Synthesis of hexanuclear molybdenum clusters containing phosphine oxide ligands

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We report the direct preparation of two new octahedral hexanuclear molybdenum cluster complexes containing phosphine oxide ligands, namely, $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$ and $[Mo_6(\mu_3\text{-}Cl)_8(OPEt_3)_2Cl_4]$, from Mo_6Cl_{12} and the corresponding phosphine oxide ligands. Both of these complexes were characterized by NMR and IR spectroscopies, cyclic voltammetry and elemental analysis. Further, a single-crystal X-ray structure determination of $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$ was obtained: $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$ crystallizes in the monoclinic space group, $P2_1/n$ with $a = 10.0685(16)$ Å, $b = 15.617(2)$ Å, $c = 15.693(3)$ Å, $\beta = 91.799(5)°$, and $R1 = 0.0288$. A *trans* arrangement of the phosphine oxide ligands was observed, where both ligands are bonded to the molybdenum cluster through the oxygen atoms. We also investigated the reaction of $[Mo_6(\mu_3\text{-}Cl)_8\{P(n\text{-}Pr)_3\}_2Cl_4]$ with a variety of oxidizing agents and found that the coordinated tri(n-propyl)phosphine ligands are cleanly oxidized by H_2O_2 to the corresponding phosphine oxides, yielding $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$.

Introduction

Octahedral hexanuclear cluster complexes containing the basic formula, $[M_6(\mu_3\text{-}X)_8L_6]^n$ comprise an important class of high nuclearity transition metal cluster complexes. The structural similarities between these octahedral hexanuclear cluster complexes and single metal octahedral complexes have been noted in the literature;[1–3] both types of complexes contain six non-bridging ligands arranged in an octahedral fashion around an octahedral hexanuclear metal core or single metal center. Despite numerous reports involving octahedral hexanuclear cluster complexes,[4–7] there are limited examples of octahedral hexanuclear cluster complexes containing mixed terminal ligands, especially with phosphine oxide ligands.

Our group is interested in investigating the preparation and reactivity of mixed terminal ligand cluster complexes containing the $[Mo_6(\mu_3\text{-}Cl)_8]^{4+}$ core. The only mixed terminal ligand octahedral hexanuclear molybdenum cluster complexes reported to date are those with the basic formula $[Mo_6(\mu_3\text{-}Cl)_8L_2Cl_4]$ (where L = neutral ligand) which are generated when strong donor ligands are reacted with the polymeric Mo_6Cl_{12}. For example, Saito *et al.* generated a family of $[Mo_6(\mu_3\text{-}Cl)_8(PR_3)_2Cl_4]$ (R = n-Pr, n-Bu and n-Pen) cluster complexes by reacting the appropriate tertiary phosphine ligand with Mo_6Cl_{12}.[8] Similarly, other neutral ligands such as pyridine, dimethylformamide and dimethylsulfoxide react with Mo_6Cl_{12}, generating $[Mo_6(\mu_3\text{-}Cl)_8L_2Cl_4]$ cluster complexes.[9,10] Notably, $[Mo_6(\mu_3\text{-}Cl)_8(OPPh_3)_2Cl_4]$ is the only known $[Mo_6(\mu_3\text{-}Cl)_8L_2Cl_4]$ complex, containing phosphine oxide ligands, reported to date.[11] Unfortunately, very little is known about this cluster complex.

Tertiary phosphine (PR_3) and tertiary phosphine oxide (OPR_3) ligands play an important role in transition metal chemistry due to the fact that the steric and electronic properties of the ligands can be tuned by modifying the substituents bonded to the phosphorus atom. It is for this reason that tertiary phosphine ligands, in particular, have played such an important role in the development of organometallic catalysts. We became interested in the preparation of cluster complexes containing phosphine oxide ligands during an attempt to grow single crystals of $[Mo_6(\mu_3\text{-}Cl)_8\{P(n\text{-}Pr)_3\}_2Cl_4]$. Unfortunately, the crystal data that was obtained could not be solved due to disorder. However, the data suggested that the phosphine ligands may have been air oxidized during the crystallization process resulting in the production of clusters containing phosphine oxide ligands.

