybdenum dinitrogen complex, trans-$Mo(N_2)_2(DPE)_2$ (I), we have recently reported that it reacts with N,N-dimethylformamide (DMF) to give the carbonyl complex, $Mo(CO)(DMF)(DPE)_2$, which is converted to trans-$Mo(CO)(N_2)(DPE)_2$ (II) upon crystallization under nitrogen atmosphere.$^{1)}$ Since CO abstraction from organic oxygen compounds is scarcely known for complexes of the early transition metals, the reaction of several oxygen-containing compounds with (I) has been invetigated. We have now found novel reactions leading to the formation of carbonyl and hydride complexes of molybdenum.

The reaction of tetrahydrofuran (THF) with (I) in benzene at reflux under nitrogen affords a dark brown solution, which becomes reddish orange on cooling. From the resulting solution (II) is obtained in 40 % yield. The bis-carbonyl complex, cis-$Mo(CO)_2(DPE)_2$ (III) is also obtained (15 %). The dark brown solution at reflux seems to contain $[Mo(CO)(DPE)_2]_n$, from which (II) must have been formed by the reaction with nitrogen gas.$^{1)}$ The formation of carbonyl complexes from THF as a CO source has been found only for a rhodium complex.$^{2)}$ On the other hand, (I) reacts with THF under argon to give the hydride $MoH_4(DPE)_2$ (IV) (45 %). The hydride (IV) is also found in the reaction products under nitrogen. Glc analysis shows that there are no detectable amounts of the expected dehydrogenation and decarbonylation products of THF, i.e., furan, propylene, and propane. By use of pyrrolidine (IV) is obtained in 75 % yield. However, no low-boiling dehydrogenation products such as pyrrole can be detected. Since 1-pyrroline is reported to be so unstable as to trimerize$^{3)}$ or add to amines,$^{4)}$ it is presumed that dehydrogenation intermediates might have reacted to give products of higher molecular weight which are not detectable by glc analysis. In contrast, (I) reacts with indoline to give (IV) with the formation of indole, the expected dehydrogenation product.



The formation of the hydride (IV) from THF, pyrrolidine, and indoline would be of particular interest since these reactions apparently occur via saturated C-H bond activation. Although it is well-known that alcohols react with group VIII metal halides to give hydrides,[5)] there is no precedent for the formation of hydrides using these hydroaromatics as a hydrogen donor.[6)] Recently homogeneous group VIII metal catalysts were reported to be active in the transfer of hydrogen from the donors such as 2-propanol, THF, pyrrolidine, 1,4-dioxane, and tetralin to a variety of acceptors.[7)] The isolation of (IV) in our reaction systems may be suggestive of the possibility of intermediacy of hydride complexes in the transfer-hydrogenation catalyst systems using the hydroaromatics as a hydrogen donor. The reported effective donors, e.g., 1,4-dioxane and tetralin are, however, not suitable for the preparation of (IV).

The complex (I) reacts with MeOH or EtOH in benzene at reflux to give (II) and (III) in only low yields. In contrast, (I) reacts with 2-propanol to give the hydride (IV) in a high yield (83 %). Acetone can be detected as a dehydrogenation product. In the case of MeOH and EtOH, however, no formation of (IV) is observed. The complex (I) is unreactive to t-BuOH.

When N,N-dimethylacetamide is used in place of DMF, no reaction has been observed. The reaction of HCOOMe with (I) in benzene at reflux under nitrogen affords (II) and (III). Glc analysis shows the formation of MeOH by the decarbonylation of HCOOMe. The ratio of (II) to (III) decreases with an increase in the reaction time. Upon refluxing for 30 min, (III) is exclusively obtained. To our knowledge, this is the first example of carbonyl complex formation utilising formate esters as a CO source. By use of MeCOOMe, only trace amounts of (III) are obtained. With $MeCOOCH=CH_2$ or $MeCOOCH_2CH=CH_2$, (I) gives acetate complexes of molybdenum.[8)]

Further investigations are now in progress.

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