Inorg. Chem. **1985**, *24*, 2846–2849

complexes of this structural type may be capable of existing in *four different* electronic configurations that correspond to formal metal–metal bond orders of 1.5 (see Table IV).

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Registry No. $[Re_2Cl_3(dppm)_2(NCCH_3)_2](PF_6)_2$, 97391-38-3; $[Re_2Cl_3(dppm)_2(NCCH_3)_2](PF_6)$, 95345-98-5; $[Re_2Cl_3(dppm)_2(NCC_2H_5)_2](PF_6)_2$, 97391-40-7; $[Re_2Cl_3(dppm)_2(NCC_2H_5)_2](PF_6)$, 95345-96-3; $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2](PF_6)_2$, 97391-42-9; $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2](PF_6)$, 95345-94-1; $[Re_2Cl_6(dppm)_2]PF_6$, 96438-01-6; $[Re_2Cl_3(dppm)_2]BF_4$, 96322-62-2; $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(dppm)_2]$, 96343-32-7; $[Re_2Cl_6(dppm)_2]H_2PO_4\cdot H_3PO_4\cdot 4H_2O$, 96322-64-4; $Re_2Cl_6(dppm)_2$, 58312-74-6; Re, 7440-15-5; cobaltocene, 1277-43-6.

Supplementary Material Available: Details of the structure solution, listings of the experimental details (Table S1), positional parameters for the hydrogen atoms (Table S2), thermal parameters (Table S3), bond distances and bond angles (Table S4), torsional angles (Table S5), and observed and calculated structure factors, and a figure showing the full atomic numbering scheme (Figure S1) for the crystal structure of $[Re_2Cl_6(dppm)_2]H_2PO_4\cdot H_3PO_4\cdot 4H_2O$ (39 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Kansas State University, Manhattan, Kansas 66506

Reactivity of Molybdenum Oxo–Imido Complexes with Organophosphines: Generation and Chemistry of $[Mo^{V}(Ntol)(S_2CNEt_2)_2]_2O$ and $Mo^{IV}(Ntol)(S_2CNEt_2)_2$

DAVID D. DEVORE and ERIC A. MAATTA*

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The oxo–imido molybdenum(VI) dithiocarbamate complex $MoO(Ntol)L_2$ (tol = *p*-tolyl; L = S_2CNEt_2) reacts with 0.5 equiv of Ph_3P or $EtPh_2P$ to produce the dinuclear Mo(V) complex $[Mo(Ntol)L_2]_2O$ and the corresponding phosphine oxide. An oxo-bridged structure for the dinuclear complex is indicated by IR and ^{17}O NMR studies. The visible spectrum of the dinuclear complex displays an intense absorption at 533 nm that does not obey the Lambert–Beer law; this observation is interpreted in terms of an equilibrium disproportionation reaction, whereby $Mo^{IV}(Ntol)L_2$ and $Mo^{VI}O(Ntol)L_2$ are produced via Mo–O bond scission in the dimer. Support for this proposition is provided by the fact that toluene solutions of $[Mo(Ntol)L_2]_2O$ react with Ph_3P or $EtPh_2P$ to produce the corresponding phosphine oxide and $Mo(Ntol)L_2$, which has been trapped as its dimethyl acetylenedicarboxylate (DMAC) adduct, $Mo(Ntol)(DMAC)L_2$. Solutions of $Mo(Ntol)L_2$ react with O_2 to regenerate $MoO(Ntol)L_2$; this reaction, in combination with the above oxygen-abstraction reaction, thus completes a catalytic cycle for the oxidation of tertiary phosphines. Solutions containing $Mo(Ntol)L_2$ react similarly with Me_2SO to afford Me_2S and $MoO(Ntol)L_2$.