In this paper we report the direct syntheses of $[Mo_6(\mu_3\text{-}Cl)_8(OPEt_3)_2Cl_4]$ and $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$ from Mo_6Cl_{12} and the corresponding phosphine oxide ligands. The characterization of these complexes includes an X-ray crystal structure analysis of $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$. In addition, we discuss how the coordinated $P(n\text{-}Pr)_3$ ligands in the $[Mo_6(\mu_3\text{-}Cl)_8\{P(n\text{-}Pr)_3\}_2Cl_4]$ complex can be oxidized by O_2, trimethylamine-*N*-oxide, and hydrogen peroxide. We compare and contrast our results to other studies involving the oxidation of coordinated phosphine ligands.

Experimental

Reagents and general procedures

Mo_6Cl_{12} and $[Mo_6(\mu_3\text{-}Cl)_8\{P(n\text{-}Pr)_3\}_2Cl_4]$ were prepared according to previously published procedures.[8,12] Air drying of $[Mo_6(\mu_3\text{-}Cl)_8(PR_3)_2Cl_4]$ did not lead to the formation of $[Mo_6(\mu_3\text{-}Cl)_8(OPR_3)_2Cl_4]$ or OPR_3 (R = Et or n-Pr). Me_3NO was purchased from Aldrich and H_2O_2 (30%) was purchased from Fisher; both of these reagents were used as received. All manipulations involving Mo_6Cl_{12} were done under an inert atmosphere using glove box techniques. The product complexes $[Mo_6(\mu_3\text{-}Cl)_8L_2Cl_4]$ (L = $OP(n\text{-}Pr)_3$ or $OPEt_3$) were found to be air stable.

Instrumentation

^{31}P and ^{1}H NMR spectra were recorded on a Varian 400 MHz Mercury Spectrophotometer equipped with a tunable probe. ^{31}P NMR spectra were proton decoupled and externally referenced to 85% H_3PO_4. The electrochemical studies were carried out in

anhydrous CH_2Cl_2 (Aldrich) using a BAS CV-27 potentiostat equipped with an *x-y* recorder. A conventional three electrode cell consisting of a platinum disk working electrode, a platinum wire auxiliary electrode and a $Ag/AgNO_3$ (0.01 M) reference electrode was used. The potentials were related to the SCE reference electrode using a value of 0.46 V *vs.* SCE for the ferrocene/ferrocenium couple in CH_2Cl_2.[13] Elemental analyses were performed by the Microanalysis Laboratory at the University of Illinois, Urbana, 61801.

Synthesis of $[Mo_6(\mu_3\text{-}Cl)_8(OPEt_3)_2Cl_4]$

67.0 mg (0.5 mmol) of $OPEt_3$ was added to a solution of 200 mg (0.20 mmol) of Mo_6Cl_{12} in 20 mL of absolute ethanol in an inert atmosphere glove box. The reaction mixture was brought out of the glove box and stirred overnight at room temperature under a N_2 atmosphere. The resulting yellow precipitate was filtered, washed with ethanol, and air dried (460 mg, 90%). ^{31}P NMR ($CDCl_3$): δ 84.37 (s, *trans*), 84.07 (s, *cis*). ^1H NMR ($CDCl_3$): δ 1.18 (m, 18H, CH_2CH_3), 1.88 (m, 12H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): 5.78 (d, CH_2CH_3), 18.85 (d, CH_2CH_3). IR (KBr) ν_{P-O} 1101 cm^{-1}. Anal. calc. for $C_{12}H_{30}O_2P_2Mo_6Cl_{12}$: C, 11.45; H, 2.38. Found C, 11.06; H, 2.39%.

