REACTIONS OF *trans*-Mo(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂ WITH ESTERS; CLEAVAGE OF C—O BONDS

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(Received February 24th, 1981)

Summary

Reactions of benzyl carboxylates, RCOOCH₂C₆H₅, (R = CH₃ or C₂H₅) with *trans*-Mo(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂ yield RH, C₆H₆ and molybdenum carbonyl complex(es), whereas C₂H₄ and H₂ also are formed when the R group is C₂H₅. The formation of the products is accounted for by assuming oxidative addition of the ester to molybdenum (cleavage of the acyl—O bond of RCOOCH₂C₆H₅), followed by extrusion of CO. Reactions of phenyl carboxylates occur similarly by way of acyl—O bond cleavage. In contrast, reaction of allyl acetate with *trans*-Mo(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂ involves the cleavage of the allyl—O bond to give propylene and a molybdenum acetate complex containing the *ortho*-metallated phosphine. Reactions of vinyl carboxylates occur similarly by way of vinyl—O bond cleavage.

Introduction

The cleavage of C—O bonds in esters promoted by transition metals has been of recent interest [1]. In a previous paper [2], we noted that decarbonylation of formate esters was promoted by *trans*-Mo(N₂)₂(dpe)₂ (dpe = Ph₂PCH₂CH₂PPh₂). The reaction is assumed to start with the initial cleavage of the C—H bond of the formyl group. During the investigation of the reaction of vinyl formate with *trans*-Mo(N₂)₂(dpe)₂, we have found formation of a formate complex arising from cleavage of the vinyl—O bond. We now wish to report cleavage of the C—O bonds of esters by Mo⁰ and the effect of the kinds of esters on the position of the cleavage.

Results and discussion
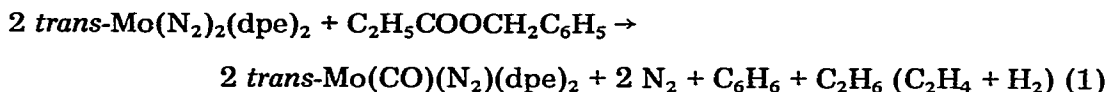
Reactions of benzyl and phenyl esters

Table 1 summarizes the products of the reactions of benzyl and phenyl carboxy-

TABLE 1

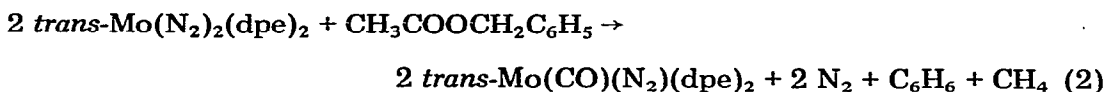PRODUCTS OF THE REACTIONS OF BENZYL AND PHENYL ESTERS WITH *trans*-Mo(N$_2$)$_2$(dpe)$_2$ [a]

Esters	Solvent	Temp. (°C)	Time (min)	Products (% yield/*trans*-Mo(N$_2$)$_2$(dpe)$_2$)			
				Organic compds.	Mo(CO)(N$_2$)	Mo(CO)$_2$	Others
C$_2$H$_5$COOCH$_2$C$_6$H$_5$	Benzene	rfx	30	C$_2$H$_4$ (44), C$_2$H$_6$ (29) C$_6$H$_5$CHO (t)	57	t	H$_2$ (45)
C$_2$H$_5$COOCH$_2$C$_6$H$_5$	Toluene	100	25	C$_2$H$_4$ (30), C$_2$H$_6$ (17) C$_6$H$_6$ (43)	52	3	H$_2$ (33)
C$_2$H$_5$COOCH$_2$C$_6$H$_5$ [b]	Toluene	100	40	C$_2$H$_4$ (2), C$_2$H$_6$ (15) C$_6$H$_6$ (39)	32[c]	5[c]	H$_2$ (19) Mo(CO)(C$_2$H$_4$) (14) [c]
CH$_3$COOCH$_2$C$_6$H$_5$	Toluene	rfx	25	CH$_4$ (20), C$_2$H$_4$ (t) C$_6$H$_6$ (50), CH$_3$COCH$_3$(t)	37	17	
C$_2$H$_5$COOC$_6$H$_5$	Benzene	rfx	30	C$_2$H$_4$ (50), C$_2$H$_6$ (4) C$_6$H$_5$OH (47)	19	36	
C$_2$H$_5$COOC$_6$H$_5$	Benzene	70	100	C$_2$H$_4$ (37), C$_2$H$_6$ (11) C$_6$H$_5$OH (45)	12	30	
CH$_3$COOC$_6$H$_5$	Benzene	rfx	15	CH$_4$ (25), CH$_3$COCH$_3$ (3) C$_6$H$_5$OH (20)	0	36	Phenoxo-Mo complex (15 mg)

