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SPECTROSCOPIC EVIDENCE FOR HEMILABILE BEHAVIOR IN A β -KETOPHOSPHONATE COMPLEX OF MOLYBDENUM(VI)

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ABSTRACT

The β -ketophosphonate complexes dichlorodioxo(diethyl(2-phenyl-2-oxoethyl)phosphonate)molybdenum(VI) (5a) and dichlorodioxo(triethylphosphonoacetate)molybdenum (VI) (5b) have been synthesized in 61-80% yield and characterized by NMR and IR spectroscopies. The crystal structure of (5a) (orthorhombic, $2_12_12_1$, a = 8.0909 (5) Å, b = 14.1432 (5) Å, c = 14.9749 (8) Å, Z = 4) shows that the β -ketophosphonate ligand is coordinated to the molybdenum atom in a bidentate binding mode. In solution, compound (5a) displays hemilabile behavior as revealed by an IR spectrum recorded in CH₃CN. Reaction of (5a) with diphenylsulfoxide (DPSO) in CH₂Cl₂ results in complete displacement of the β -ketophosphonate ligand and formation of dichlorodioxobis(diphenylsulfoxide)-molybdenum(VI) (8) in 96% yield.

INTRODUCTION

A multidentate, chelating ligand which is able to coordinate to a metal through a combination of donor atoms in which one ligand component is either displaced by an incoming ligand or leaves an open coordination site, has been described as hemilabile. Ligands which demonstrate hemilabile behavior in solution have been known for some time

and a few isolated examples of their use in transition metal catalyzed organic transformations have been documented. Figure 1 shows several transition metal complexes containing this unique type of ligand which have been used successfully in homogeneous catalysis. The cobalt complex (1) contains two ether-functionalized phosphine ligands and is an extremely active catalyst for the homologation of methanol to ethanol¹ and a thioether-phosphine rhodium complex (2) efficiently catalyzed the transfer hydrogenation of ketones.² Mirkin has also reported related rhodium hydrogenation catalytsts.³ Braunstein reported that a βketophosphine complex of palladium (3) catalyzed the telomerization of butadiene and carbon dioxide to give a variety of oxygenated products.⁴ All of the above examples of hemilabile ligands contain both soft phosphorus and hard oxygen or sulfur donor atoms. Cole-Hamilton demonstrated that the molybdenum dioxo complex (4) successfully catalyzed the epoxidation of olefins and tentatively suggested that the high activity of the complex was due to the hemilabile nature of the β -ketophosphonate ligand, one of the few reported examples of a hemilabile ligand containing the same atom as part of the donor set.⁵ We recently communicated our own studies on the high activity of a closely related complex in the catalytic oxidation of diaryl and dialkyl sulfides.⁶ In order that further exploitation of this type of ligand in homogeneous catalysis may be achieved, we felt it necessary to establish unambiguously the hemilabile nature of the functionalized phosphonate ligand, and the results of this study are described below.

EXPERIMENTAL

<u>General Data.</u> All reactions were conducted under dry, pre-purified N₂ using standard Schlenk-line and catheter-tubing techniques. IR spectra were recorded on a Mattson Galaxy 6020 (FT) spectrometer. All ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker AC-300 spectrometer and referenced to internal tetramethylsilane (¹H), CDCl₃ (¹³C) and external H₃PO₄ (³¹P). Microanalyses were performed by Atlantic Microlab.

Solvents were purified as follows: benzene, hexane, THF and ether, distilled from sodium/benzophenone; CH₂Cl₂, distilled from CaH₂, CDCl₃ (Cambridge Isotope Laboratories), used as received.

Reagents were obtained as follows: diphenylsulfoxide (Aldrich), recrystallized from CH_2Cl_2 /hexane; acetonitrile (Fisher Scientific), distilled from CaH_2 ; triethyl phosphonoacetate (Aldrich); MoO_2Cl_2 (Alfa), used as received. Diethyl (2-phenyl-2-oxoethyl)phosphonate was prepared according to the literature procedure.⁷

<u>Dichlorodioxo(diethyl(2-phenyl-2-oxoethyl)phosphonate)molybdenum(VI)</u> (5a). A flame-dried Schlenk flask was charged with $Mo_2O_2Cl_2$ (1.85 g, 9.30 mmoles), THF (2.5 mL), and a stirrer bar. A solution of diethyl (2-phenyl-2-oxoethyl)phosphonate (2.38 g, 9.30