Introduction

An important aspect of the reactivity of *cis*-dioxomolybdenum(VI) complexes is their ability to function as oxygen atom transfer reagents. By far, the most extensively studied class of such reactions involves oxygen atom transfer to tertiary-phosphine substrates.[1-21] In all cases, the initial products of these reactions are an oxomolybdenum(IV) species and a tertiary-phosphine oxide as depicted in eq 1. However, in most but not

$$Mo^{VI}O_2L_2 + R_3P \rightarrow Mo^{IV}OL_2 + R_3PO \qquad (1)$$

all[22] instances, the nascent $Mo^{IV}OL_2$ species is rapidly intercepted by unreacted $Mo^{VI}O_2L_2$, producing an oxo-bridged Mo(V) dimer, $Mo_2O_3L_4$ (eq 2). The ultimate isolation of $Mo^{IV}OL_2$ products

$$Mo^{IV}OL_2 + Mo^{VI}O_2L_2 \rightarrow Mo^{V}{}_2O_3L_4 \qquad (2)$$

in these systems depends upon the reversibility of eq 2; that is, the $Mo^{V}{}_2O_3L_4$ species must participate in the disproportionation equilibrium depicted in eq 3.[23] Disproportionation of the

$$Mo^{V}{}_2O_3L_4 \rightleftharpoons Mo^{VI}O_2L_2 + Mo^{IV}OL_2 \qquad (3)$$

$Mo^{V}{}_2O_3L_4$ species is markedly dependent on the nature of the donor atoms provided by the ligands L. Thus, S,S chelates (dithiocarbamates,[1,3,9] dithiophosphates,[3,24] dithiophosphinates,[3]

Table I. Molar Absorptivity (λ = 533 nm) vs. Concentration of $[Mo(Ntol)(S_2CNEt_2)_2]_2O$ in Toluene Solution

concn, M	molar abs	concn, M	molar abs
9.6×10^{-6}	9120	3.86×10^{-5}	14560
1.93×10^{-5}	14040	1.11×10^{-4}	15800

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[22] In those cases where the ancillary ligands L in the $Mo^{IV}OL_2$ species possess sufficient bulk, the dimerization reaction of eq 2 is apparently obviated by steric constraints. See ref 19 and 21.

[23] For a cogent discussion of the kinetics of these reactions, including a summary of previous studies, see ref 20.

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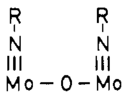
thioxanthates,[8] and possibly xanthates[25]) are effective in promoting the equilibrium of eq 3, while O,O and O,N chelates (acetylacetonate and 8-hydroxyquinolinate[3,9]) are not.

Structural similarities between analogous oxo and organoimido (NR) transition-metal complexes are well-documented.[26] However, parallels in the reactivity of such species have been established in relatively few cases.[27] We report here the results of a study of the reactions of organophosphines with *cis*-oxo(*p*-tolylimido)bis(diethyldithiocarbamato)molybdenum(VI), $MoO(Ntol)(S_2CNEt_2)_2$; these results demonstrate that many of the reaction patterns observed for oxo complexes of Mo(VI), Mo(V), and Mo(IV) are indeed displayed by their organoimido analogues.

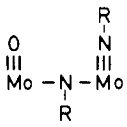
Results

When 0.5 equiv of Ph_3P or $EtPh_2P$ is added to a CH_2Cl_2 solution of $MoO(Ntol)(S_2CNEt_2)_2$, the corresponding phosphine oxide, R_3PO, is produced along with an intensely violet dinuclear Mo(V) species, $Mo_2O(Ntol)_2(S_2CNEt_2)_4$, as shown in eq 4. A priori, two core structures (A and B) are conceivable for the dinuclear complex.[28] However, the IR spectrum of the dinuclear complex is devoid of any band attributable to ν(MoO) in the 850–1000-cm^{-1} region, thus implicating the oxo-bridged structure A. Definitive evidence for structure A was obtained from ^{17}O NMR studies. The ^{17}O NMR spectrum of $Mo_2O(Ntol)_2(S_2CNEt_2)_4$ displays a single broad resonance at 643 ppm, a region characteristic of μ-bridging oxo species.[29] In contrast, the oxo-ligand resonance in the spectrum of $MoO(Ntol)(S_2CNEt_2)_2$ appears at 1002 ppm, a position within the range observed for terminal oxo species.

