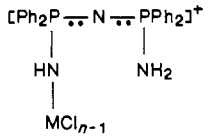
The infrared spectrum of **7** showed characteristic absorptions for P–N bonds between 1130 and 1270 cm^{-1}. The electron ionization mass spectrum for **7** consisted of the parent ion (m/z 739). The elemental analysis was compatible with structure **7**. The ^1H-decoupled ^{31}P NMR spectrum showed a single resonance line at 46.2 ppm.

The electron withdrawal property of transition-metal atoms causes a deshielding effect on the phosphorus chemical shifts of all the cyclometallaphosphazenes compared to the nonmetallated cyclophosphazene analogues (Table I).

Stability of Vanadium, Tungsten, and Rhenium in Their Highest Oxidation States. Compounds **4**–**7** provide examples of stable species of vanadium, tungsten, and rhenium in their highest oxidation state. It appears that the phosphazene skeleton has an ability to stabilize transition metals in their highest oxidation states.

Mechanism of the Formation of Cyclometallaphosphazenes. The interaction of the transition-metal halides MCl_n (VCl_4, $MoCl_5$, WCl_6, $ReCl_5$) with the linear phosphazene salt **1** appears to be a sequential process. The first step is the formation of an acyclic intermediate



followed by the subsequent cyclization step through the elimination of HCl. We have not isolated this acyclic intermediate; however, we have been able to monitor the progress of the reactions of the various metal halides with the linear phosphazene salt **1** by using $^{31}P\{^1H\}$ NMR spectroscopy. A typical series of spectra obtained for the reaction of WCl_6 with **1** at different reaction times are illustrated in Figure 1.

Conclusion

We have so far demonstrated that transition-metal atoms can be incorporated into sulfur–nitrogen[13] and phosphorus–nitrogen[7,8] ring skeletons through different synthetic strategies. The ready synthesis of these metallacycles has opened up a new topic of research in inorganic heterocyclic chemistry. The presence of metal–halogen bonds in compounds **2**–**7** offers opportunities for carrying out varieties of nucleophilic substitution reactions.

Acknowledgment. We are grateful for support by the Deutsche Forschungsgemeinschaft. K.V.K. thanks the Alexander von Humboldt Foundation for a fellowship.

Registry No. **3**, 101653-99-0; **4**, 110589-08-7; **5**, 110589-09-8; **6**, 110589-10-1; **7**, 110589-11-2.

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Contribution from the Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980, Japan

Ligand Isotopic Exchange of *cis*-Bis(acetylacetonato)dioxomolybdenum(VI) in Acetylacetone

Akira Nagasawa, Hideaki K. Tanaka, Masayuki Miyoshi, and Kazuo Saito*[1]

Received February 25, 1987

The ligand exchange of *cis*-bis(acetylacetonato)dioxomolybdenum(VI) in acetylacetone has been studied kinetically with the ^{14}C-labeling technique. The rate law was rate = $(k_1 + k_2[H_2O])$[complex] at 5.0, 15.0, 25.0, and 35.0 °C; k_1 and k_2 are 1.05×10^{-3} s^{-1} and 8.27×10^{-3} M^{-1} s^{-1} at 25 °C, respectively. ΔH^* and ΔS^* are 64 ± 2 and 64 ± 1 kJ mol^{-1} and −86 ± 5 and −71 ± 4 J K^{-1} mol^{-1} for k_1 and k_2, respectively. Dilution of the solvent with acetonitrile and deuteriation of the acidic hydrogens of the solvent and of water decreased both rate constants. Application of pressure to the solution up to 92 MPa at 5 °C caused no significant change in the rate law, and the rates themselves, i.e. ΔV^*'s, were ca. 0 cm^3 mol^{-1}. The mechanism of the reaction is discussed on the basis of these data.

Introduction

The kinetics of ligand substitution reactions of molybdenum(VI) complexes has been studied mainly in aqueous solution.[2-4] The participating species are not specified in some cases, since there are various molybdenum(VI) species, including dimers and polymers, in aqueous media depending on the pH and the concentration.[5] Anation and hydrolysis are sometimes accompanied by a change in the coordination number. Most aqua complex ions have oxide as an inert ligand and given regiospecificity on substitution.[4]

Some complexity may be ignored in the reactions in organic solvents. We have demonstrated the importance and usefulness of the solvent-exchange rate of the metal solvate involving bidentate ligands by the use of acetylacetonato complexes in acetylacetone (Hacac).[6,7] For Mo^{VI} complexes the solvent-exchange reactions in organic solvents have been less investigated, although a few reports have also been published on isotopic ^{18}O exchange between solvent water and MoO_4^{2-}.[8]

