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REACTIONS OF (η-ALLYL)DICARBONYLMOLYBDENUM(II) COMPLEXES WITH PHOSPHORUS AND ARSENIC DONOR LIGANDS

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Summary

Reaction of $[MoX(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2]$ with the arsines $Ph_2AsCH_2CH_2AsPh_2$ (dae) and $Ph_2AsCH_2AsPh_2$ (dam) yields complexes of stoichiometry $[MoX(CO)_2(\eta\text{-}C_3H_5)dae]$ (where X = Cl, Br or I) and $[MoX(CO)_2(\eta\text{-}C_3H_5)]_2dam$ (where X = Cl or Br). The former are isomorphous with the known $Ph_2PCH_2CH_2PPh_2$ complexes, whereas the latter probably contain halogen and dam bridges. Under forcing conditions the corresponding ditertiary phosphines form the molybdenum(O) derivatives cis-$Mo(CO)_2[Ph_2P(CH_2)_nPPh_2]_2$ (where n = 1 or 2).

Introduction

The tertiary phosphines PPh_3 and $P(n\text{-}C_4H_9)_3$ react under mild conditions with $[MoX(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2]$, where X = Cl or Br, to form molybdenum(O) derivatives $[Mo(CO)_2(PR_3)_2(MeCN)_2]$ and $[Mo(CO)_2(PR_3)_3MeCN]$ [1,2]. However, under similar conditions the ditertiary phosphines

$Ph_2PCH_2PPh_2$(dpm) and $Ph_2PCH_2CH_2PPh_2$(dpe) simply displace the MeCN ligands in these starting materials with no evidence of reduction [3]. We have extended these studies to include the reactions of the corresponding arsines, and have used forcing reaction conditions to prepare molybdenum(O)-ditertiary phosphine derivatives.

Experimental

All preparations were carried out under dry nitrogen gas using solvents and reactants freed from moisture and oxygen by standard procedures. The complexes $[MoX(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2]$, where X = Cl, Br or I, were prepared by literature methods [4].

Infrared spectra were recorded on solid samples using a Perkin-Elmer 237 spectrophotometer and a Beckman-RIIC FS 720 interferometer. 'H NMR spectra were measured on a JEOL PS 100 instrument using tetramethylsilane as internal standard. Molecular weights were measured in acetone solution at 37°C on a Mechrolab 301A Osmometer.

Carbon and hydrogen analyses were determined by microanalytical techniques (Dr.Strauss, Oxford).

Preparation of $[MoX(CO)_2(\eta\text{-}C_3H_5)dae]$, where X = Cl, Br or I

A solution of 1.0 mmol (0.49 g) dae in 20 cm^3 acetone was added to 1.0 mmol $[MoX(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2]$ dissolved in 15 cm^3 acetone. The solution was stirred and warmed to 50°C for 0.5 hr and the solvent evaporated to low bulk at room temperature. On cooling the products (complexes I-III) crystallised out as orange solids which were filtered off and recrystallised from $CHCl_3$/petroleum ether. Yields 40-60%.

Preparation of $[MoX(CO)_2(\eta\text{-}C_3H_5)]_2dam$, where X = Cl or Br

1 mmol (0.47 g) dam and 0.5 mmol $[MoX(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2]$ were dissolved separately in the minimum quantity of acetone and then stirred together at room temperature. The products (IV and V) were filtered off and recrystallised as above. Yields 40-50%.

No other products were identified in the dae or dam reactions even in refluxing acetone or acetonitrile in the presence of a large excess of ligand.

Preparation of cis-$Mo(CO)_2[Ph_2P(CH_2)_nPPh_2]$, where n = 1 or 2

1 mmol $[MoX(CO)_2(\eta-C_3H_5)(MeCN)_2]$ was heated under reflux in 30 cm^3 MeCN with 3 mmol dpe or dpm for 2 hr. The yellow product which precipitated from solution on cooling was filtered off, washed with a little acetone and recrystallised from $CHCl_3$/petroleum ether (yields up to 70%).

Reactions of $[MoCl(CO)_2(\eta-C_3H_5)(MeCN)_2]$ with PPh_3 and $AsPh_3$

1:2 mol ratios of $[MoCl(CO)_2(\eta-C_3H_5)(MeCN)_2]$ and ZPh_3 (Z = P or As) were dissolved in the minimum volume of acetone maintained at ice-salt temperatures. After 1 hr the solution was filtered and treated dropwise with petroleum ether to precipitate products VI and VII as yellow solids, which were recrystallised from CH_2Cl_2/petroleum ether. Yields 66 and 22% respectively. Complex VII was also formed when the $AsPh_3$ reaction was carried out in boiling MeCN.