[a] *trans*-Mo(N$_2$)$_2$(dpe)$_2$ = 0.07 mmol, ester = 0.7 mmol, solvent = 3 ml, rfx; refluxed, t; trace, Mo(CO)(N$_2$); *trans*-Mo(CO)(N$_2$)(dpe)$_2$ (1/2 C$_6$H$_6$ was included as a crystal solvent when benzene was used as a solvent), Mo(CO)$_2$; *cis*-Mo(CO)$_2$(dpe)$_2$, Mo(CO)(C$_2$H$_4$); Mo(CO)(C$_2$H$_4$)(dpe)$_2$. [b] Under argon. [c] The yields were estimated from the IR spectrum of the complex mixture by using the molar extinction coefficient of ν(C≡O) of an independently synthesized authentic sample.

lates with $trans$-Mo(N$_2$)$_2$(dpe)$_2$. Treatment of $trans$-Mo(N$_2$)$_2$(dpe)$_2$ with C$_2$H$_5$-COOCH$_2$C$_6$H$_5$ in toluene at 100°C for 25 min affords a dark brown solution with evolution of H$_2$, C$_2$H$_4$ and C$_2$H$_6$. The solution changes to orange on cooling under nitrogen, and from the resulting solution $trans$-Mo(CO)(N$_2$)(dpe)$_2$ and benzene are obtained. The dark brown solution obtained at reflux contains the five-coordinate Mo(CO)(dpe)$_2$ [3]. The total amount of C$_2$H$_4$ and C$_2$H$_6$ is roughly equal to that of benzene. The amount of H$_2$ is roughly equal to that of C$_2$H$_4$. In the reaction conducted under argon, the amount of C$_2$H$_4$ evolved is small, because in the absence of a large amount of N$_2$, C$_2$H$_4$ can be coordinated to Mo(CO)(dpe)$_2$ [4]. The formation of these products indicates that all of the C$_2$H$_5$—COOCH$_2$C$_6$H$_5$, C$_2$H$_5$CO—OCH$_2$C$_6$H$_5$, and C$_2$H$_5$COOCH$_2$—C$_6$H$_5$ bonds are cleaved in the reaction. The reaction may be expressed by eq. 1:

$$2\ trans\text{-Mo(N}_2)_2(\text{dpe})_2 + C_2H_5COOCH_2C_6H_5 \rightarrow$$

$$2\ trans\text{-Mo(CO)(N}_2)(\text{dpe})_2 + 2\ N_2 + C_6H_6 + C_2H_6\ (C_2H_4 + H_2)\ (1)$$

A similar reaction of CH$_3$COOCH$_2$C$_6$H$_5$ with $trans$-Mo(N$_2$)$_2$(dpe)$_2$ may be expressed by eq. 2:

$$2\ trans\text{-Mo(N}_2)_2(\text{dpe})_2 + CH_3COOCH_2C_6H_5 \rightarrow$$

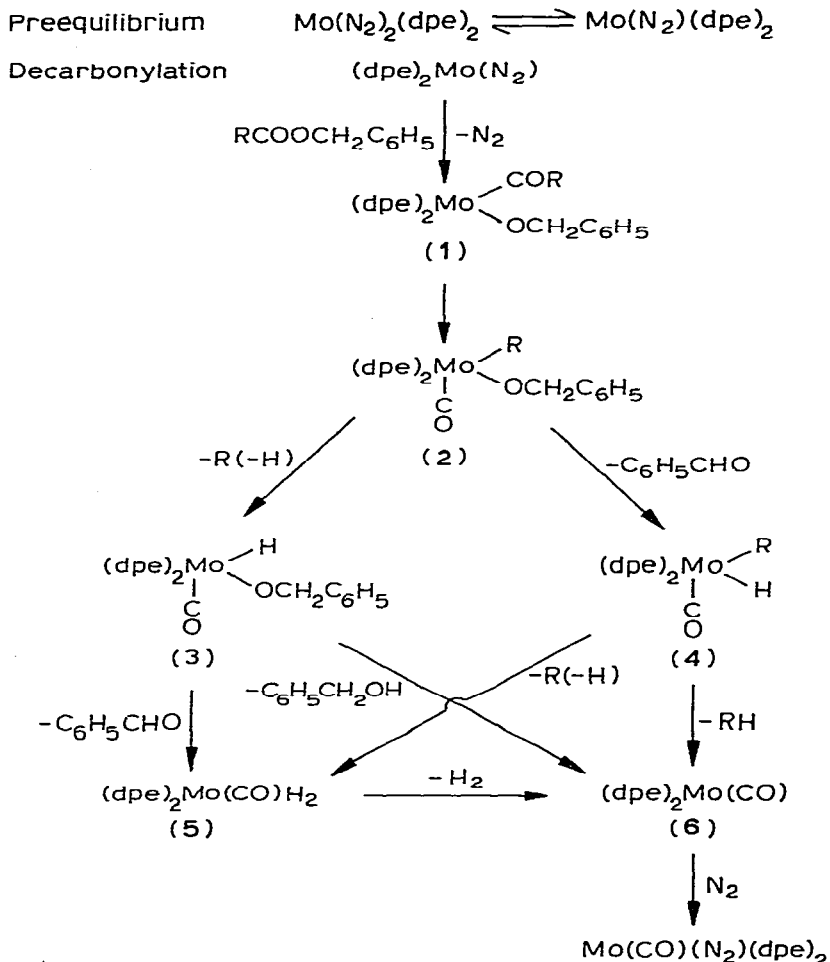$$2\ trans\text{-Mo(CO)(N}_2)(\text{dpe})_2 + 2\ N_2 + C_6H_6 + CH_4\ (2)$$

But the amount of CH$_4$ is smaller than that of C$_6$H$_6$ and the fit to the stoichiometry of the reaction (eq. 2) is unsatisfactory. Trace amounts of C$_2$H$_4$ and acetone also are obtained. However, the methyl-group balance, detected in the form of CH$_4$, C$_2$H$_4$, and acetone in Table 1 does not equal the amount of benzene. In contrast with C$_2$H$_5$COOCH$_2$C$_6$H$_5$, CH$_3$COOCH$_2$C$_6$H$_5$ is not suitable for the synthesis of Mo(CO)(N$_2$)(dpe)$_2$, since a considerable amount of cis-Mo(CO)$_2$-(dpe)$_2$ is formed.

In order to explain the observations shown in Table 1, we propose a mechanism for the reaction of benzyl carboxylates as illustrated in Scheme 1. The first step is oxidative addition of the ester to yield the acyl(benzyloxy)molybdenum complex 1. The acyl complex is assumed to be converted to an alkyl complex 2 by the well-known acyl—alkyl rearrangement. In the reaction of CH$_3$COOCH$_2$C$_6$H$_5$, formation of a small amount of acetone, which is considered to be generated by a coupling reaction between 1 and 2, is confirmed. This provides additional evidence for the postulated mechanism. Complex 2 is considered to undergo β-elimination to give alkane or benzaldehyde. The resulting complex, 3 or 4, is assumed to undergo subsequent reductive elimination to produce the five-coordinate carbonyl complex 6 and benzyl alcohol or alkane. Alternatively, 3 or 4 would undergo β-elimination to give 5 and benzaldehyde or alkene, and from 5 hydrogen may be reductively eliminated to afford 6. In fact, formation of a small amount of benzaldehyde is observed. Benzaldehyde and benzyl alcohol thus formed are known to be decarbonylated by $trans$-Mo-(N$_2$)$_2$(dpe)$_2$ to give benzene and carbonyl complexes [2].

Recently Yamamoto et al. reported the reaction of aryl carboxylates with bis(1,5-cyclooctadiene)nickel in the presence of phosphine ligands. The formation of the products was accounted for by assuming oxidative addition of the
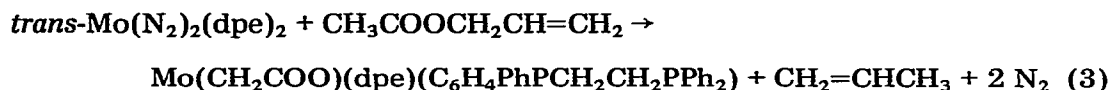
SCHEME 1

