Inorganica Chimica Acta, 103 (1985) 111–112

Synthesis of Molybdenum(IV) Aryloxides

SHARON BESHOURI, TIMOTHY W. COFFINDAFFER, SHAHIN PIRZAD and IAN P. ROTHWELL*

Department of Chemistry, Purdue University, West Lafayette, Ind. 47907, U.S.A.

Received November 26, 1984

Abstract

The reaction of the molybdenum(IV) dimethylamido complex $Mo(NMe_2)_4$ with a series of alkylated phenols has been examined. Only mononuclear, paramagnetic products were obtained from the reaction in contrast to the di- and polynuclear products obtained with aliphatic alcohols. The stoichiometry of the final products is dependent on the size of the phenol, 4-methylphenol (HOAr-4Me) leading to the octahedral $Mo(OAr\text{-}4Me)_4(HNMe_2)_2$ while 2,6-di-isopropylphenol ($HOAr\text{-}2,6Pr^i_2$) will only substitute three of the amido ligands to give $Mo(OAr\text{-}2,6Pr^i_2)_3(NMe_2)(HNMe_2)$. Treatment of the hydride $MoH_4(PMe_2Ph)_4$ with 4-methylphenol also leads to a mononuclear molybdenum(IV) aryloxide, $Mo(OAr\text{-}4Me)_4(PMe_2Ph)_2$ with the evolution of H_2.

Introduction

In a recent series of papers [1–4], we reported the reactivity of the dinuclear dimethylamides $M_2(NMe_2)_6$ (M = Mo, W) towards aryl-alcohols. Although only simple substitution products were obtained for tungsten, a number of dinuclear products containing various metal–metal bond orders were obtained from the reaction of the molybdenum amide [4]. The products obtained were found to be extremely sensitive to the steric requirements of the aryloxide group. We have extended this study to the discrete, mononuclear molybdenum(IV) complex $Mo(NMe_2)_4$ [5]. Chisholm and co-workers have shown that alcoholysis of this complex can lead to a series of molybdenum(IV) alkoxides whose molecularity is strongly dependent on the size of the alkyl substituent [6]. The use of isopropyl-alcohol results in the dinuclear $Mo_2(OPr^i)_8$ for which both spectroscopic [6] and structural data [7] is consistent with the presence of a molybdenum–molybdenum double bond. In contrast we wish to report here our findings that only mononuclear, paramagnetic aryloxides can be obtained by this reaction. Related mononuclear aryloxides of molybdenum(IV) have also been obtained by use of the hydride $Mo(H)_4(PMe_2Ph)_4$.

Results and Discussion

We have examined the reactivity of $Mo(NMe_2)_4$ with a series of alkylated phenols of varying steric demand. The products along with their analytical and some spectroscopic data are collected in Table I. The sterically less demanding 4-methyl and 3,5-dimethylphenols react rapidly (>4 equiv) with purple $Mo(NMe_2)_4$ in hexane to produce deep brown solutions from which crystals of product (1) and (2) are obtained on standing, eqn. 1. Data is consistent with

$$Mo(NMe_2)_4 + 4HOAr\text{-}4Me \longrightarrow Mo(OAr\text{-}4Me)_4(HNMe_2)_2\ (1) + 2HNMe_2 \qquad (1)$$

these complexes containing octahedral molybdenum(IV) metal centers, presumably with *trans*-coordinated dimethylamine ligands similar to $Mo(OSiMe_3)_4(HNMe_2)_2$ which has been structurally characterized [6]. The lack of ready dissociation of dimethylamine from these complexes to generate polynuclear compounds $[Mo(OAr)_4]_n$, analogous to those seen with alkoxides [6], is consistent with the poorer σ-donor ability of aryloxides compared to alkoxides [1].

With the more sterically demanding 2,6-methylphenol, total substitution of amido groups is seen but the product isolated (3) contains only one coordinated dimethylamine ligand, eqn. 2. Presumably the extra steric pressure of the 2,6-dialkyl substitutents

$$Mo(NMe_2)_4 + 4HOAr\text{-}2,6Me_2 \longrightarrow Mo(OAr\text{-}2,6Me_2)_4(HNMe_2)\ (3) + 3HNMe_2 \qquad (2)$$

prevents further coordination of dimethylamine. The structure of this five coordinate complex is uncertain and the prediction of either a square pyramidal or tbp geometry is not straightforward. However, a stoichiometrically similar adamantoxide has been isolated by Wilkinson [8] and shown to adopt a tbp structure with axial $HNMe_2$.