The corresponding bromo- and iodo-starting materials reacted with PPh_3 in acetone at low temperatures to produce cis-$Mo(PPh_3)_2(CO)_4$ in low yields (15-20%).

Reactions of $[MoCl(CO)_2(\eta-C_3H_5)]_2$dam with other ligands

(a) Pyridine. 0.5 mmol (0.46 g) of complex IV was dissolved in 5 cm^3 $CHCl_3$ and treated with 2 cm^3 pyridine. The solution was stirred at room temperature and the product $[MoCl(CO)_2(\eta-C_3H_5)py_2]$ precipitated by the dropwise addition of petroleum ether. Yield 65%.

(b) Tetraphenylarsonium chloride. 0.5 mmol (0.46 g) of complex IV dissolved in 5 cm^3 CH_2Cl_2 was stirred at room temperature with 0.5 mmol (0.21 g) Ph_4AsCl dissolved in the minimum volume of CH_2Cl_2. Addition of petroleum ether (40-60) precipitated $Ph_4As[Mo_2(CO)_4(\eta-C_3H_5)_2Cl_3]$ in 90% yield.

(c) $Ph_2PCH_2PPh_2$. 1.0 mmol (0.93 g) of complex IV was mixed with 2.0 mmol (0.77 g) dpm in 15 cm^3 acetonitrile and refluxed 1.5 hr. The

TABLE 1

ANALYTICAL AND SELECTED INFRARED DATA (cm^{-1})

Complex	Analyses found (calcd.)(%) C	H	Decomp. point (^{o}C)	Mol.wt found (calcd.)	ν(C-O)[a]	ν(M-X)
$MoCl(CO)_2(\eta-C_3H_5)dae$ (I)	52.0 (52.1)	3.9 (4.1)	171	710 (715)	1935 1850	242
$MoBr(CO)_2(\eta-C_3H_5)dae$ (II)	48.2 (49.0)	4.1 (3.8)	173	746 (759)	1940 1850	161
$MoI(CO)_2(\eta-C_3H_5)dae$ (III)	46.0 (46.2)	3.6 (3.6)	185	788 (806)	1940 1855	139
$[MoCl(CO)_2(\eta-C_3H_5)]_2dam$ (IV)	41.5 (41.9)	3.0 (3.2)	156		1948, 1932 1868, 1848	249 217(m)
$[MoBr(CO)_2(\eta-C_3H_5)]_2dam$ (V)	38.2 (41.3)	3.1 (3.2)	133	990 (1018)	1944, 1932 1870, 1850	188 166(m)
$(Ph_3P-C_3H_5)[Mo_2(CO)_4(\eta-C_3H_5)Cl_3]$ (VI)	46.5 (46.8)	4.0 (3.8)			1942, 1927 1850(br)	273 230(m)
$(Ph_3As-C_3H_5)[Mo_2(CO)_4(\eta-C_3H_5)_2Cl_3]$ (VII)	43.9 (44.4)	3.3 (3.6)			1940, 1930 1855, 1843	271 229(m)

[a] Recorded on Nujol mulls, all bands are strong unless otherwise noted

solid which separated out on cooling was recrystallised from $CHCl_3$/petroleum ether and identified as cis-$Mo(CO)_2(dpm)_2$. Yield 85%.

Results and Discussion

Ditertiary arsine reactions

Analytical and spectroscopic data (Tables 1 and 2) show that the reactions of $[MoX(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2]$ with dae are completely analogous to those of dpe under mild conditions. Thus the cis-carbonyls and the η^3-allyl group are retained in each of the products, and both MeCN ligands are replaced by a chelating molecule of dae. In the room temperature NMR spectra, the arsine methylene protons appeared as an AA'BB' pattern, while the signals for the allyl ligand were typical of symmetrical η^3-allyls. At low temperatures however, the spectra of complexes I-III lost all fine structure and by -120°C up to six separate broad signals were observed for the allyl and methylene protons (Fig.1), indicating that the deceptively simple room temperature