$$Mo^{VI}O(Ntol)(S_2CNEt_2)_2 + 0.5R_3P \rightarrow 0.5Mo^{V}{}_2O(Ntol)_2(S_2CNEt_2)_4 + 0.5R_3PO \quad (4)$$

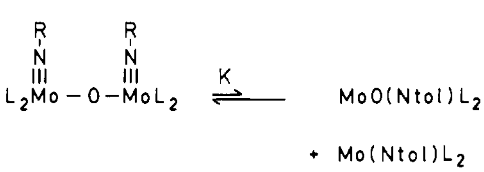


A



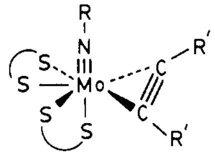
B

Further information concerning the dinuclear complex is available from visible spectroscopy. The electronic spectrum of $[Mo(Ntol)(S_2CNEt_2)_2]_2O$ in toluene displays an intense absorption at 533 nm. However, this band does not obey the Beer–Lambert law, as shown in Table I. Similar, albeit more marked, deviations from Beer law behavior have been observed previously in the spectra of $Mo_2O_3(S_2CNR_2)_4$[1,30] and $Mo_2O_3(S_2PPh_2)_4$[3] complexes. We interpret these results as being indicative of the equilibrium disproportionation reaction shown in eq 5. Experimental support for eq 5 is provided by our observation that toluene solutions of $[Mo(Ntol)(S_2CNEt_2)_2]_2O$ react with Ph_3P or $EtPh_2P$ to afford the corresponding phosphine oxide and the reactive Mo(IV) species, $Mo(Ntol)(S_2CNEt_2)_2$. While we have not as yet isolated an analytically pure sample of $Mo(Ntol)(S_2CNEt_2)_2$, we have been able to trap this species as its dimethyl acetylenedicarboxylate (DMAC) adduct as shown in eq 6. The nonequivalence of the DMAC methyl groups in the ^1H NMR spectrum of the adduct suggests that the alkyne is positioned cis to the tolylimido group; furthermore, simple bonding arguments (analogous to those presented to describe similar oxomolybdenum alkyne complexes[31]) predict that the alkyne should be contained in the plane perpendicular to the molybdenum–imido bond, leading to the pentagonal-bipyramidal structure shown in C.



$$L_2\overset{\overset{R}{|}}{\overset{N}{\overset{|||}{Mo}}}-O-\overset{\overset{R}{|}}{\overset{N}{\overset{|||}{Mo}}}L_2 \overset{K}{\rightleftharpoons} MoO(Ntol)L_2 + Mo(Ntol)L_2 \quad (5)$$

$$[Mo(Ntol)(S_2CNEt_2)_2]_2O + EtPh_2P + 2DMAC \rightarrow 2Mo(Ntol)(DMAC)(S_2CNEt_2)_2 + EtPh_2PO \quad (6)$$



C

Toluene solutions containing $Mo(Ntol)(S_2CNEt_2)_2$ react with O_2 (1 atm) to regenerate $MoO(Ntol)(S_2CNEt_2)_2$ (eq 7). This reaction, combined with the above oxygen-abstraction reaction involving $MoO(Ntol)(S_2CNEt_2)_2$ and organophosphines, thus completes a catalytic cycle for phosphine oxidation using O_2. Similarly, toluene solutions of $Mo(Ntol)(S_2CNEt_2)_2$ react with dimethyl sulfoxide to form $MoO(Ntol)(S_2CNEt_2)_2$ and dimethyl sulfide, as shown in eq 8. The oxo analogue of the above tolylimido species, $MoO(S_2CNEt_2)_2$, displays similar reactivity toward O_2,[1,32] DMAC,[31,33] and Me_2SO.[32,34]

$$Mo(Ntol)(S_2CNEt_2)_2 + {}^1/_2O_2 \rightarrow MoO(Ntol)(S_2CNEt_2)_2 \quad (7)$$

$$Mo(Ntol)(S_2CNEt_2)_2 + Me_2SO \rightarrow MoO(Ntol)(S_2CNEt_2)_2 + Me_2S \quad (8)$$