Synthesis of $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$

52 mg (0.36 mmol) of $OP(n\text{-}Pr)_3$ was added to a solution containing 190 mg (0.19 mmol) of Mo_6Cl_{12} in 20 mL of absolute ethanol in an inert atmosphere glove box. The reaction mixture was brought out of the glove box and stirred overnight at room temperature under a N_2 atmosphere. The resulting yellow precipitate was filtered, washed with ethanol, and air dried (220 mg, 80%). ^{31}P NMR ($CDCl_3$): δ 79.36 (s, *trans*), 79.00 (s, *cis*). ^1H NMR ($CDCl_3$): δ 1.05 (m, 18H, $PCH_2CH_2CH_3$), 1.5 (m, 12, $PCH_2CH_2CH_3$), 1.8 (m, 12, $PCH_2CH_2CH_3$). IR (KBr) ν_{P-O} 1086 cm^{-1}. Anal. calc. for $C_{18}H_{42}O_2P_2Mo_6Cl_{12}$: C, 15.97; H, 3.13. Found C, 15.87; H, 2.99%.

Oxidation of $[Mo_6(\mu_3\text{-}Cl)_8\{P(n\text{-}Pr)_3\}_2Cl_4]$ with H_2O_2

90 mg (0.068 mmol) of $[Mo_6(\mu_3\text{-}Cl)_8\{P(n\text{-}Pr)_3\}_2Cl_4]$ was dissolved in 30 mL of acetone. 1.5 mL of 30% H_2O_2 was added to this solution and then stirred under N_2 at room temperature for 2 d. After reducing the volume of the reaction mixture to approximately 5 mL, solid precipitated. This solid was collected, washed with water and air dried (83 mg, 90%). ^{31}P NMR ($CDCl_3$): δ 79.31 (s, *trans*), 78.96 (s, *cis*). Anal. calc. for $C_{18}H_{42}O_2P_2Mo_6Cl_{12}\cdot H_2O$: C, 15.76; H, 3.23. Found C, 15.37; H, 2.98%.

Oxidation of $[Mo_6(\mu_3\text{-}Cl)_8\{P(n\text{-}Pr)_3\}_2Cl_4]$ with Me_3NO

30 mg (0.022 mmol) of $[Mo_6(\mu_3\text{-}Cl)_8\{P(n\text{-}Pr)_3\}_2Cl_4]$ was dissolved in 10 mL of distilled THF. To this solution 3.5 mg (0.047 mmol) of Me_3NO was added and the resulting solution was stirred under N_2 at room temperature for 15 min. The solution was reduced to dryness under vacuum. ^{31}P NMR (acetone-d_6): δ 45.77 (s, $OP(n\text{-}Pr)_3$), other smaller peaks were present at 55.89, 31.2 and 31.05.

X-Ray data

Data collection and refinement. Single crystals of $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$ were grown *via* solvent diffusion out of $CHCl_3$ and hexanes. Two different types of yellow crystals were observed. A crystal representative of the major crystalline form (or major isomer) was chosen and mounted using oil (Paratone-N, Exxon) to a thin glass fiber and centered on a Bruker CCD Smart System diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation at 193 K. Data collection and reduction were performed using the Bruker SMART v5 and Bruker Saint v5 package of programs. The

structure was solved by direct methods and refined by full-matrix least-squares on F^2 using Bruker SHELXTL v5. Inversion symmetry was imposed on the host complex and the proposed model includes two disordered sites for each idealized propyl moiety.

Crystal data. $C_{18}H_{42}Cl_{12}Mo_6O_2P_2\cdot(CHCl_3)_2$, M = 1592.23, monoclinic, a = 10.0685(16), b = 15.617(2), c = 15.693(3) Å, β = 91.799(5)°, T = 193 K, space group $P2_1/n$, Z = 2, μ(Mo-Kα) = 2.542 mm^{-1}, 18342 reflections measured, 4492 independent reflections (R_{int} = 0.0507), for all data $R1$ = 0.0491 and $wR2$ = 0.0672, for 3341 intensities with $I > 2\sigma$ $R1$ = 0.0288 and $wR2$ = 0.0626.

CCDC reference number 180468.

See http://www.rsc.org/suppdata/dt/b2/b200792d/ for crystallographic data in CIF or other electronic format.