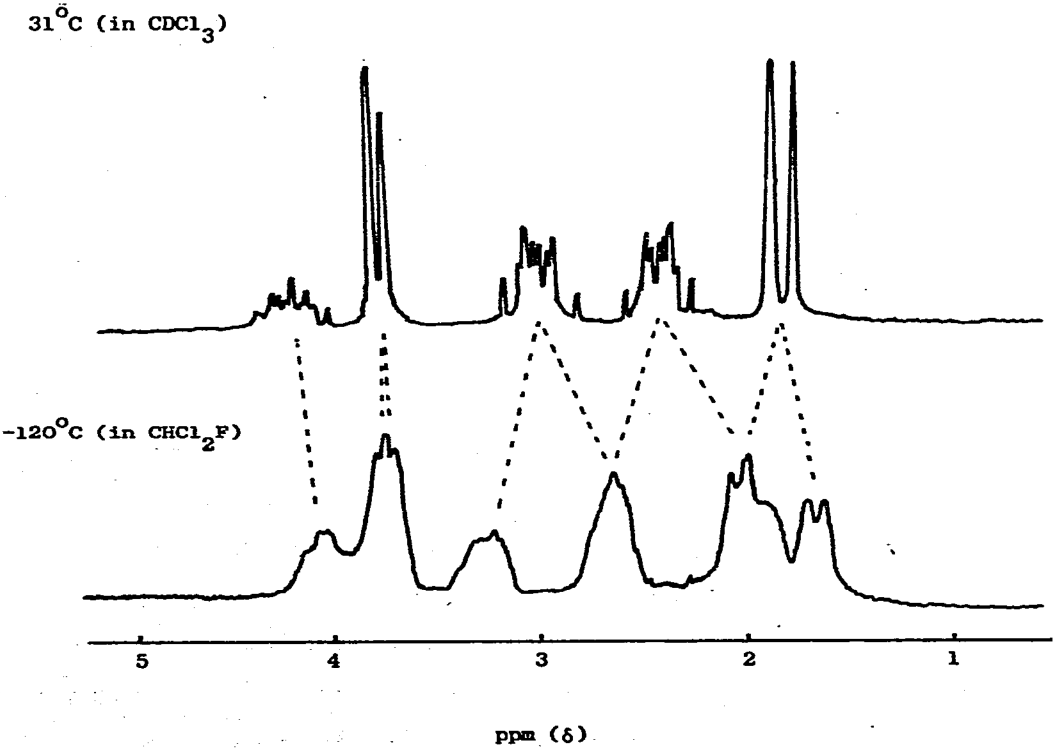


Fig.1. Variable temperature ¹H NMR of $[MoBr(CO)_2(\eta\text{-}C_3H_5)dae]$.

TABLE 2

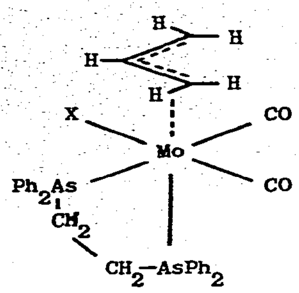
^{1}H NMR DATA[a] IN $CDCl_3$ (δ in ppm rel. to TMS, J in Hz)

Complex	η^3-C_3H_5			Methylene and	Aromatic
	H_{anti}	H_{syn}	H	η^1-C_3H_5 protons	protons
I	1.87d(10.1)	3.68d(6.5)	4.04tt	2.84m	7.44m
II	1.78d(10.0)	3.70d(6.5)	4.11tt	2.92m	7.51m
III	1.75d(10.2)	3.79d(6.7)	4.30tt	3.04m 2.40m	7.40m
IV	1.58d(10.0)	3.68d(6.2)	4.44tt	3.14s	7.30m
V	1.60d(10.0)	3.88d(6.3)	4.64tt	3.44s	7.36m
VI[b]	0.83d(9.8)	3.55d(6.7)	3.67tt	4.02br, PCH_2 5.55m, CH_2=CH	7.72m
VII	0.86d(9.8)	3.35d(6.7)	3.70tt	4.10d(7.0)$AsCH_2$ 5.53m, CH_2 5.64m, CH	7.70m

[a] d = doublet, tt = triplet of triplets, m = multiplet, br = broad

[b] ^{31}P decoupled spectrum

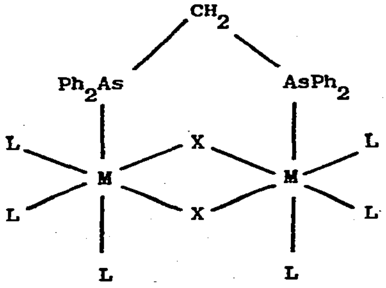
spectra were caused by the stereochemical nonrigidity of the molecule. The low temperature splitting of the allyl signals revealed the nonequivalence of the two ends of the allyl group, and consequently a molecular structure which lacks a plane of symmetry through the allyl group is indicated. In the solid state, complexes I–III were found to be isomorphous with their dpe analogues, and consequently the type of structure recently found for $[MoX(CO)_2(\eta$-$C_3H_5)dpe]$, where X = Cl or I [5] seems likely at least for complexes I and III.