Discussion

Previously,[35] we found that the reaction of $MoO(Ntol)(S_2CNEt_2)_2$ with HCl leads to removal of the oxo ligand with concomitant formation of $Mo(Ntol)Cl_2(S_2CNEt_2)_2$, as shown in eq 9. It is striking that organophosphine nucleophiles also remove the oxo ligand from $MoO(Ntol)(S_2CNEt_2)_2$ (eq 10). The

$$MoO(Ntol)(S_2CNEt_2)_2 + 2HCl \rightarrow Mo(Ntol)Cl_2(S_2CNEt_2)_2 + H_2O \quad (9)$$

$$MoO(Ntol)(S_2CNEt_2)_2 + R_3P \rightarrow Mo(Ntol)(S_2CNEt_2)_2 + R_3PO \quad (10)$$

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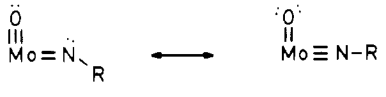
bonding of the oxo and *p*-tolylimido ligands in $MoO(Ntol)(S_2CNEt_2)_2$ can be described as a resonance hybrid of the two extreme canonical structures D and E. Since in similar complexes both tolylimido and oxo ligands are susceptible to removal by HCl,[36] the result of eq 9 suggests that the solution structure of $MoO(Ntol)(S_2CNEt_2)_2$ is polarized toward canonical form E. Thus, if the reaction shown in eq 10 occurs via direct attack of the phosphine nucleophile on a multiply bonded ligand (oxo or Ntol),[37] one would expect initial coordination of R_3P to the (less basic) imido nitrogen atom; subsequent rearrangement could then occur to produce the thermodynamically favored products R_3PO and $Mo(Ntol)(S_2CNEt_2)_2$. Alternatively, the phosphine could initially coordinate directly to the molybdenum center,[38] forcing a pair of π-bonding electrons onto one of the multiply bonded atoms;[39] subsequent migration of phosphorus to oxygen and electron transfer could again yield the observed products. On the basis of steric considerations, we favor the former pathway.



D E

$Mo(Ntol)(S_2CNEt_2)_2$ produced via eq 10 is intercepted by unreacted $MoO(Ntol)(S_2CNEt_2)_2$, leading to equilibrium formation of $[Mo(Ntol)(S_2CNEt_2)_2]_2O$ (eq 5). The intense absorption at 533 nm in the visible spectrum of the dinuclear species is characteristic of mono-oxo-bridged Mo(V) dimers and likely arises from a transition into an antibonding component of the Mo–O–Mo three-center bond.[30,40,41] Because of our inability to isolate pure $Mo(Ntol)(S_2CNEt_2)_2$, we have not been able to determine the value of the equilibrium constant K in eq 5. However, two pieces of evidence suggest that disproportionation of $[Mo(Ntol)(S_2CNEt_2)_2]_2O$ is not as extensive as in $[MoO(S_2CNEt_2)_2]_2O$. First, throughout a similar range of concentrations, changes in the apparent molar absorptivity of $[MoO(S_2CNEt_2)_2]_2O$ solutions[30] are much larger than the corresponding changes for $[Mo(Ntol)(S_2CNEt_2)_2]_2O$ solutions (Table I). Second, solutions of $[MoO(S_2CNEt_2)_2]_2O$ display ^{17}O NMR resonances due to both $MoO_2(S_2CNEt_2)_2$ and $MoO(S_2CNEt_2)_2$ as well as those due to the bridging and terminal oxygen atoms of the undissociated dimer.[29a] In the ^{17}O NMR spectrum of $[Mo(Ntol)(S_2CNEt_2)_2]_2O$, no resonance due to $MoO(Ntol)(S_2CNEt_2)_2$ was observed, suggesting that most of this dimer remains intact in solution.