Molybdenum(VI) gives a discrete complex, *cis*-bis(acetylacetonato)dioxomolybdenum(VI), that is stable in dry organic solvents.[9] Craven et al.[10] investigated the intramolecular site

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0020-1669/87/1326-4035$01.50/0

exchange of two nonequivalent methyl positions of coordinated acac⁻ (trans-to-oxo and cis-to-oxo) by ^{1}H NMR line shape analysis in $CHCl_3$ and benzene and found no intermolecular exchange between the complex and Hacac on the NMR time scale at ambient temperature. We have studied the exchange kinetics of the reaction (eq 1) by the ^{14}C-labeling technique under atmospheric and elevated pressure.

$$[Mo(O)_2(acac^*)_2] + Hacac = [Mo(O)_2(acac)_2] + Hacac^* \quad (1)$$

Experimental Section

Materials. Preparation of *cis*-Bis(acetylacetonato)dioxomolybdenum(VI), *cis*-[Mo^{VI}(O)$_2$(acac)$_2$]. The crude product[11] was recrystallized by dissolving the complex (5 g) in a mixture of Hacac (25 cm^3), ethanol (25 cm^3), and 3 M HCl (1 cm^3, M = mol dm^{-3}) at ca. 60 °C and setting it aside overnight at room temperature. The lemon yellow crystals were filtered off, washed with Hacac–acetone mixture (1:10, v/v), dried in vacuo, and identified by elemental analysis and IR spectroscopy (KBr pellet);[12] yield 3.5 g (54% from sodium molybdate dihydrate).

^{14}C-labeled complex was obtained by dissolving 2.0 g of [Mo(O)$_2$(acac)$_2$] in a mixture of [2-^{14}C]Hacac[6] (2.3 × 10^6 Bq mol^{-1}, 10 cm^3), ethanol (10 cm^3), and 3 M HCl (0.5 cm^3) with stirring at 60 °C and set aside overnight at room temperature. Crystals were filtered off, washed with acetone, and dried in vacuo. The specific radioactivity of the product was ca. 0.3 μCi g^{-1}.

Solvents. Hacac and CH_3CN were purified, and [*methylene*-$^2H_2$]-Hacac (Dacac, 71% deuteriated) was prepared and purified according to the methods previously described.[7] The water content of these solvents was less than 0.01 M.

Kinetic Procedure. Reactions under Ambient Pressure. Kinetic runs were carried out similarly to the procedure reported in the literature.[7] The thermostated solvent (10 cm^3) was mixed with the complex (ca. 40 mg) by shaking for 1 min to dissolve the powder. Six portions (1 cm^3 each) were pipetted out one by one at appropriate time intervals and immediately poured into test tubes in a cold methanol bath at −50 °C. The solvent was removed in vacuo at −5 °C to recover the complex, which was dissolved in 2 cm^3 of Hacac–CH_3CN mixture (1:99 by volume). The solution (1 cm^3) was mixed with the liquid scintillator (14 cm^3 of toluene containing 0.1% *p*-terphenyl and 0.04% *p*-bis(5-phenyl-2-oxazolyl)-benzene), and the radioactivity was counted. The water content of the reaction mixture remained constant during the kinetic run within ±5% (Karl Fischer method). The conditions were [[Mo(O)$_2$(acac)$_2$]] = (0.984–1.78) × 10^{-2} mol kg^{-1}, [H_2O] = 0.025–0.273 mol kg^{-1}, and temperature 5.0–30.0 (±0.1) °C.

Reactions under Elevated Pressures. The solution of ^{14}C-labeled complex (ca. 60 mg in 15 cm^3) was prepared at ca. −5 °C, dispensed into five poly(trifluoroethylene) (Diflon) cylindrical vessels (1.4 cm in diameter and 4.5 cm in height) doubly stoppered with Diflon pistons and silicone-rubber O-rings,[13] and frozen in a methanol bath at −60 °C. To start the run, the vessel was dipped into a mixture of salt and ice at ca. −5 °C for 7 min and placed in the pressure container.[7] The pressure was applied through methanol at 5 °C for a given period. The vessel was desealed at −5 °C, a portion of the solution (1 cm^3) immediately chilled at −50 °C to quench the reaction, and the residual solution submitted to the Karl Fischer titration. The complex was recovered crystalline, and the radioactivity was measured as noted above. The water contents of six portions of solution for one kinetic run coincided with one another within a ±10% fluctuation. The conditions were [[Mo(O)$_2$(acac)$_2$]] = (1.16–1.55) × 10^{-2} mol kg^{-1}, [H_2O] = 0.027–0.242 mol kg^{-1}, temperature 5.0 °C, and pressure 0.10, 43.6, and 92.1 MPa.

