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Olefin Disproportionation by Molybdenum(0) Complexes and Aluminum Halides[1]

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Synopsis. $MoN_2(PPh_3)_2 \cdot PhMe$ and $Mo(CO)(PPh_3)_2$ were activated by aluminum halides to give catalysts effective for the disproportionation of 2-pentene.

Halide complexes of molybdenum or tungsten in combination with organoaluminum have been known to be effective for olefin disproportionation.[2–4] We wish to report new molybdenum catalyst systems, free of metal alkyls, for the disproportionation of 2-pentene. Metal alkyl-free catalysts comprised of tungsten combounds have been briefly reported before.[5,6]

Treatment of $MoN_2(PPh_3)_2 \cdot PhMe$[7] (**1**) with $AlCl_3$ in bromobenzene afforded a brown suspension, which was effective for the disproportionation of 2-pentene to 2-butene and 3-hexene at ambient temperature. The system became active with an increase in the Al/Mo ratio, but the large excess of $AlCl_3$ promoted the alkylation of the solvent (Table 1). In the evaluation of other molybdenum(0) complexes, it was found that $Mo(CO)(PPh_3)_2$ (**2**) also was a satisfactory catalyst precursor. $AlCl_3$ could not produce catalytic systems in combination with other molybdenum(0) compounds, except that some activity was produced with *trans*-$Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$[7] (Table 2).

Table 1. Effect of $AlCl_3$/Mo molar ratio
1: 0.05 mmol, 2-pentene: 9.4 mmol, PhBr: 4 ml, reaction time: 2 hr.

Al/Mo ratio	Olefin yield, mol%[a]		
	C_4	C_5	C_6
1	t [b]	99	t [b]
3	5.6	81	5.2
6	17	51	17
9	19	43	19
12	16	47	15

a) mol% of each olefin to the amount of 2-pentene used. b) t; trace.

Table 2. Effect of molybdenum(0) complexes
Complex: 0.05 mmol, 2-pentene: 9.4 mmol, PhCl: 4 ml.

Molybdenum complex	$AlCl_3$/Mo ratio	Reaction time, hr	Olefin yield, mol%		
			C_4	C_5	C_6
$MoN_2(PPh_3)_2 \cdot PhMe$ (**1**)	9	2	6.8	64	6.8
$Mo(CO)(PPh_3)_2$ (**2**)	9	2	12	33	12
trans-$Mo(N_2)_2(dpe)_2$[a]	20	24	2.2	40	2.2
cis-$Mo(CO)_2(dpe)_2$[a]	20	72	0.0	43	0.0
trans-$Mo(CO)_4(PPh_3)_2$	9	2	0.1	43	0.1
$Mo(CO)_6$	6	120	0.2	19	0.2
$Mo(Ph_2PCH_2PPh_2)_3$	17	120	0.1	22	0.1
$Mo(CO)_3(PhH)$	9	72	0.0	40	0.0

a) dpe=1,2-bis(diphenylphosphino)ethane.

To determine the effectiveness of Lewis acids as cocatalyst with **1**, parallel preparations were made with several aluminum and other metal halides. Among the aluminum halides the order of the activity was $AlCl_3 \gg AlBr_3 > AlEtCl_2$ (Table 3). With **2** the activity decreased in the same order. The system derived from other aluminum compounds such as AlI_3, $AlEt_2Cl$, or $AlEt_3$ was not effective. Other metal halides such as LiCl, $MgCl_2$, $BF_3 \cdot Et_2O$, $TiCl_4$, $MoCl_5$, $FeCl_3$, $ZnCl_2$, or $SnBr_4$ were ineffective, whereas very little activity was produced by $ZrCl_4$. It is likely that traces of moisture provides HCl from $AlCl_3$ and that it is an alternative cocatalyst. Treatment of **2** with HCl in bromobenzene afforded a reddish brown suspension, which exhibited, however, no activity.

Table 3. Effect of Lewis acids
1: 0.05 mmol, 2-pentene: 9.4 mmol, PhCl: 4 ml.

Lewis acid	Acid/Mo ratio	Reaction time, hr	Olefin yield, mol%		
			C_4	C_5	C_6
$AlCl_3$	9	2	6.8	64	6.8
$AlBr_3$	12	20	3.7	39	4.7
$AlEtCl_2$	20	20	1.6	82	1.0
$ZrCl_4$	9	24	0.3	43	0.3