Increasing the steric demand of the aryloxide by use of 2,6-di-isopropyl- or 2-tert-butyl, 6-methylphenol results in the substitution of only three amido ligands to generate a five coordinate complex of stoichiometry $Mo(OAr)_3(NMe_2)(HNMe_2)$, (4) and

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*Author to whom correspondence should be addressed.

0020-1693/85/$3.30

TABLE I. Analytical and Physical Data.

Complex	%C	%H	%N	g	μ_{eff} B.M.
$Mo(OAr\text{-}4Me)_4(HNMe_2)_2$ (1)	62.42 (62.53)	6.86 (6.89)	4.65 (4.56)	1.9405	1.10
$Mo(OAr\text{-}3,5Me_2)_4(HNMe_2)_2$ (2)	65.03 (64.46)	7.52 (7.15)	4.15 (4.17)	1.9366	–
$Mo(OAr\text{-}2,6Me_2)_4(HNMe_2)$ (3)	65.24 (65.32)	6.87 (6.90)	2.30 (2.24)	1.9300	1.31
$Mo(OAr\text{-}2Bu^t, 6Me)_3(NMe_2)(HNMe_2)$ (4)	66.72 (65.81)	8.63 (8.77)	3.66 (4.15)	1.9629	1.25
$Mo(OAr\text{-}2,6Pr^i)_3(NMe_2)(HNMe_2)$ (5)	67.02 (67.06)	8.97 (8.93)	3.51 (3.91)	1.9308	–
$Mo(OAr\text{-}4Me)_4(PMe_2Ph)_2$ (6)	65.09 (66.00)	6.32 (6.29)	7.33 (7.74)	1.9271	1.79

(5), eqn. 3. Clearly a large number of isomers are possible for this complex.

$$Mo(NMe_2)_4 + 3HOAr\text{-}2,6Pr^i{}_2 \longrightarrow Mo(OAr\text{-}2,6Pr^i{}_2)_3(NMe_2)(HNMe_2)\ (5) + 2HNMe_2 \qquad (3)$$

Another route to analogous molybdenum(IV) phenoxides that we have explored is the displacement of hydrogen from the tetra-hydride $MoH_4(PMe_2Ph)_4$ [9]. Addition of 4-methylphenol to this complex in benzene results in the rapid evolution of dihydrogen and the formation of an intense red solution from which the bis-phosphine adduct (6) can be obtained, eqn. 4. Addition of free phosphine to the bis-amine adduct also generates this complex. Presumably *trans*-phosphine ligands are present analogous to the amine complex. All of the compounds (1)–(6) are paramagnetic at room temperature giving magnetic moments between 1 and 2 B.M. as determined by Evan's method in benzene solution. A broad resonance was also present in the EPR spectrum (Table I) for these d^2-complexes.

$$MoH_4(PMe_2Ph)_2 + 4HOAr\text{-}4Me \longrightarrow Mo(OAr\text{-}4Me)_4(PMe_2Ph)_2\ (6) + 4H_2 + 2PMe_2Ph \qquad (4)$$

Experimental

All manipulations were carried out under an inert atmosphere of dry N_2. The compounds $Mo(NMe_2)_4$ and $MoH_4(PMe_2Ph)_4$ were prepared by the literature methods. Phenolic reagents were purchased (Aldrich Co.) and dried prior to use. Analyses were carried out by Galbraith Analytical Services. The synthesis of compounds (1)–(5) involved essentially identical reaction conditions and hence the procedure for the synthesis of only (1) is outlined in detail.

Preparation of $Mo(OAr\text{-}4Me)_4(HNMe_2)_2$ (1)

To a solution of $Mo(NMe_2)_4$ (0.52 g) in hexane was added 4-methylphenol (0.87 g; 4.2 equiv.). The initially purple solution immediately darkened to deep-brown and over a period of 1 hour brown crystals of product (1) were given. Yield = 78%.

Preparation of $Mo(OAr\text{-}4Me)_4(PMe_2Ph)_2$ (6)

To a solution of $MoH_4(PMe_2Ph)_4$ (1.0 g) in benzene was added 4-methylphenol (0.70 g; 4.4 equiv.). Bubbles of H_2 were immediately formed and the resulting deep-red solution was evaporated to a red oil from which the product was obtained as a red powder on addition of hexane. Yield = 65%.

Acknowledgement

Financial support for this research from the National Science Foundation is gratefully acknowledged.

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