Results and discussion

With our preparation of $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$ and $[Mo_6(\mu_3\text{-}Cl)_8(OPEt_3)_2Cl_4]$ we established that trialkylphosphine oxide ligands can be directly incorporated into mixed terminal ligand octahedral hexanuclear cluster complexes. As with single metal octahedral complexes, both *cis*- and *trans*-isomers are possible when cluster complexes containing the basic formula $[Mo_6(\mu_3\text{-}Cl)_8L_2L'_4]$ (where L and L′ are different monodentate ligands) are prepared. Saito and co-workers reported different ^{31}P NMR spectroscopic resonances for *cis*- and *trans*-$[Mo_6\text{-}(\mu_3\text{-}Cl)_8(PR_3)_2Cl_4]$, and Willer *et al.* reported that ^{31}P NMR spectroscopy can be used to distinguish between *cis*- and *trans*-$[Re_6(\mu_3\text{-}S)_8(PEt_3)_2Br_4]$.[8,14] The ^{31}P NMR spectral data for $[Mo_6(\mu_3\text{-}Cl)_8(OPEt_3)_2Cl_4]$ and $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$ indicate the presence of one major product (or isomer) and one minor product. Numerous attempts to separate the isomers using column chromatography were unsuccessful and led to decomposition of the complex. Based on the report that the reaction of Mo_6Cl_{12} with tertiary phosphines resulted in the formation of *trans*-$[Mo_6(\mu_3\text{-}Cl)_8(PR_3)_2Cl_4]$ in greater than 90% yield, we predicted that the *trans* isomer of $[Mo_6\text{-}(\mu_3\text{-}Cl)_8(OPR_3)_2Cl_4]$ was our major product and the *cis* isomer the minor product in our ^{31}P NMR spectrum.[8] An X-ray diffraction study of $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$ was conducted in order to unambiguously determine the relative orientation of the tertiary phosphine oxide ligands about the cluster core in this complex.

Our phosphine oxide complexes display IR spectra typical for phosphine oxide ligands coordinated to transition metal centers (ν(P–O) at 1086 and 1101 cm^{-1}).[15] In addition, the ν(P–O) for $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$ is 61 cm^{-1} lower than ν(P–O) of free $OP(n\text{-}Pr)_3$, while ν(P–O) for $[Mo_6(\mu_3\text{-}Cl)_8\text{-}(OPEt_3)_2Cl_4]$ is 51 cm^{-1} lower than ν(P–O) of free $OPEt_3$. Cotton *et al.* observed a similar trend for the P–O stretching frequencies of free and coordinated $OPPh_3$ and $OPMe_3$ and a variety of transition metal complexes containing these ligands.[16]

The structure of $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$ is shown in Fig. 1 and selected bond distances and angles are reported in Table 1. The Mo–Cl terminal bond lengths of Mo(2)–Cl(5) (2.4103(11) Å) and Mo(3)–Cl(6) (2.4220(12) Å) are significantly different (difference = 0.0117 Å). Even though there is a large difference between the Mo–Cl terminal bond lengths, they are still within the observed range for previously reported terminal Mo–Cl bond lengths in structurally similar cluster complexes (2.4018(22)–2.445(7) Å).[8,17,18] In addition, the bond lengths of the 24 electron cluster core are similar to those reported for other $[Mo_6(\mu_3\text{-}Cl)_8]^{4+}$ containing clusters. For example, $[Mo_6(\mu_3\text{-}Cl)_8\{OP(n\text{-}Pr)_3\}_2Cl_4]$ has an average Mo–(μ_3-Cl) bond length of 2.473(4) Å and an average Mo–Mo bond length of 2.601(3) Å. Values for similar molybdenum cluster complexes are 2.4556(17) to 2.506(7) Å, and 2.5889(5) to 2.6277(8) Å,

Table 1 Selected bond lengths (Å) and angles (°) for [Mo$_6(\mu_3$-Cl)$_8$-{OP(n-Pr)$_3$}$_2$Cl$_4$]