A rhenium analogue of $[Mo(Ntol)(S_2CNEt_2)_2]_2O$ has been prepared by Rowbottom and Wilkinson.[42] The complex $[Re(NC_6H_5)(S_2CNEt_2)_2]_2O$ is obtained by the action of aniline on $[ReO(S_2CNEt_2)_2]_2O$. Note however that this d^2 dimer should contain a linear N–Re–O–Re–N grouping by analogy to the known[43] structure of $[ReO(S_2CNEt_2)_2]_2O$.

When $[Mo(Ntol)(S_2CNEt_2)_2]_2O$ solutions are treated with $EtPh_2P$ in the presence of dimethyl acetylenedicarboxylate, the bright yellow $Mo(Ntol)(DMAC)(S_2CNEt_2)_2$ complex (C) is produced (eq 6). To our knowledge, this is the first example of an organoimido–alkyne complex, and its isolation provides additional support for the occurrence of the disproportionation equilibrium shown in eq 5. The IR spectrum of this alkyne complex features an absorption at 1819 cm^{-1}, assignable as $\nu(C\equiv C)$ of coordinated DMAC. The position of this band is some 30 cm^{-1} lower than the corresponding absorption in the spectrum of its oxo analogue, $MoO(DMAC)(S_2CNEt_2)_2$.[31] This observation indicates that back-donation of electron density from the Mo atom to the alkyne (primarily from Mo d_{xy} to alkyne π^*) is more pronounced in the tolylimido complex. However, this interaction does not sufficiently weaken the triple bond so as to render the bound alkyne susceptible to protonation: $Mo(Ntol)(DMAC)(S_2CNEt_2)_2$ is inert to HCl in CH_2Cl_2 solution.

When a toluene solution containing $MoO(Ntol)(S_2CNEt_2)_2$ is treated with an excess of PPh_3 under an O_2 atmosphere, the color of the solution rapidly changes from orange to purple (reflecting dimer formation) and remains purple until all of the PPh_3 is oxidized to $OPPh_3$, whereupon the original orange color is restored. Although we have not investigated the kinetics of this reaction, we can say qualitatively that this catalytic oxidation is significantly slower than that catalyzed by the analogous dioxomolybdenum system.[1] We believe that this difference in rates is due primarily to the smaller extent of disproportionation in the $[Mo(Ntol)(S_2CNEt_2)_2]_2O$ system as compared with that of its oxo analogue.

Finally, it is interesting to note the difference in reactivity with O_2 of $Mo(Ntol)(S_2CNEt_2)_2$ as compared with that of another d^2 *p*-tolylimido complex, $Re(Ntol)Cl_3(PPh_3)_2$.[44] The rhenium complex reacts with O_2 in refluxing toluene to afford primarily the nitroso complex $Re(ONtol)Cl_3(OPPh_3)$ (eq 11), while the

$$Re(Ntol)Cl_3(PPh_3)_2 + O_2 \rightarrow Re(ONtol)Cl_3(OPPh_3) \qquad (11)$$

molybdenum species reacts with O_2 to yield $MoO(Ntol)(S_2CNEt_2)_2$ (eq 7) and not the nitroso species $Mo(ONtol)(S_2CNEt_2)_2$, even though the similar complex $Mo(ONC_6H_5)(S_2CNEt_2)_2$ is known.[45]

Experimental Section

All manipulations were carried out either in vacuo or under atmospheres of dry nitrogen, except as noted. Solvents employed were dried over appropriate reagents and distilled directly from the reaction vessels. $H_2{}^{17}O$ (46.5 atom % ^{17}O) was purchased from the Mound facility of Monsanto Research Corp., Miamisburg, OH. All other chemicals were of reagent grade and were used as received from standard sources. *p*-Tolyl azide was prepared from the reaction of the corresponding diazonium tetrafluoroborate salt with NaN_3 in an Et_2O/H_2O mixture; the azide was dried, distilled at 10^{-3} torr, and stored at −20 °C in the dark. $MoO(S_2CNEt_2)_2$ was prepared as described in the literature.[3]