Calculation of the Rate. The data were analyzed by the simplified McKay equation (eq 2),[14] where x_0 and x_t are the radioactivity of the

$$R = 2[[Mo(O)_2(acac)_2]](\ln (x_0/x_t))/t \quad (2)$$

complex at time zero and t, respectively.

Apparatus. UV absorption and ^{1}H NMR spectra were recorded on a Hitachi 330 spectrophotometer and a Varian EM-390 NMR spectrometer, respectively. An Aloka LSC-903 liquid scintillation counter was used for ^{14}C β-radioactivity counting. A Metrohm E-547 automatic titrator was used for the Karl Fischer titration.

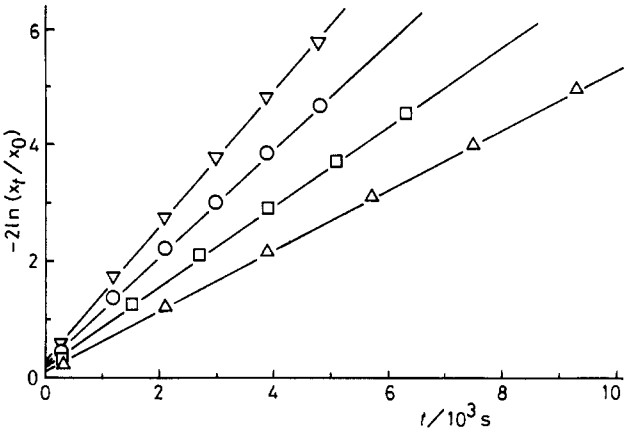

Figure 1. McKay plots for the ligand isotopic exchange of *cis*-[Mo(O)$_2$(acac)$_2$] ((1.28–1.37) × 10^{-2} mol kg^{-1}) in acetylacetone at 15.0 °C. Concentration of water: (△) 0.027 mol kg^{-1}; (□) 0.086 mol kg^{-1}; (○) 0.163 mol kg^{-1}; (▽) 0.232 mol kg^{-1}.

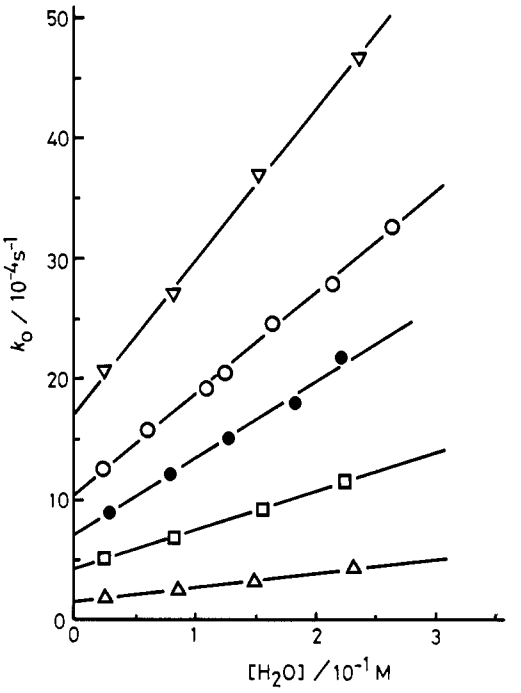

Figure 2. Influence of water concentration on the ligand isotopic exchange rate constant (k_0) of *cis*-[Mo(O)$_2$(acac)$_2$] ((0.984–1.78) × 10^{-2} mol kg^{-1}) in acetylacetone at ambient pressure. Temperature: (△) 5.0 °C; (□) 15.0 °C; (○) 25.0 °C; (●) 25.0 °C (in 71% deuteriated-methylene acetylacetone containing D_2O (71 atom %)); (▽) 35.0 °C.

Results

Stability of the Complex in Solution. Two ^{1}H NMR signals of the complex (2.1 and 5.8 ppm vs tetramethylsilane) remained unchanged with time in the presence of Hacac in $CDCl_3$, indicating no contribution from *trans*-[Mo(O)$_2$(acac)$_2$] and hydrolyzed species. No change in UV spectra was observed at ≥330 nm in neat Hacac or in the presence of Hacac in CH_3CN. The stability of the complex in the presence of excess Hacac or in neat Hacac was thus verified.