Mo(1)–O(1)	2.080(3)	Mo(1)–Cl(2)	2.4721(11)
Mo(1)–Cl(4)	2.4679(11)	Mo(2)–Cl(5)	2.4103(11)
Mo(1)–Cl(3)	2.4694(11)	Mo(3)–Cl(6)	2.4220(12)
Mo(1)–Cl(1)	2.4706(11)	P(1)–O(1)	1.489(3)
O(1)–Mo(1)–Cl(4)	90.67(10)	O(1)–Mo(1)–Cl(2)	93.05(10)
O(1)–Mo(1)–Cl(3)	91.89(10)	Cl(4)–Mo(1)–Cl(2)	176.28(4)
Cl(4)–Mo(1)–Cl(3)	90.15(4)	Cl(3)–Mo(1)–Cl(2)	89.79(4)
O(1)–Mo(1)–Cl(1)	92.10(10)	Cl(1)–Mo(1)–Cl(2)	90.07(4)
Cl(4)–Mo(1)–Cl(1)	89.74(4)	P(1)–O(1)–Mo(1)	171.1(2)
Cl(3)–Mo(1)–Cl(1)	176.01(4)		
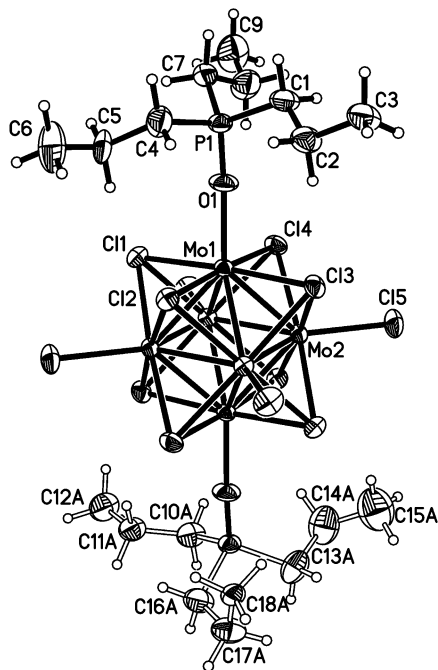
Fig. 1 SHELXTL (Bruker, 1998) plot of *trans*-[Mo$_6(\mu_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$] showing 35% probability ellipsoids for non-H atoms and circles of arbitrary size for H atoms.

respectively.[8,17–19] The Mo–Cl–Mo bond angles of *trans*-[Mo$_6(\mu_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$] are also in agreement with those reported for *cis*-[Mo$_6(\mu_3$-Cl)$_8$(PEt$_3$)$_2$Cl$_4$].[17]

Examining the OP(n-Pr)$_3$ ligand, the Mo(1)–O(1) bond length of 2.080(3) Å lies within the observed range (Mo–O = 2.065–2.370 Å) for monodentate tertiary phosphine oxide ligands coordinated to molybdenum centers.[20–23] In addition, the P(1)–O(1) bond length of 1.489(3) Å, is within the range observed for tertiary phosphine oxide ligands coordinated to transition metal centers.[20–27] However, ∠Mo(1)–O(1)–P(1), 171.1(2)°, is larger than the average ∠Mo–O–P (approximately 155°). In fact, [MoCl$_2$(NH)O(OPEtPh$_2$)$_2$], which contains a ∠Mo–O–P of 171.9(6)°, is the only other complex reported to contain an ∠Mo–O–P larger than that found in *trans*-[Mo$_6$-(μ_3-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$].[28] This high angle indicates linear coordination.