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 1330 spectrophotometer and were calibrated with the use of a polystyrene film. ^1H (400 MHz) and ^{17}O (54.2 MHz) NMR spectra were obtained on an IBM/Bruker WM-400 instrument and are referenced to internal Me_4Si and external H_2O, respectively. Visible spectra were measured on a Cary 14 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories.

Preparation of $MoO(Ntol)(S_2CNEt_2)_2$. A portion of tolyl azide (0.173 g; 1.3 mmol) was added to a stirred solution of $MoO(S_2CNEt_2)_2$ (0.50 g; 1.2 mmol) in CH_2Cl_2 (40 mL) at room temperature. Immediate gas evolution was observed, and the solution acquired an intense violet color. After 1 h, the solution was orange. The solution was filtered and evaporated to dryness. The orange solid residue was triturated with hexane (3 × 25 mL), collected by filtration, and dried in vacuo to yield the product as an orange powder. Anal. Calcd for $C_{17}H_{27}N_3OS_4Mo$: C, 39.75; H, 5.30; N, 8.18. Found: C, 39.23; H, 5.39; N, 7.98. ^1H NMR ($CDCl_3$): δ 7.21 (AB quartet, J_{AB} = 7.5 Hz, 4 H, $C_6H_4CH_3$), 3.82 (m, 8 H, NCH_2CH_3), 2.42 (s, 3 H, $C_6H_4CH_3$), 1.29 (t, 12 H, NCH_2CH_3).

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^{17}O NMR ($C_6H_4CH_3$): δ 1002 ($\Delta\nu_{1/2}$ = 600 Hz). IR: 1512 (s), 1440 (s), 1355 (w), 1301 (w), 1282 (s), 1209 (m), 1169 (w), 1154 (w), 1096 (w), 1076 (w), 1006 (w), 969 (w), 921 (w), 874 (s), 852 (w), 829 (m), 784 (w), 647 (w), 496 (w), 438 (w) cm^{-1}.

Preparation of [Mo(Ntol)(S_2CNEt_2)$_2$]$_2$O. A portion of PPh_3 (0.128 g; 0.49 mmol) was added to a stirred solution of MoO(Ntol)(S_2CNEt_2)$_2$ (0.500 g; 0.97 mmol) in CH_2Cl_2 (25 mL) at room temperature. After 12 h, the violet solution was taken to dryness, and the purple residue was triturated with Et_2O (3 × 25 mL), collected by filtration, and dried in vacuo. Analysis of the Et_2O washings by IR and ^{31}P NMR spectroscopy revealed the presence of Ph_3PO. Elemental analysis of the purple product indicates that the dimeric complex is obtained as the CH_2Cl_2 solvate. Anal. Calcd for $C_{35}H_{56}N_6OS_8Cl_2Mo_2$: C, 38.35; H, 5.15; N, 7.67. Found: C, 38.38; H, 5.30; N, 7.89. ^1H NMR (CD_2Cl_2): δ 7.22 (AB quartet, J_{AB} = 8 Hz, 4 H, $C_6H_4CH_3$), 3.80 (m, 8 H, CH_2CH_3), 2.30 (s, 3 H, $C_6H_4CH_3$), 1.36–1.20 (m, 12 H, CH_2CH_3). ^{17}O NMR ($C_6H_4CH_3$): δ 643 ($\Delta\nu_{1/2}$ = 1300 Hz). IR: 1495 (s), 1432 (s), 1354 (m), 1323 (m), 1302 (w), 1273 (s), 1212 (m), 1171 (w), 1149 (m), 1096 (w), 1077 (m), 1007 (m), 988 (w), 916 (w), 852 (m), 831 (m), 784 (w), 754 (w), 441 (w) cm^{-1}.