Preequilibrium $\qquad$ $Mo(N_2)_2(dpe)_2 \rightleftharpoons Mo(N_2)(dpe)_2$

Decarbonylation $\qquad$ $(dpe)_2Mo(N_2)$

$$RCOOCH_2C_6H_5 \Big\downarrow -N_2$$

$$(dpe)_2Mo\!\!\begin{array}{c} COR \\ OCH_2C_6H_5 \end{array}$$
$$(1)$$

$$(dpe)_2Mo\!\!\begin{array}{c} R \\ | \\ C \\ \| \\ O \end{array}\!\!OCH_2C_6H_5$$
$$(2)$$

$-R(-H)$ $\swarrow$ $\qquad$ $\searrow$ $-C_6H_5CHO$

$$(dpe)_2Mo\!\!\begin{array}{c} H \\ | \\ C \\ \| \\ O \end{array}\!\!OCH_2C_6H_5$$
$$(3)$$

$$(dpe)_2Mo\!\!\begin{array}{c} R \\ | \\ C \\ \| \\ O \end{array}\!\!H$$
$$(4)$$

$-C_6H_5CH_2OH$ $\qquad$ $-R(-H)$

$-C_6H_5CHO$ $\Big\downarrow$ $\qquad\qquad$ $\Big\downarrow -RH$

$$(dpe)_2Mo(CO)H_2 \xrightarrow{\ -H_2\ } (dpe)_2Mo(CO)$$
$$(5) \qquad\qquad\qquad\qquad (6)$$

$$\Big\downarrow N_2$$

$$Mo(CO)(N_2)(dpe)_2$$

ester to nickel, involving the cleavage of the acyl—O bond followed by decarbinylation. As shown in Table 1, the reaction of $C_2H_5COOC_6H_5$ with *trans*-Mo-$(N_2)_2(dpe)_2$ proceeds similarly to give C_2H_4, PhOH, and carbonyl complexes. A considerable amount of C_2H_6 also is formed and the molar ratio of C_2H_6 and C_2H_4 increases gradually with time. But the source of hydrogen transferred has not been clarified. The reaction of $CH_3COOC_6H_5$ with *trans*-Mo(N_2)_2(dpe)_2 gives CH_4, PhOH, *cis*-Mo(CO)_2(dpe)_2, and a molybdenum phenoxide. The IR spectrum of the phenoxide shows a characteristic intense band at 1260 cm^{-1} [1c]. But we could not determine the structure of the complex since it proved difficult to purify. It is noteworthy that no monocarbonyl complex was obtained from $CH_3COOC_6H_5$.

Reactions of allyl and vinyl esters

Transition metal-promoted cleavage of the allyl—O bonds of allyl esters has been utilized for organic synthesis [5] and in the preparation of π-allyl complexes [6]. Treatment of *trans*-Mo(N_2)_2(dpe)_2 with $CH_3COOCH_2CH=CH_2$

results in the formation of propylene and brown crystals. The latter exhibit strong IR bands at 1618 and 1308 cm^{-1}, which are ascribed to the asymmetric and symmetric C—O stretching frequencies of a unidentate acetate ligand [7]. Elemental analysis allows the empirical formula Mo(CH$_3$COO)(dpe)$_2$ to be deduced for the complex. The complex is diamagnetic, however, and the origin of hydrogen used in the formation of propylene cannot be considered other than the dpe·ligand. An intense shoulder peak at 744 cm^{-1} absent from the IR spectrum of the parent compound is assigned to the C—H out-of-plane deformation mode of an *ortho*-disubstituted benzene [8]. Thus we formulate the complex as Mo(CH$_3$COO)(dpe)(C$_6$H$_4$PhPCH$_2$CH$_2$PPh$_2$). The reaction may be expressed as follows:

trans-Mo(N$_2$)$_2$(dpe)$_2$ + CH$_3$COOCH$_2$CH=CH$_2$ →

$$Mo(CH_2COO)(dpe)(C_6H_4PhPCH_2CH_2PPh_2) + CH_2=CHCH_3 + 2\ N_2 \quad (3)$$

It has long been known that aromatic amines, imines, and phosphines react with reactive transition metal complexes to give chelated *ortho*-metallated complexes [8,9].