In refluxing acetonitrile no reduction to Mo(O) occurred in the presence of excess dae, although under these conditions the corresponding ditertiary phosphine (dpe) caused reductive elimination of allyl halide and yielded cis-[$Mo(CO)_2(dpe)_2$] in high yields.

$Ph_2AsCH_2AsPh_2$ did not react in an analogous manner to either dae or dpm. The complexes formed (IV and V) had an allyl to dam ratio of 2:1, and an NMR investigation of various mixtures of [$MoX(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2$] and dam in $CDCl_3$ gave no indication of more than this one type of complex. The chemical shifts of the methylene protons of the coordinated arsine fell between the values normally found for monodentate and chelated dam and were consistent with a bridging mode of coordination [6]. In order that the Mo(II) atom retains its 18e configuration, more than one bridging ligand must be present, and a dam and halide bridged structure analogous to that reported for the isoelectronic complexes [$Re_2(CO)_6Cl_2$dam] [7] and [$W_2(CO)_4(NO)_2X_2$dam] [6] seems likely therefore.

Support for this type of structure was obtained from far-infrared studies. For the rhenium complex [$Re_2(CO)_6Cl_2$dam], Colton [8] assigned

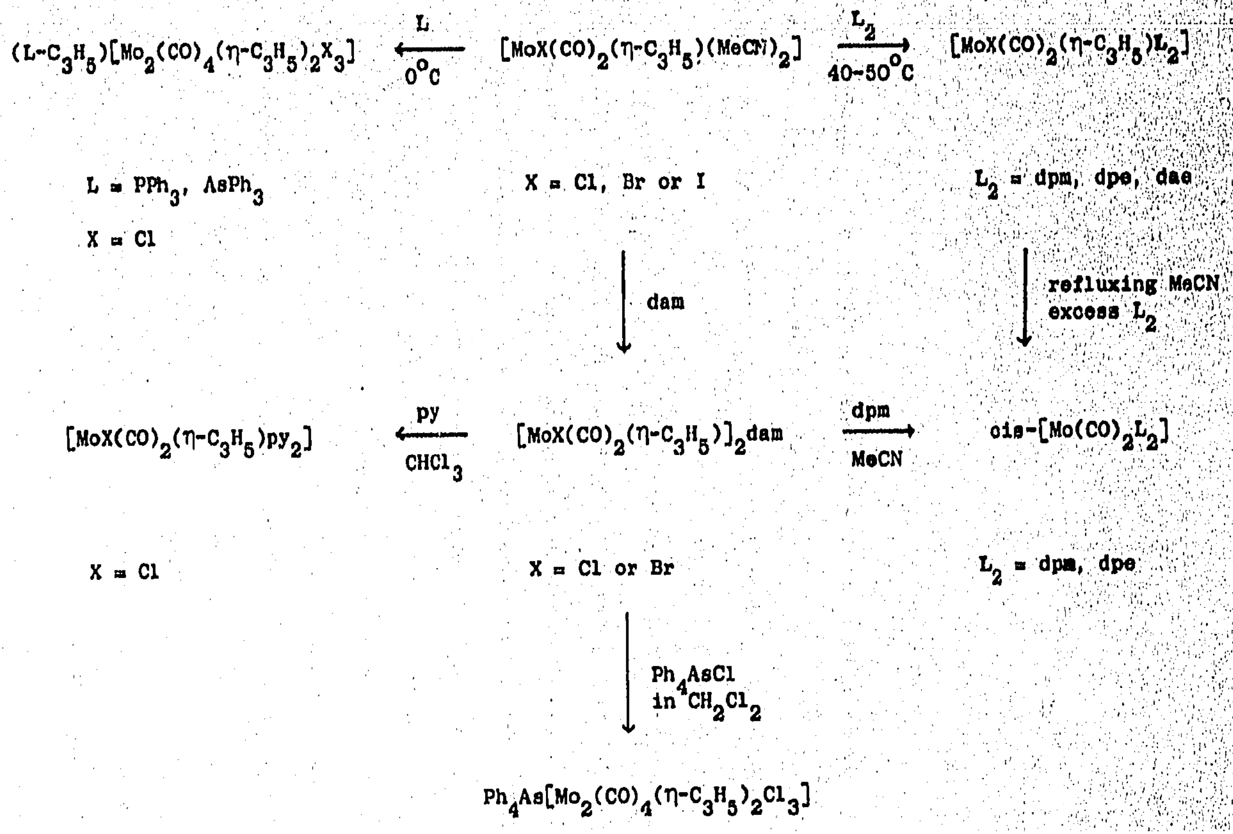


M = Mo, X = Cl or Br, 3L = 2CO and $\eta^3\text{-}C_3H_5$

M = Re, X = Cl, L = CO

M = W, X = halide, 3L = 2CO and NO

REACTION SCHEME



bands at 283(s) and 230(m) to ν(Re–Cl) bridging stretches. Complexes IV and V exhibited a similar pattern of halogen sensitive bands, whereas complexes (I)–(III), which contain only terminal Mo–X linkages showed single strong M–X stretches (Table 1). Variable temperature NMR studies indicate that complexes IV and V are also fluxional in solution. The sharply defined room temperature allyl signals become broad featureless bands by –40°C and then revert at still lower temperatures to a normal AM_2X_2 spectrum shifted to slightly lower fields. The non-splitting of the low temperature allyl signals indicates that the molecule finally adopts a symmetrical structure with the allyl groups probably <u>trans</u> to the arsenic ligands and <u>cis</u> to both bridging halides. The non-formation of the iodo-complex under similar reaction conditions may reflect the weaker bridging capacity of this halide ion.