Electrochemical studies of [Mo$_6(\mu_3$-Cl)$_8$(OPEt$_3$)$_2$Cl$_4$] and [Mo$_6(\mu_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$] have also been conducted. Interestingly, cyclic voltammetric data for both complexes display quasi-reversible oxidative waves at $E_{1/2}$ = 1.91 V vs. SCE, and irreversible reductive waves at −1.36 V vs. SCE. Thus, the Et *versus* n-Pr substituents of the phosphine oxide ligands do not appear to affect the electrochemistry of [Mo$_6(\mu_3$-Cl)$_8$-(OPEt$_3$)$_2$Cl$_4$] and [Mo$_6(\mu_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$]. The cyclic voltammogram of (Bu$_4$N)$_2$[Mo$_6(\mu_3$-Cl)$_8$Cl$_6$] is reported to have an oxidative wave ($E_{1/2}$ = 1.56 V vs. SCE) as well as a quasi-reversible reductive wave ($E_{1/2}$ = −1.53 V vs. SCE); both

of these redox processes are assigned as single electron processes.[29] The redox potentials for the tertiary phosphine oxide cluster complexes appear at more positive potentials as compared to the [Mo$_6(\mu_3$-Cl)$_8$Cl$_6$]$^{2-}$ complex, which is expected based on the difference in the overall charges of these cluster complexes.

Oxidation studies

Free tertiary phosphines are readily oxidized by a variety of oxidants, including O$_2$, H$_2$O$_2$ and oxometal complexes.[30] However, the oxidation of coordinated tertiary phosphine ligands to coordinated phosphine oxide ligands is not as common.[31] We report here our findings on the reaction of [Mo$_6(\mu_3$-Cl)$_8$-{P(n-Pr)$_3$}$_2$Cl$_4$] with three different oxidizing agents: O$_2$, H$_2$O$_2$, and trimethylamine-*N*-oxide (Me$_3$NO).

Initial oxidation studies were conducted using O$_2$ as the oxidant, based on other reports of coordinated tertiary phosphine ligands being converted to coordinated tertiary phosphine oxide ligands in the presence of air or O$_2$.[32] Molecular oxygen was bubbled through a 1 : 2 MeCN : CH$_2$Cl$_2$ solution containing [Mo$_6(\mu_3$-Cl)$_8${P(n-Pr)$_3$}$_2$Cl$_4$] for 6 hours. The ^{31}P NMR spectrum of the product obtained from this reaction indicated the presence of a trace amount of [Mo$_6$-(μ_3-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$], confirming our suspicion that coordinated P(n-Pr)$_3$ can be oxidized by molecular oxygen (based on our previous attempts to recrystallize [Mo$_6$-(μ_3-Cl)$_8${P(n-Pr)$_3$}$_2$Cl$_4$]). However, the oxidation by O$_2$ was not a clean reaction; in addition to a substantial amount of unreacted [Mo$_6(\mu_3$-Cl)$_8${P(n-Pr)$_3$}$_2$Cl$_4$] present after the reaction, approximately 15 other signals were present in the ^{31}P NMR spectrum of this product. We did not investigate this reaction further since it was clear that the oxidation of [Mo$_6(\mu_3$-Cl)$_8${P(n-Pr)$_3$}$_2$Cl$_4$] with O$_2$ was not an efficient means of preparing [Mo$_6(\mu_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$].