Treatment of *trans*-Mo(N$_2$)$_2$(dpe)$_2$ with CH$_3$COOCH=CH$_2$ gives yellow crystals, the IR spectrum of which shows strong bands characteristic of acetate complexes. No evolution of C$_2$H$_4$ was observed. The ^{1}H NMR spectrum of the complex shows a resonance of coordinated ethylene at δ 0.63 and 0.69 ppm. An intense peak in the IR spectrum at 746 cm^{-1} suggests an *ortho*-metallated phenyl ring. Thus we formulate the complex as Mo(CH$_3$COO)(C$_2$H$_4$)(dpe)-(C$_6$H$_4$PhPCH$_2$CH$_2$PPh$_2$). The strong coordination ability of the C$_2$H$_4$ ligand prohibits its evolution, as is distinct from propylene. Reactions with HCOO-CH=CH$_2$ and C$_2$H$_5$COOCH=CH$_2$ give analogous carboxylate complexes, whereas in the former case decarbonylation, generally observed for formate esters [2], also occurs. The results are summarized in Table 2.

Alkyl carboxylates such as CH$_3$COOC$_2$H$_5$ and C$_2$H$_5$COOC$_2$H$_5$ did not react with *trans*-Mo(N$_2$)$_2$(dpe)$_2$ under similar condistions.

Reaction patterns of esters

Interactions of the esters with *trans*-Mo(N$_2$)$_2$(dpe)$_2$ would lead to cleavage of the esters at three positions as shown below.

$$R_1 \overset{\text{A}}{\rule{1cm}{0.4pt}} \underset{\underset{O}{\parallel}}{C} \overset{\text{B}}{\rule{1cm}{0.4pt}} O \overset{\text{C}}{\rule{1cm}{0.4pt}} R_2 \quad (4)$$

Table 3 summarizes the mode of cleavage deduced from the results of the product analysis. Cleavage at A occurs only in the case of formate esters. In the molecule shown, the estimated homolytic bond dissociation energies (BDE) of B and C indicate that benzyl esters should cleave at C. Allyl esters also are expected to cleave at C because of the similarity of the allyl to the benzyl group. The allyl ester does this, while the benzyl esters react with cleavage at B. It appears that in the benzyl esters, coordination to Mo^0 would result in weakening of bond B to overcome the ca. 20 kcal difference between bonds B and C. This is presumably a result of the initial interaction of molybdenum

TABLE 2

CARBOXYLATE COMPLEXES OF MOLYBDENUM

Compound	Yield (%)	IR (cm^{-1})		NMR (δ)		Analysis Found (Calcd.) (%)	
		ν(CO)	δ(CH)[a]	RCOO	C$_2$H$_4$	C	H
Mo(CH$_3$COO)(dpe)(C$_6$H$_4$PhPCH$_2$CH$_2$PPh$_2$)	46	1618 1308	744	1.55s		67.6 (68.2)	6.5 (5.3)
Mo(CH$_3$COO)(C$_2$H$_4$)(dpe)(C$_6$H$_4$PhPCH$_2$CH$_2$PPh$_2$)	72	1612 1318	746	1.33s	0.63 0.69	69.5 (68.8)	5.3 (5.5)
Mo(C$_2$H$_5$COO)(C$_2$H$_4$)(dpe)(C$_6$H$_4$PhPCH$_2$CH$_2$PPh$_2$)	75	1606 1275	742	0.71t 1.57q	1.09 1.27	69.5 (69.0)	5.7 (5.6)
Mo(HCOO)(C$_2$H$_4$)(dpe)(C$_6$H$_4$PhPCH$_2$CH$_2$PPh$_2$)	29	1610 1370	748	—	—	—[b]	

[a] Aromatic C—H out-of-plane deformation frequencies of σ-bonded *ortho*-disubstituted aryl groups. [b] Satisfactory analysis could not be obtained due to impurities (carbonyl complexes).

TABLE 3

MODE OF CLEAVAGE OF ESTERS (eq. 4) BY THE REACTIONS WITH *trans*-Mo(N$_2$)$_2$(dpe)$_2$

Esters (R = CH$_3$ or C$_2$H$_5$)	BDE [a] (kcal/mol)		Mode of cleavage	
	B	C	Expected	Found
RCOOCH$_2$C$_6$H$_5$	95 [b]	74 [b]	C	B
RCOOC$_6$H$_5$	82 [b]	102	B	B
RCOOCH$_2$CH=CH$_2$			C	C
RCOOCH=CH$_2$		99	B	C
RCOOC$_2$H$_5$	96	87		no reaction

[a] Estimated homolytic bond dissociation energies (R = CH$_3$) taken from ref. 11. [b] Calculated by using the values from refs. 12—14.

and the π-electrons of the benzene ring, assisting the attack of the metal at the carbonyl group, which leads to the acyl—O bond cleavage (Type B).