Fig 1. Catalytically Active Transition Metal Complexes Containing Hemilabile Ligands.

mmoles) in THF (2.5 mL) was then added via cannular. After stirring for 1 h, the solvent was removed under oil pump vacuum and the residue treated with ether (15 mL). Pale blue crystals formed which were collected by filtration, washed with ether (5 mL) and dried under oil-pump vacuum. A second crop was analogously isolated following further addition of ether (15 mL) to the filtrate. The crops were combined to give (**5**b) (3.40 g, 7.44 mmoles, 80 %). IR (cm⁻¹, Nujol mull): v(C=O) 1644, v(P=O) 1192, v(Mo=O) 961, 914 cm⁻¹. ¹H NMR (CDCl₃): δ 8.09 (d, J = 7.9 Hz, 2H of C₆H₅, o), 7.74 (t, J = 7.4 Hz, 1H of C₆H₅, p), 7.55 (t, J = 7.8 Hz, 2H of C₆H₅, m), 4.35 (m, 2CH₂O), 4.02 (d, $J_{HP} = 22.4$ Hz, CH₂P), 1.33 (t, J = 7.1 Hz, 2CH₃). ¹³C{¹H} NMR (CDCl₃): δ 197.27 (s, br, CO), 136.72-129.38 (5C of C₆H₅.), 135.19 (d, $J_{CP} = 5.5$ Hz, C₆H₅, i), 66.06 (d, $J_{CP} = 6.9$ Hz, OCH₂), 32.67 (d, $J_{CP} = 136.5$ Hz, CH₂), 16.03 (d, $J_{CP} = 6.3$ Hz, CH₃). ³¹P{¹H}</sup> NMR (CDCl₃): δ 25.4 (s). Anal. Calcd for C₁₂H₁₇Cl₂MoO₆P (454.96 g/mole): C, 31.67; H, 3.77. Found: C, 31.55; H, 3.77.

<u>Dichlorodioxo(triethylphosphonoacetate)molybdenum(VI) (5b).</u> A flame-dried Schlenk flask was charged with $Mo_2O_2Cl_2$ (2.664 g, 13.40 mmoles), THF (5 mL), and a stirrer bar. A solution of diethyl (2-phenyl-2-oxoethyl)phosphonate (3.000 g, 13.40 mmoles) in THF (5 mL) was then added via cannular. After stirring for 1 h, the solvent was removed under oil pump vacuum, the residue dissolved in ether (15 mL), reduced to half volume and cooled to -

20 °C. Blue cubes formed which were collected by filtration, washed with ether (3 x 5 mL) and dried under oil-pump vacuum. A second crop was analogously isolated after storing the filtrate for several days at -20 °C. The crops were combined to give (**5b**) (3.458 g, 61 %). IR (cm⁻¹, Nujol mull): v(C=O) 1642, v(P=O) 1192, v(Mo=O) 961, 916 cm⁻¹. ¹H NMR (CDCl₃): δ 4.47 (q, CH₂OC), 4.34 (q, CH₂OP J = 6.9 Hz), 3.24 (d, J_{HP} = 21.0 Hz, CH₂P), 1.33 (overlapping multiplets, 3CH₃). ³¹P{¹H} NMR (CDCl₃): δ 24.9 (s). Anal. Calcd for C₇H₁₇Cl₂MoO₇P (410.95 g/mole): C, 22.71; H, 4.08. Found: C, 22.75; H, 4.08.

Dichlorodioxobis(diphenylsulfoxide)molybdenum(VI) (8). A flame-dried Schlenk flask was charged with (5a) (0.238 g, 0.523 mmoles), CH_2Cl_2 (10 mL), and a stirrer bar. Then diphenylsulfoxide (1.052 g, 5.201 mmoles) was added as a solid. The solution was stirred for 90 min. and the solvent removed under oil-pump vacuum. The residue was treated with benzene (5 mL) and a blue powder was obtained which was washed with benzene (3 x 5 mL), collected by filtration and dried under oil-pump vacuum to give (8) (0.302 g, 0.501 mmoles, 96 %). IR (cm⁻¹, nujol mull): v(S=O) 1001, 966 cm⁻¹, v(Mo=O) 936, 909 cm⁻¹. ¹H NMR (CDCl₃): δ 7.63-7.36 (m, 4C₆H₅). Anal. Calcd for C₂₄H₂₀Cl₂MoO₄S₂ (603.15 g/mole): C, 47.77; H, 3.34. Found: C, 47.72; H, 3.35.