The reaction of **2** with $AlCl_3$ in bromobenzene yielded a reddish brown complex, which had a band at 1900 cm^{-1} assigned to $\nu(CO)$ in its IR spectrum. This band is *ca.* 90 cm^{-1} higher than that of **2**. The shift is reasonable because the electron density in the molybdenum atom would be decreased by the interaction of molybdenum(0) base with the Lewis acid, resulting in a decrease in back π-bonding from the molybdenum to the CO ligand. Bencze and Markó have recently reported highly reactive adducts of halocarbonyl complexes of tungsten with $AlCl_3$, which also show higher shifts of $\nu(CO)$.[8] In the reaction of **2** with $AlEtCl_2$ or $AlBr_3$, $\nu(CO)$ was similarly shifted to higher frequency by 15 cm^{-1} or 165 cm^{-1}, respectively. Accordingly, the increment of $\nu(CO)$ falls in the usually accepted order of Lewis acidity, $AlBr_3 > AlCl_3 > AlEtCl_2$, while the order of effectiveness for the disproportionation was $AlCl_3 \gg AlBr_3 > AlEtCl_2$.

When $AlCl_3$ was added to **1** in bromobenzene, the absorbance at 1905 cm^{-1} attributed to $\nu(NN)$ disappeared. Since N_2 is a weaker π-acceptor than CO, a decrease in back donation from the molybdenum must weaken the Mo–N_2 bond so much, resulting in liberation of N_2 from the complex. Other molybdenum(0) complexes such as *cis*-$Mo(CO)_2(Ph_2PCH_2CH_2PPh_2)_2$ and *trans*- Mo(CO)$_4$(PPh$_3$)$_2$ were also observed to interact with AlCl$_3$; ν(CO) bands of these complexes were shifted to higher frequencies by *ca.* 70—100 cm^{-1}. As described above, they were, however, not effective as catalyst precursors. The molecular weight of **2** was found to be 1290 by the vapor pressure osmometric method, indicating that **2** has a dimeric structure (Calcd 1296). Since **1** can be easily converted to **2** in the presence of CO and has the empirical formula analogous to **2**, it may also have a dimeric structure. It is to be noted that the 6-coordinate mononuclear molybdenum(0) complexes did not afford active catalyst systems by the addition of aluminum halides, but that the complexes, **1** and **2**, presumed to have unusual dimeric structures showed a remarkable catalytic activity.

Recently Lewandos and Pettit have reported that arene-W(CO)$_3$ complexes can act as catalyst precursors for olefin disproportionation.[9] These systems are, however, not notably effective, and prolonged heating to 98 °C is necessary in order to activate the catalyst systems. We have observed that **2** itself also exhibited very little disproportionation activity at 98 °C, while the addition of AlCl$_3$ markedly stimulated the activity. Although Wang and Menapace suggested a W(IV) (d^2) catalytic intermediate in the WCl$_6$-*n*-BuLi sistem,[10] Mo(IV) (d^2) complexes such as MoCl$_4$(EtCN)$_2$ or MoCl$_4$(PPh$_3$)$_2$ could neither act as catalysts by themselves nor be activated by AlCl$_3$.

The systems using bromobenzene or chlorobenzene as the solvent were clearly superior to those using benzene or *n*-hexane (Table 4). In the case of the latter solvents the system became almost heterogeneous, suggestive of active species having some ionic character. The complex **1** was recovered quantitatively after being allowed to stand for a long time in bromobenzene or chlorobenzene, ruling out the posibility that the oxidative addition of the solvent occurred. The disproportionation was completely inhibited using iodobenzene, which rapidly reacted with **1**. If the catalyst was prepared in toluene and 2-pentene was added, almost exclusive and rapid alkylation of toluene took place.

TABLE 4. SOLVENT EFFECT
1: 0.05 mmol, AlCl$_3$: 0.45 mmol, 2-pentene: 9.4 mmol, solvent: 4 ml, reaction time: 2 hr.

Solvent	Olefin yield, mol%		
	C$_4$	C$_5$	C$_6$
PhMe	0	2.8	0
PhH	0.7	44	0.7
PhCl	6.8	64	6.8
PhBr	19	43	19
PhI	0	100	0

It has been established that in the transition metal-olefin interaction, two factors are operating, *i.e.*, σ-donation from the olefin to the metal and back π-bonding from the metal to the olefin. The magnitude of the contribution of these two factors are partly dependent on the electron density on the metal atom. The fact that AlCl$_3$ is the most effective cocatalyst with the molybdenum complexes may be explained in terms of moderate decrease in the electron density on the molybdenum by adduct formation, as indicated by the increase in ν(CO). The most active catalyst systems reported for homogeneous olefin disproportionation are composed of halide complexes of either molybdenum or tungsten and organoaluminum compounds. In those systems metal halides are supposed to react with organoaluminum to produce, transiently, molybdenum(0) or tungsten(0) complexes with formation of aluminum halides, leading to catalyst systems similar to our combinations. We may conclude that in the catalyst systems previously reported, organoaluminum functions not only as a reducing agent but also as an electron modifier of the reduced molybdenum or tungsten.

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