Reaction of [Mo$_6(\mu_3$-Cl)$_8${P(n-Pr)$_3$}$_2$Cl$_4$] with excess H$_2$O$_2$ over a period of two days resulted in a clean conversion of [Mo$_6(\mu_3$-Cl)$_8${P(n-Pr)$_3$}$_2$Cl$_4$] to [Mo$_6(\mu_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$]. The product that was isolated, in almost quantitative yield, was identified as [Mo$_6(\mu_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$] by ^{31}P NMR spectroscopy and elemental analysis. As expected the major isomer was determined to be *trans*-[Mo$_6(\mu_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$-Cl$_4$] using ^{31}P NMR spectroscopy. Shorter reaction times resulted in the observation of unreacted starting material and an intermediate product, proposed to be [Mo$_6(\mu_3$-Cl)$_8${OP-(n-Pr)$_3$}{P(n-Pr)$_3$}Cl$_4$], based on the ^{31}P NMR chemical shift. H$_2$O$_2$ is a common oxidant used to oxidize non-coordinated tertiary phosphines to the corresponding phosphine oxides.[33] In addition, there are reports involving the H$_2$O$_2$ driven oxidation of strained chelating phosphine ligands to dangling phosphine oxides.[34,35] For example, Brill *et al.* reported that the oxidation of [(η^5-C$_5$H$_5$)Co(P–P)I]I (where P–P = Ph$_2$P(CH$_2$)$_4$PPh$_2$ and is coordinated through both P donor atoms) by H$_2$O$_2$ yields [(η^5-C$_5$H$_5$)Co(P–P(O))I$_2$] (where P–P(O) = Ph$_2$P(CH$_2$)$_4$P(O)Ph$_2$ and is only coordinated through the P atom).[34] However, to the best of our knowledge, the oxidation of [Mo$_6(\mu_3$-Cl)$_8$-{P(n-Pr)$_3$}$_2$Cl$_4$] to [Mo$_6(\mu_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$] is the only report of an apparently coordinated monodentate tertiary phosphine ligand being oxidized to a coordinated tertiary phosphine oxide ligand. One possible explanation for the observed reactivity is that the cluster complex, [Mo$_6(\mu_3$-Cl)$_8$-{P(n-Pr)$_3$}$_2$Cl$_4$], is in equilibrium with trace amounts of [Mo$_6(\mu_3$-Cl)$_8${P(n-Pr)$_3$}Cl$_4$] and free P(n-Pr)$_3$. Since H$_2$O$_2$ is capable of oxidizing free P(n-Pr)$_3$, the dissociated P(n-Pr)$_3$ could be oxidized by H$_2$O$_2$ and then coordinate to the molybdenum cluster core as OP(n-Pr)$_3$. Mechanisitic studies need to be conducted to determine whether or not this is occurring.

The third oxidant that we investigated was trimethylamine-*N*-oxide. Me$_3$NO has frequently been used as a decarbonylating agent in the substitution of carbonyl ligands coordinated to

transition metal centers.[36] Me$_3$NO is proposed to nucleophilically attack a CO ligand, generating CO$_2$, Me$_3$N, and an open coordination site at the metal center. Using this strategy, carbonyl ligands are often replaced with tertiary phosphine ligands, transforming M–CO to M–PR$_3$ moieties. Since most free tertiary phosphines, including triphenylphosphine and trimethylphosphine, are not oxidized by Me$_3$NO under decarbonylation conditions,[36] tertiary phosphines can be reacted directly with transition metal carbonyl complexes in the presence of Me$_3$NO. The only free phosphine reported to be oxidized by Me$_3$NO is PPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe,[37] however, there are a few examples where the uncoordinated phosphorus atom of η^1-bidentate phosphine ligands is oxidized by Me$_3$NO. For example, the uncoordinated phosphorus atoms in [Cp$_2$-Rh$_2$(CO)(μ-η^1:η^1-CF$_3$C$_2$CF$_3$){η^1-Ph$_2$P(CH$_2$)$_4$PPh$_2$}] and [Cr-(CO)$_5$(η^1-dppe)] are oxidized to uncoordinated (or dangling) phosphine oxides.[38,39] The oxidation of [Cr(CO)$_5$(η^1-dppe)] is believed to be a metal assisted oxidation.