Reaction of MoO(Ntol)(S_2CNEt_2)$_2$ with Excess R_3P (R_3P = Ph_3P, $EtPh_2P$) in the Presence of O_2. A solution of MoO(Ntol)(S_2CNEt_2)$_2$ (1.05 g; 2.04 mmol) in toluene (60 mL) was stirred with Ph_3P (1.85 g; 7.08 mmol; 3.5 equiv) at room temperature under one atm of O_2. The dark purple characteristic of [Mo(Ntol)(S_2CNEt_2)$_2$]$_2$O was evident until ca. 36 h later, at which time the solution was orange-brown. Solvent was evaporated and the residue was triturated with absolute ethanol (2 × 40 mL) and diethyl ether (40 mL), leaving an orange powder that was identified as MoO(Ntol)(S_2CNEt_2)$_2$ by comparison of its IR spectrum to that of an authentic sample. The combined washings were taken to dryness, yielding a white solid identified as Ph_3PO as determined by IR and ^{31}P NMR spectroscopy. A similar experiment performed with 3.4 equiv of $EtPh_2P$ required 20 h for completion; the reaction products were determined to be MoO(Ntol)(S_2CNEt_2)$_2$ and $EtPh_2PO$.

Similar results were obtained in a large-scale reaction using MoO(Ntol)(S_2CNEt_2)$_2$ (0.70 g; 1.36 mmol) and Ph_3P (12.48 g; 47.6 mmol; 35 equiv) in toluene (80 mL). In this case, the reaction mixture was heated to 50 °C for 10 h, after which heating was discontinued and the system was stirred until completion (an additional 72 h).

Reaction of MoO(Ntol)(S_2CNEt_2)$_2$ with 3 Equiv of Ph_3P and 3 Equiv of Me_2SO. To 50 mL of a toluene solution containing MoO(Ntol)(S_2CNEt_2) (0.96 g; 1.87 mmol) and PPh_3 (1.47 g; 5.6 mmol) was added 5.6 mmol of dimethyl sulfoxide in toluene (10 mL). The violet solution was stirred under N_2 at 55 °C for 24 h, after which time the reaction mixture was burnt orange. The formation of dimethyl sulfide was confirmed by GC/MS analysis. Evaporation of solvent and trituration of the residue as described above allowed the separation and recovery of MoO(Ntol)(S_2CNEt_2)$_2$ and Ph_3PO.

Preparation of Mo(Ntol)(DMAC)(S_2CNEt_2)$_2$. A solution of MoO(Ntol)(S_2CNEt_2)$_2$ (1.39 g; 2.7 mmol) in toluene (60 mL) was stirred with $EtPh_2P$ (0.64 g; 3.0 mmol) under an N_2 atmosphere at 55 °C for 1 h. A solution of dimethyl acetylenedicarboxylate (1.92 g; 13.5 mmol) in toluene (20 mL) was then added, and the mixture was stirred at 55 °C for an additional 15 h. The dark yellow solution was filtered, and toluene was removed in vacuo. The residue was triturated with Et_2O (3 × 25 mL), affording a brown powder. The powder was dissolved in a minimum amount of toluene from which yellow-brown crystals were obtained upon incremental addition of hexane. These crystals were washed with 1–2 mL of acetone, yielding a bright yellow powder which was recrystallized from acetone, affording the product as bright yellow needles. The product thus obtained is the acetone hemisolvate; drying in vacuo yields the unsolvated product. Anal. Calcd for $C_{23}H_{33}N_3O_4S_4Mo$: C, 43.18; H, 5.20; N, 6.57. Found: C, 43.39; H, 5.33; N, 6.38. ^1H NMR ($CDCl_3$): δ 7.00 (AB quartet, J_{AB} = 8.3 Hz, 4 H, $C_6H_4CH_3$), 3.93–3.50 (m, 8 H, CH_2CH_3), 3.87 (s, 3 H, DMAC(CH_3)), 3.86 (s, 3 H, DMAC(CH_3)), 2.27 (s, 3 H, $C_6H_4CH_3$), 1.35–1.15 (m, 12 H, CH_2CH_3). IR: 1819 (m), 1802 (s), 1790 (s), 1512 (sh), 1500 (s), 1436 (s), 1357 (w), 1301 (w), 1276 (m), 1238 (w), 1211 (s), 1175 (w), 1152 (m), 1089 (w), 1079 (w), 1036 (w), 1019 (w), 1008 (w), 983 (w), 916 (w), 902 (w), 852 (w), 837 (w), 826 (w), 811 (w), 782 (w), 735 (m), 603 (w), 435 (w) cm^{-1}.