Crystal Structure of (5a). A clear, colorless prism of (5a) was grown from CH₂Cl₂/hexane at -25 °C and mounted for data collection on a Enraf Nonius CAD-4 diffractometer which was controlled with a DEC MicroVAX computer and the Enraf Nonius VAX/VMS CAD4 Express control program. Cell constants were obtained from 25 reflections with $35^\circ < 2\theta <$ 41.4°. Data were corrected for Lorentz and polarization factors and reduced to F_0^2 and $(F_0)^2$ using the program XCAD. The SHELXTL program package was implemented to determine the orthorhombic acentric space group and apply the absorption correction. The structure was determined by direct methods using the program XS with the successful location of the four heavy atoms, molybdenum, two chlorines and one phosphorus. The remaining non-hydrogen atoms were found from one subsequent difference-Fourier map. The structure was refined with XL. Refinement continued with all atoms refined anisotropically. Hydrogen atoms were placed in calculated positions, these being dependent on both the type of bonding at the carbon, and the temperature (153 K) with the aromatic hydrogens calculated with d(C-H) = 0.950 and U_H set equal to $1.2U_{(parent)}$ and methyl hydrogens were initially determined with a rotational Fourier about the central carbon atom that was further optimized for tetrahedral geometry with d(C-H) = 0.980; U_H set equal to 1.5U(parent) and methylene hydrogens were placed in tetrahedral positions with d(C-H) = 0.990; U_H set equal to 1.2U(parent).

RESULTS AND DISCUSSION

Synthesis and Properties

The addition of one equivalent of β -ketophosphonate to a suspension of molybdenum dioxide dichloride in THF yielded, after work-up (see Experimental section), compounds (5a) and (5b) in 61-80% yield [(i)]. In the pure form the compounds are colorless both in the solid state and in solutions of polar solvents such as THF and dichloromethane. On exposure to moist air, however, both solutions and the solids gradually turn pale blue in color. In addition, compounds are stable indefinitely when stored under dry nitrogen at room temperature.



The bidentate binding mode for the β -ketophosphonate ligands in solution was confirmed by infra-red spectroscopy, and in the solid state by X-ray crystallography (vide infra) of (**5a**). The infra-red spectra of (**5a**) and (**5b**) were recorded as Nujol mulls and contained the expected bands at 961 and 916-914 cm⁻¹ corresponding to the *cis* disposition of the two oxo ligands. An intense band centered at 1192 cm⁻¹ was assigned to the phosphoryl groups coordinated to the Mo(VI) center and represents a shift of -59 and -79 cm⁻¹ for (**5a**) and (**5b**), respectively, when compared directly to the free ligands. Equally intense bands at 1644 cm⁻¹ and 1642 cm⁻¹ have been assigned to the coordinated carbonyl groups. Very minor shifts (<2 cm⁻¹) in the absorptions of v(P=O) and v(C=O) in both (**5**) and the free ligand were observed in dichloromethane solution across a wide concentration range.

Crystal Structure Analysis of (5a)

A single crystal of compound (5a) was grown from a solution of dichloromethane/hexane and the crystal structure was solved. An ORTEP representation of (5a) with the atomic numbering scheme is shown in Figure 2 and crystallographic data, selected bond distances and angles are listed in Tables I and II. The structure revealed that the central molybdenum



Fig 2. ORTEP Diagram of the Structure of (5a).

atom is surrounded by two chloride atoms and four oxygen atoms in a highly distorted octahedral coordination environment with Cl(1)-Mo-Cl(2) = 157.53(6)° and O(1)-Mo-O(2) = 102.9(2)° although such distortions are not uncommon for six-coordinate dioxo-molybdenum complexes of the type *cis*-[MoO₂X₂L] where L is a bidentate, chelating ligand. The crystal structure analysis confirms that the β -ketophosphonate ligand is bound to the molybdenum atom in a bidentate fashion with a bite angle of 77.50(12)°, close to the angle found in the related β -carbamoyl- and β -keto-phosphonate complexes MoO₂Cl₂[*i*-C₃H₇O)₂P(O)CH₂C(O)N(C₂H₅)₂] (78.9° (1)) (6)⁸ and MoO₂Cl₂L (L = (1R)-*endo*-(+)-3-(diethoxyphosphoryl)camphor) (78.6° (3)) (4).⁹ The phosphonate oxygen-Mo bond distance (Mo-O(3)) of 2.174 (4) Å in (5a) is shorter than that found in (6) (2.220(2) Å) but similar to that found in (4) (2.183(7) Å) and the carbonyl oxygen-Mo bond distance (Mo-O(6)) of 2.349 (3) Å is longer than that found in (6) (2.246(2) Å) but markedly shorter than that found in (4) (2.402(7) Å). The longer O(6)-Mo distance of the carbonyl oxygen-Mo bond compared to O(3)-Mo suggests that the carbonyl group is weakly bound to the