Attempts to replace bridging dam by dpm resulted in no reaction under mild conditions and complete disruption and reduction of the complex with the formation of cis-$[Mo(CO)_2(dpm)_2]$ in high yield in refluxing MeCN. Reaction of complex IV with pyridine and with Ph_4AsCl resulted in displacement of the arsine ligand and formation of the known products $[MoCl(CO)_2(\eta\text{-}C_3H_5)py_2]$ and $Ph_4As[Mo_2(CO)_4(\eta\text{-}C_3H_5)_2Cl_3]$ (Reaction scheme).

Ditertiary phosphine reactions

Reaction of dpe and dpm with $[MoX(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2]$, where X = Cl, Br or I, led to the initial formation of the complexes $[MoX(CO)_2(\eta\text{-}C_3H_5)L_2]$, where L_2 = dpe or dpm [3]. In the presence of excess ligand in boiling MeCN reduction of Mo(II) to Mo(O) occurred with the formation of <u>cis</u>-$[Mo(CO)_2(L_2)_2]$. This reductive elimination reaction can be accomplished in polar solvents other than acetonitrile and is similar to the reaction between the nitrile starting materials and the tertiary phosphines PPh_3 and $P(n\text{-}C_4H_9)_3$. However, in these latter reactions there is no report of any intermediate Mo(II) complex of the type $[MoX(CO)_2(\eta\text{-}C_3H_5)(PR_3)_2]$ as a precursor of the reduced products.

We have reinvestigated the reactions of the nitrile starting materials with PPh_3 under very mild conditions, and have extended the investigation to include $AsPh_3$ as well. In no instance have we been able to isolate $[MoX(CO)_2(\eta\text{-}C_3H_5)(ZPh_3)_2]$, where Z = P or As and X = Cl, Br or I. The only molybdenum compounds which were identified positively in these reactions were the salts $(Ph_3Z\text{-}C_3H_5)[Mo_2(CO)_4(\eta\text{-}C_3H_5)_2Cl_3]$, and the reduced product <u>cis</u>-$Mo(PPh_3)_2(CO)_4$. Dieck <u>et al</u> observed similar products in their studies on the phosphine reactions [1,2]. The differing reactivities of PPh_3 and $P(n\text{-}C_4H_9)_3$ (which cause reduction) compared with $PHPh_2$, $Ph_2PCH_2PPh_2$ and $Ph_2PCH_2CH_2PPh_2$ (which form stable molybdenum(II) adducts under ambient conditions) may be related to variations in the electronic and/or steric effects of the phosphines. A valid comparison between the electronic effects of monodentate and bidentate phosphines is difficult to obtain, but the steric requirements of the ligands are well documented [9], and have been shown to increase along the series $Ph_2PCH_2PPh_2 < Ph_2PCH_2CH_2PPh_2 < PHPh_2 < P(n\text{-}C_4H_9)_3 < PPh_3$, with the two phosphines which readily cause reduction having cone angles greater than 130°, whereas the remainder have cone angles between 120 and 130° [9].

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