Preparation of ^{17}O-Enriched MoO(Ntol)(S_2CNEt_2)$_2$ and [Mo(Ntol)(S_2CNEt_2)$_2$]$_2$O. The starting material in these preparations was ^{17}O-enriched MoO_2(S_2CNEt_2)$_2$, which was synthesized by the method of J. W. McDonald as described in ref 29d. This species was reduced by Ph_3P to provide labeled MoO(S_2CNEt_2)$_2$, which was subsequently oxidized with *p*-tolyl azide as described above to yield ^{17}O-enriched MoO(Ntol)(S_2CNEt_2)$_2$. Treatment of this species with 0.5 equiv of Ph_3P as above afforded the ^{17}O-enriched dimer [Mo(Ntol)(S_2CNEt_2)$_2$]$_2$O.

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Registry No. MoO(Ntol)(S_2CNEt_2)$_2$, 75900-17-3; $Mo^V{}_2O$(Ntol)$_2$(S_2CNEt_2)$_4$, 97391-47-4; Mo(Ntol), 97391-48-5; Mo(Ntol)(DMAC)(S_2CNEt_2)$_2$, 9739-49-6; Ph_3P, 603-35-0; $EtPh_2P$, 607-01-2; Ph_3PO, 791-28-6; $EtPh_2PO$, 1733-57-9; MoO(S_2CNEt_2)$_2$, 25395-92-0; Me_2SO, 67-68-5; tolyl azide, 2101-86-2.

Notes

Contribution from the Department of Chemistry,
The Royal Military College of Science,
Shrivenham, Wiltshire, SN6 8LA, United Kingdom,
and The Materials Quality Assurance Directorate,
Woolwich, London, SE18 6TD, United Kingdom

Preparation, Characterization, and Properties of Platinum(0) Complexes with Tri-*n*-butyl Phosphite, Tri-*n*-butylarsine, and Tri-*n*-butylstibine

D. H. Goldsworthy,[1a] F. R. Hartley,*[1a] G. L. Marshall,[1b] and S. G. Murray*[1a]

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Our current interest in the chemistry of long-alkyl-chain phosphine complexes of group 8–10 metals[2,34] prompted us to examine the chemistry of low-valent metal compounds with the less well studied ligands of phosphite, arsine, and stibine, especially their reactivity toward oxidative addition. In particular, by development of coordinative unsaturation at the metal center, some progress toward the synthesis of highly reactive metal complexes, capable of reacting with C–H bonds, might be achieved, with the greater electron-acceptor ability of phosphites compared with that of phosphines to promote oxidative addition. It was hoped that the greater flexibility within the P–O–R linkages compared with that of P–R[3] would also enable easier access to the metal center by an incoming substrate; this should also be the case for the larger donor atoms of arsenic and antimony. The *n*-butyl group would be expected to impart a greater degree of solubility to these complexes, compared to shorter alkyl chain derivatives, without hindering access to the metal as observed for larger *n*-alkyl groups.[2,4]

Experimental Section

All manipulations and reactions were carried out under an atmosphere of white spot nitrogen that had previously been passed through a column

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