chemical formula	C ₁₂ H ₁₇ Cl ₂ MoO ₆ P
formula weight	455.07
space group	212121
<i>a</i> , Å	8.0909 (5)
<i>b</i> , Å	14.1432 (5)
<i>c</i> , Å	14.9749 (8)
<i>V</i> , Å ³	1713.6 (2)
Z	4
$\rho_{caic} g/cm^3$	1.764
λ (Å)	0.71073
abs coeff, mm ⁻¹	1.193
temperature	153 (2) K
R ^a	0.0288
\mathbf{R}_{w}^{b}	0.0727

TABLE I. Crystallographic Data for (5a).

 ${}^{a}\mathbf{R} = \Sigma ||F_{0}| - |F_{c}|/\Sigma |F_{0}|. \ \ \, {}^{b}\mathbf{R}_{w} = [\Sigma_{w}(|F_{0}|^{2} - |F_{c}|^{2})^{2}/\Sigma_{w} \ \, (|F_{0}|^{2})^{2}]^{1/2}; \ \, w = 1/\sigma^{2}(|F_{0}|).$

molybdenum center compared to the phosphoryl group and similar observations were made for complex (4).⁹ The oxo ligands have the predicted *cis* geometry¹⁰ and have bond distances of 1.676 and 1.680 Å, similar to the terminal oxo ligands in (6) (1.687(8) and 1.677(9) Å) but slightly longer than those found in (4) (1.658(8) and 1.655(9) Å).

Hemilabile Behavior of (5a)

When a ³¹P NMR spectrum (CH₂Cl₂) of (**5a**) was recorded in the presence of one equivalent of acetonitrile (CH₃CN), the spectrum contained a very broad singlet centered at 25.2 ppm suggestive of the dynamic behavior of (**5a**) in the presence of acetonitrile. Furthermore, precipitation of the solid from an acetonitrile solution of (**5a**) by the addition of an excess of diethyl ether resulted in complete recovery of the starting material. The dynamic behavior of (**5a**) with acetonitrile in solution may result from several modes of reactivity including: 1) complete displacement of the β -ketophosphonate ligand from the molybdenum center yielding a bis(acetonitrile) complex; 2) displacement of the phosphoryl group by an acetonitrile ligand and 3) displacement of the carbonyl group by an acetonitrile ligand.

Mo(1)-O(1)	1.676(4)	
Mo(1)-O(2)	1 680(4)	
$M_0(1)-O(3)$	2 174(4)	
$M_0(1) - O(6)$	2.174(4) 2.349(3)	
$M_0(1)$ - $O(0)$	2.349(3)	
$M_0(1) - Cl(2)$	2.379(2)	
O(3) D(1)	1.492(4)	
$\mathcal{D}(\mathbf{J})$ - $\mathbf{r}(\mathbf{I})$	1.403(4)	
P(1) O(3)	1.540(4)	
P(1) - O(4)	1.334(4)	
$\Gamma(1)$ - $C(3)$	1.790(3)	
C(1) C(2)	1.479(9)	
O(5) C(2)	1.4/0(0)	
C(3) - C(3)	1.495(7)	
C(5) - C(4)	1.400(0)	
C(5) - C(0)	1.212(6)	
C(0) - O(0)	1.222(0)	
C(7) C(9)	1.470(7)	
C(7) = C(0)	1.300(7)	
C(1)- $C(12)$	1.399(7)	
C(0) - C(0)	1.401(8)	
C(10) $C(11)$	1.301(0)	
$O(1) M_0(1) O(2)$	1.370(8)	
O(1) - MO(1) - O(2)	01.4(2)	
O(1) - MO(1) - O(3)	71.4(2) 165 5(2)	
O(2) - MO(1) - O(3)	168 0(2)	
O(1) - MO(1) - O(0)	88 2(2)	
O(2) - MO(1) - O(0)	77.50(12)	
O(3) - MO(1) - O(0)	(12)	
O(1) - MO(1) - O(1)	95.7(2)	
O(2) - MO(1) - O(1)	93.4(2) 84.01(12)	
O(5) - MO(1) - O(1)	70.24(10)	
O(0) - MO(1) - O(1)	9.24(10)	
O(1) - MO(1) - CI(2)	90.4(2)	
O(2) - MO(1) - CI(2)	93.4(2)	
O(5) - MO(1) - CI(2)	80.42(10)	
O(0)-MO(1)-O(2)	157 52(6)	
D(1) - MO(1) - CI(2)	127.2(0)	
P(1) - O(3) - MO(1)	137.3(2)	
C(1) - O(4) - F(1)	121.0(3)	
C(2) - C(1) - O(4)	100.0(3)	
C(3) - O(3) - P(1)	120.3(3) 107.2(4)	
C(4) - C(3) - O(3)	116 2(4)	
C(0) - C(3) - F(1)	121 1(5)	
O(0)- $C(0)$ - $C(1)$	121.1(3) 121 $O(4)$	
O(0)- $C(0)$ - $C(3)$	141 7(2)	
U(0) - U(0) - MO(1)	141.7(5)	