Both phenyl esters and vinyl esters are expected to cleave at B, but the vinyl esters react with cleavage at C. This also is attributed to the interaction of vinyl π electrons with Mo^0. The poor reactivity of aliphatic esters also suggests the importance of such interaction.

Experimental

All reactions were carried out under prepurified nitrogen unless otherwise noted. Solvents were dried and distilled by using standard techniques. *trans*-Mo(N$_2$)$_2$(dpe)$_2$ was prepared by a known method [10]. All other reagents were commercially available. IR spectra were taken as KBr pellets on a Nihon-Bunko IRA-2 spectrometer. ^{1}H (60 MHz) NMR spectea were recorded on a Hitachi R-40 spectrometer.

Reaction of benzyl propionate

Benzyl propionate (115 mg, 0.7 mmol) was added to a Schlenk-type flask containing *trans*-Mo(N$_2$)$_2$(dpe)$_2$ (66 mg, 0.07 mmol) in toluene (3 ml). The mixture was heated at 100°C for 25 min. During the reaction, samples of the reaction gas were withdrawn by a syringe through a serum cap. GLC analysis on molecular sieve 5A and Porapak Q columns showed formation of H$_2$, C$_2$H$_4$, and C$_2$H$_6$ in 33, 30, and 17% yield, respectively. After cooling under nitrogen, GLC analysis of the liquid phase showed formation of benzene in 43% yield. Addition of n-hexane deposited orange crystals, which were filtered, washed with n-hexane, and dried in vacuo to yield *trans*-Mo(CO)(N$_2$)(dep)$_2$ (34 mg, 52%). Anal. Found: C, 66.7; H, 5.3; N, 3.2. Calcd. for C$_{53}$H$_{48}$N$_2$OP$_4$Mo: C, 67.1; H, 5.1; N, 3.0%. A small amount of yellow microcrystals of *cis*-Mo(CO)$_2$-(dpe)$_2$ (3%) also was obtained.

Other reactions of benzyl esters were carried out in similar manner.

Reaction of phenyl acetate

Phenyl acetate (95 mg, 0.7 mmol) was added to a solution of *trans*-Mo(N$_2$)$_2$-(dpe)$_2$ (66 mg, 0.07 mmol) in benzene (3 ml). The mixture was heated under

reflux for 15 min. GLC analysis of the gas phase showed formation of CH_4 (25%). After cooling, GLC analysis of the liquid on an inositol/Uniport B column indicated formation of phenol (20%) and acetone (3%). Addition of n-hexane deposited yellow microcrystals of cis-$Mo(CO)_2(dpe)_2$ (24 mg, 36%) and a black powder (15 mg). The IR spectrum of the powder exhibited a strong $\nu(C-O)$ band at 1260 cm^{-1} which is characteristic of phenoxides, but it was contaminated by impurities. Its purification by recrystallization was unsuccessful and we could not determine the structure.

Other reactions of phenyl esters were carried out in similar manner.

Reaction of allyl acetate

Allyl acetate (200 mg, 2.0 mmol) was added to a solution of trans-$Mo(N_2)_2$-$(dpe)_2$ (190 mg, 0.2 mmol) in benzene (6 ml). When heated under reflux for 10 min, the mixture turned reddish brown. GLC analysis of the gas phase on a VZ-7 column showed formation of propylene (59%). Addition of n-hexane deposited brown crystals of $Mo(CH_3COO)(dpe)(C_6H_4PhPCH_2CH_2PPh_2)$ (87 mg, 46%).

Reaction of vinyl acetate

Vinyl acetate (86 mg, 1.0 mmol) was added to a solution of trans-$Mo(N_2)_2$-$(dpe)_2$ (95 mg, 0.1 mmol) in benzene (4 ml). When heated under reflux for 40 min, the mixture turned orange brown. GLC analyses of the gas phase showed no formation of H_2, C_2H_4, or 1,3-butadiene. Addition of n-hexane deposited yellow crystals of $Mo(CH_3COO)(C_2H_4)(dpe)(C_6H_4PPhCH_2CH_2PPh_2)$ (70 mg, 72%).

Other reactions of vinyl esters were carried out in similar manner.

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