Kinetic Feature of the Reaction. McKay plots, −2 ln (x_t/x_0) vs t, gave straight lines by at least 80% extent of the exchange reaction (Figure 1). The observed rate constant

$$k_0 = R/[[Mo(O)_2(acac)_2]] \quad (3)$$

did not change with the lot and the concentration of the labeled complex (Table I). Therefore, the ligand isotopic exchange took

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(13) The sample solution (ca. 2 cm^3) was sealed with a piston, onto which a small amount of the same solution (ca. 0.5 cm^3) was poured and stoppered with another piston. This was found to be effective to protect the sample from the methanol or the moisture outside the piston when pressurized.
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Table I. Rate Constants and Activation Parameters for the Ligand Isotopic Exchange of *cis*-$[Mo(O)_2(acac)_2]$ in Hacac[a]

temp/°C	press./MPa	$[Mo^{VI}]/10^{-2}$ mol kg^{-1}	$[H_2O]/10^{-2}$ mol kg^{-1}	$k_o/10^{-4}$ s^{-1}	$k_1/10^{-4}$ s^{-1}	$k_2/10^{-3}$ kg mol^{-1} s^{-1}
5.0	0.10	1.13	2.81	1.89 ± 0.02	1.54 ± 0.05	1.14 ± 0.03
		1.09	8.85	2.52 ± 0.02		
		1.06	15.5	3.33 ± 0.03		
		1.40	16.2	3.31 ± 0.08		
		1.16	23.9	4.29 ± 0.04		
		1.16[b]	2.68	1.89 ± 0.01	1.61 ± 0.01	1.05 ± 0.01
		1.16[b]	12.7	2.93 ± 0.02		
		1.16[b]	24.2	4.12 ± 0.02		
	43.6	1.34[b]	15.9	3.12 ± 0.11		
	92.1	1.39[b]	4.45	2.07 ± 0.04	1.60 ± 0.02	1.06 ± 0.01
		1.55[b]	15.8	3.26 ± 0.11		
		1.34[b]	23.6	4.10 ± 0.20		
15.0	0.10	1.28	2.66	5.22 ± 0.03	4.31 ± 0.15	3.10 ± 0.10
		1.37	8.61	6.90 ± 0.05		
		1.32	16.3	9.28 ± 0.09		
		1.29	23.2	11.6 ± 0.10		
25.0	0.10	1.56	2.51	12.6 ± 0.1	10.5 ± 0.3	8.02 ± 0.18
		0.984	6.27	15.8 ± 0.2		
		0.984	11.3	19.2 ± 0.4		
		1.78	12.9	20.5 ± 0.4		
		0.984	17.0	24.5 ± 0.2		
		0.984	22.1	27.9 ± 1.2		
		1.77	27.3	32.6 ± 0.2		
	0.10	1.08	2.98[c]	9.01 ± 0.1	5.59 ± 0.81[d]	5.39 ± 0.53[d]
		1.37	8.07[c]	12.2 ± 0.1		
		1.05	13.0[c]	15.2 ± 0.2		
		1.23	18.4[c]	18.1 ± 0.2		
		1.12	22.3[c]	21.7 ± 0.3		
30.0	0.10	1.26	2.82	20.7 ± 0.05	17.1 ± 0.6	12.0 ± 0.40
		1.26	8.54	27.0 ± 0.3		
		1.33	16.0	36.8 ± 0.4		
		1.32	24.6	46.6 ± 0.4		
$\Delta H^{\ddagger}$/kJ mol^{-1}					64.4 ± 1.4	63.9 ± 0.9
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}					−85.5 ± 5.0	−70.6 ± 3.3
$\Delta V^{\ddagger}$/cm^3 mol^{-1}					+0.2 ± 0.4	−0.4 ± 0.4
k^H/k^D					1.9 ± 0.3	1.5 ± 0.2

[a] Rate equation: rate = $(k_1 + k_2[H_2O])$[complex]. Errors are calculated on 70% confidence level. [b] Different lot of the complex was used. [c] 71% deuteriated Hacac and water were used (see text). [d] Estimated value as in Dacac (100%) containing D_2O (100%) from the data obtained in the experiments using 71% deuteriated Hacac and water.