TABLE II. Selected Bond Lengths [Å] and Angles [deg] for (5a).

In order to obtain more information about the possible species present in solution, an IR spectrum of (5a) was recorded in acetonitrile. The spectrum is shown in Figure 3 and is surprisingly revealing when compared directly to the free ligand and compound (5a) in solution. The comparison clearly indicates that there are two carbonyl absorptions present at 1636 and 1686 cm⁻¹ which have been assigned to coordinated and uncoordinated keto groups, respectively. Analysis of the phosphonate region of the spectrum however, is also informative and shows exclusively the presence of a metal-coordinated (P=O) functional group at 1181 cm⁻¹ and the lack of a discreet band at 1251 cm⁻¹ which would correspond to a free uncoordinated β -ketophosphonate ligand. The infra-red spectrum of the free ligand was also recorded in acetonitrile to confirm the assignments.

We have interpreted the observations described above in the following manner: the lack of uncoordinated phosphoryl clearly indicates that no free ligand is present in solution and the appearance of two absorptions in the carbonyl region suggests the presence of two distinct complexes, one in which the carbonyl group is displaced from the metal by an acetonitrile ligand (7), and compound (5a) [eq. (ii)]. Moreover, further evidence for the formation of (7) is given by the observation of a weak absorption at 2287 cm⁻¹, typical of an acetonitrile ligand coordinated to molybdenum e.g. $Mo(CH_3CN_3)(CO)_3$.¹¹ The conclusion from the above observations is that complex (5a) is acting in a hemilabile fashion in acetonitrile.



Our earlier observations that compound (5a) acts as an active catalyst in the oxidation of sulfides such as dimethylsulfide and diphenylsulfide to the corresponding sulfoxide prompted us to investigate the possible hemilabile behavior of (5a) in the presence of a sulfoxide ligand. When (5a) was treated with an excess of diphenyl sulfoxide (DPSO) in CH₂Cl₂, no dynamic behavior was observed by ³¹P at room temperature, although a sharp peak at 21.2 corresponding to free β -ketophosphonate ligand was seen. The subsequent work-up of the reaction mixture resulted in the isolation of the new compound dichlorodioxobis(diphenylsulfoxide)molybdenum (8) [eq. (iii)]. Similar reaction of (5a) with other oxygen containing donor ligands such as dimethylformamide and DMSO also



Figure 3. Infra-red Spectrum of (5a) Recorded in CH₃CN Showing Coordinated and Uncoordinated Carbonyl groups.

resulted in complete displacement of the β -ketophosphonate ligand. Thus, the hemilabile activity of complex (5a) is highly dependent on the donor ability of the incoming ligand.



In summary, we have shown that a β -ketophosphonate complex of molybdenum can act in a hemilabile fashion in the presence of the weakly coordinating ligand acetonitrile. The transition to complete displacement of the coordinated ligand, however, can be achieved by choosing a strongly displacing ligand such as diphenyl sulfoxide. These factors are clearly of importance when proposing a hemilabile ligand-metal system for a desired homogeneous catalytic reaction.

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