In this study we reacted [Mo$_6$(μ$_3$-Cl)$_8${P(n-Pr)$_3$}$_2$Cl$_4$] with two equivalents of Me$_3$NO for a 15 minute period; surprisingly the ^{31}P NMR spectral analysis of the product showed that the major product was that of *free* OP(n-Pr)$_3$. Thus the oxidation of [Mo$_6$(μ$_3$-Cl)$_8${P(n-Pr)$_3$}$_2$Cl$_4$] with Me$_3$NO involved phosphine oxidation as well as phosphine oxide ligand loss. There are two reports in the literature that discuss the oxidation of coordinated phosphine ligands to free phosphine oxides *via* Me$_3$NO oxidation;[39,40] [Re$_2$(CO)$_9$]$_2$(μ-dppf) (where dppf = 1,1′-bis(diphenylphosphino)ferrocene) is oxidized to [Re$_2$(CO)$_9$(η^1-dppfO)], and [Cp$_2$Rh$_2$(CO)(μ-η^1:η^1-CF$_3$C$_2$CF$_3$){μ-η^1:η^1-Ph$_2$P(CH$_2$)$_2$PPh$_2$}Cr(CO)$_5$] is oxidized to [Cp$_2$Rh$_2$(CO)(μ-η^1:η^1-CF$_3$C$_2$CF$_3$){η^1-Ph$_2$P(CH$_2$)$_2$P(O)Ph$_2$}]. In the oxidation of [Cp$_2$Rh$_2$(CO)(μ-η^1:η^1-CF$_3$C$_2$CF$_3$){μ-η^1:η^1-Ph$_2$P(CH$_2$)$_2$PPh$_2$}- Cr(CO)$_5$] it was suggested that a Cr–P bond is broken prior to P oxidation based on the fact that the uncoordinated phosphorus atom in [Cp$_2$Rh$_2$(CO)(μ-η^1:η^1-CF$_3$-C$_2$CF$_3$){η^1-Ph$_2$P(CH$_2$)$_4$PPh$_2$}] can be oxidized by Me$_3$NO (*vide supra*).

Interestingly, since dppf can not be oxidized with Me$_3$NO it has been proposed that during the oxidation of dppf in [Re$_2$(CO)$_9$]$_2$(μ-dppf), the bridging ferrocenyl moiety dissipates charge causing the phosphorus atom to be more susceptible to nucleophilic attack than free dppf.[40] By analogy, since P(n-Pr)$_3$ is not oxidized when it is reacted with Me$_3$NO under the same conditions as [Mo$_6$(μ$_3$-Cl)$_8${P(n-Pr)$_3$}$_2$Cl$_4$],[41] we suspect that the [Mo$_6$(μ$_3$-Cl)$_8$]$^{4+}$ core promotes the stoichiometric oxidation of coordinated P(n-Pr)$_3$ to free OP(n-Pr)$_3$. One way the molybdenum core could facilitate the oxidation reaction is if it is electron deficient enough to make the coordinated phosphine ligands susceptible to nucleophilic attack by Me$_3$NO.

Summary

We have reported the preparation of two new molybdenum cluster complexes containing tertiary phosphine oxide ligands, [Mo$_6$(μ$_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$] and [Mo$_6$(μ$_3$-Cl)$_8$(OPEt$_3$)$_2$Cl$_4$], as well as a crystal structure determination of *trans*-[Mo$_6$-(μ$_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$]. In addition, we investigated the reactivity of [Mo$_6$(μ$_3$-Cl)$_8${P(n-Pr)$_3$}$_2$Cl$_4$] with different oxidizing agents. Notably, the reaction of [Mo$_6$(μ$_3$-Cl)$_8${P(n-Pr)$_3$}$_2$Cl$_4$] with H$_2$O$_2$ and Me$_3$NO, generates [Mo$_6$(μ$_3$-Cl)$_8${OP(n-Pr)$_3$}$_2$Cl$_4$] and free OP(n-Pr)$_3$, respectively. The chemistry involving the [Mo$_6$(μ$_3$-Cl)$_8$]$^{4+}$ core yields novel results and warrants further investigation. Our future studies will focus on the mechanisms of these oxidation reactions.

Acknowledgements

References and notes

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41 When free $P(n\text{-}Pr)_3$ was reacted with Me_3NO under the same conditions as described for the oxidation of $[Mo_6(\mu_3\text{-}Cl)_8\{P(n\text{-}Pr)_3\}_2Cl_4]$ with Me_3NO, $6.0 \pm 2.5\%$ of the product was $OP(n\text{-}Pr)_3$ and the remainder was unreacted $P(n\text{-}Pr)_3$. The same procedure was followed without the addition of Me_3NO; in this case $7.6 \pm 5.1\%$ of the product was $OP(n\text{-}Pr)_3$. Therefore, within experimental error, the same percentage of phosphine oxide is formed in the absence and presence of Me_3NO.