Table II. Rate Constants for the Ligand Isotopic Exchange of *cis*-$[Mo(O)_2(acac)_2]$ in a Hacac–CH_3CN Mixture at 25.0 °C under Ambient Pressure[a]

[Hacac]/([Hacac] + [CH_3CN])	$[Mo^{VI}]/10^{-2}$ mol kg^{-1}	$[H_2O]/10^{-2}$ mol kg^{-1}	$k_o/10^{-4}$ s^{-1}	$k_1/10^{-4}$ s^{-1}	$k_2/10^{-3}$ kg mol^{-1} s^{-1}
0.198	1.35	6.09	4.10 ± 0.07	1.49 ± 0.28	4.21 ± 0.16
	1.15	15.7	8.01 ± 0.14		
	1.28	25.1	12.1 ± 0.1		
0.379	1.25	5.97	6.25 ± 0.11	4.11 ± 1.71	4.03 ± 0.98
	1.25	15.7	11.0 ± 0.3		
	1.28	25.2	14.0 ± 0.2		
0.558	1.32	15.6	12.5 ± 0.2		
0.714	1.30	5.97	10.2 ± 0.1	7.25 ± 1.30	5.27 ± 0.74
	1.15	16.2	16.2 ± 0.2		
	1.37	25.0	20.2 ± 0.1		
0.860	1.36	5.53	12.3 ± 0.1	9.59 ± 1.60	5.37 ± 0.92
	1.20	15.6	18.5 ± 0.4		
	1.53	25.3	22.9 ± 0.4		

[a] Errors are calculated on a 70% confidence level.

place exclusively. The k_o vs $[H_2O]$ plots (Figure 2) at any observed temperature gave straight lines with intercepts to give the rate formula eq 4. Pressure up to 92 MPa gave almost no effect on

$$k_o = k_1 + k_2[H_2O] \quad (4)$$

the rate formula and rates themselves (Figure 3). Values of k_1 and k_2 and the activation parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$, are shown in Table I. Replacement of the acidic protons of Hacac and H_2O by deuterium decreased both k_1 and k_2 (Figure 2). The deuterium isotope effect (k^H/k^D) in Table I was calculated on the reasonable assumption that the effect of the enolate proton overwhelms that of a proton at the 3-position of Hacac. k_1 decreased on dilution of the solvent Hacac with CH_3CN, whereas k_2 did so only slightly (Figure 5,[15] Table II).

Discussion

The rate formula shows a participation of water. Moderate $\Delta H^{\ddagger}$, negative $\Delta S^{\ddagger}$, negligibly small absolute values of $\Delta V^{\ddagger}$, and significant and moderate k^H/k^D values are common for both k_1 and k_2. Therefore, rate-determining steps of both k_1 and k_2 paths should be assigned to analogous processes. A plausible mechanism is shown in Figure 4.

(15) Supplementary material.

Table III. Kinetic Data for Reactions of Octahedral Mo^{VI} Complexes

complex[a]	reactn	solvent	k_o(25 °C)/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	ref
$[Mo(O)_2(acac)_2]$	site exch	$CDCl_3$	1.2	90	+57	19
		$CHCl_3$	4.0	52	−59	10[b]
		acetone	1.1	62	−37	19
		various[c]		69–110	−6–+115	19
	ligand exch	Hacac	1.1×10^{-3}	64	−86	this work
Mo^{VI}–ox	hydrolysis	H_2O (pH 7.9–8.9)	1.95			20
Mo^{VI}–oxs	hydrolysis	H_2O (pH 7.5–8.5)	0.85			21
Mo^{VI}–cat	hydrolysis	H_2O (pH 7.3–7.8)	7.76			22
$[Mo(O)_2(OH)_2(as)]^{3-}$	hydrolysis	H_2O (pH 7.4–8.1)	0.9			23
$[Mo(O)_3(nta)]^{3-}$	hydrolysis	H_2O (pH 6.1–7.0)	1.8×10^{-3}	85	−12	23
$[Mo(O)_3L]^{n-}$	hydrolysis	H_2O (basic[d])	0.020–79[e]			24
			1.9–660[f]			24

[a] Hox = 8-hydroxyquinoline; H_2oxs = 8-hydroxyquinoline-5-sulfonic acid; H_2cat = catechol; H_3as = 1,2-dihydroxyanthraquinone-3-sulfonic acid; H_3nta = nitrilotriacetic acid; L = amino polycarboxylate ions, e.g. iminodiacetate(2−), nta^{3-}, ethylenediamine-*N*,*N*′-diacetate(2−), ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate(4−). [b] Activation parameters are recalculated on the basis of the data given in the reference. [c] Organic solvents including dioxane, CD_2Cl_2, *N*,*N*-dimethylformamide, benzene, and nitromethane. [d] $[OH^-]$ = 0.007–0.183 M. [e] The k_1 value (s^{-1}) of the rate formula $k_o = (k_1 + k_2K_{OH}[OH^-])/(1 + K_{OH}[OH^-])$, where K_{OH} is the association constant between the complex and OH^-. [f] The k_2 value (s^{-1}) of the formula in footnote *e*.

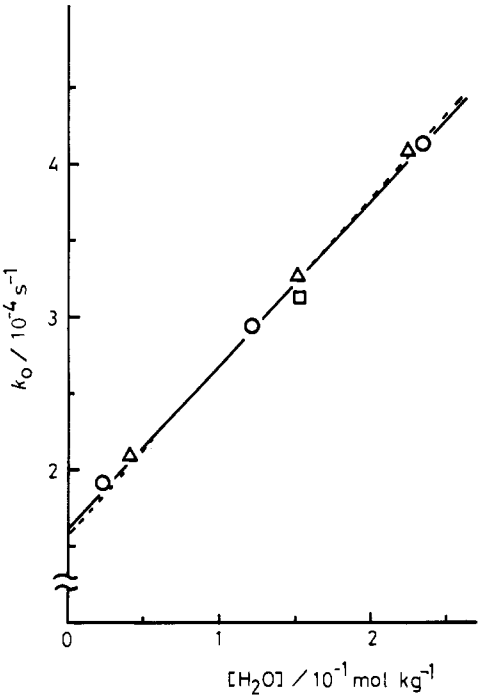

Figure 3. Dependence of k_o on the concentration of water for the ligand isotopic exchange of *cis*-$[Mo(O)_2(acac)_2]$ in acetylacetone at 5.0 °C under ambient and elevated pressures ([Complex] = (1.16–1.55) × 10^{-2} mol kg^{-1}). Pressure: (○, solid line) 0.10 MPa; (□) 43.6 MPa; (△, broken line) 92.1 MPa.

Catalytic Effect of Water. In the presence of a large excess of water with the complex in CH_3CN, the UV absorption spectrum changed gradually, probably due to hydrolysis (Figure 6[15]).[16] However, the present system contains only a small excess of water, and no hydrolyzed species was detected by the UV absorption and ^1H NMR spectroscopy. Hence, the contribution of hydrolysis in the present exchange can be ignored, and the influence of water concentration upon the rate should be understood as a catalytic effect.

A water molecule can interact with the complex in place of $acac^-$ to give an intermediate with a unidentate $acac^-$ and a water molecule (**4** in Figure 4). This species is converted into **2**, and a process similar to the noncatalytic path is followed (vide infra). Such a mechanism has been proposed for the interpretation of the catalytic effect of water in ligand exchange of $[M^{III}(acac)_3]$ (M = Co, Cr, Fe, V, Ru, Rh, Al) in Hacac.[6,7] Those reactions gave activation parameters and k^H/k^D's for k_2 analogous to those of k_1, as the present exchange does. Therefore, a similar sort of participation of water may be considerable for this reaction.

Reaction Mechanism. A regiospecificity is generally observed for the ligand substitution of oxo–transition metal complexes.[4] The oxo ligand is substitution inert,[8] and ligands at trans-to-oxo positions are more labile in substitution than those at cis-to-oxo sites.[4,17] Structural data of the present complex show a similar trend: Mo–O bond lengths at trans- and cis-to-oxo positions are 2.19 and 1.98 Å, respectively.[18] In the present exchange, substitution should take place at trans-to-oxo Mo–O first, with rate constants k_a and k_c for the k_1 and k_2 paths, respectively, to give intermediates **2** and **4**. The reversed step, i.e. recombination of the free end of $acac^-$ onto the trans-to-oxo position (rate constants k_{-a} and k_{-c}), may be much faster than the chelate-opening process, since only negligible amounts of Mo complexes with unidentate $acac^-$ or Hacac are present in Hacac (vide supra, NMR). The observed rate constant is expressed as

$$k_1 = k_a k_b/(k_{-a} + k_b) \quad (5)$$

where k_b is the rate constant to give **1′** from **2**. k_1 is the smallest rate constant of the ligand substitutions of octahedral oxo–molybdenum(VI) complexes, in which substitution at trans-to-oxo positions may predominantly take place (Table III). The slow

(16) In a very dilute solution of the complex in CH_3CN, UV absorption spectra of the complex changed with time at 25 °C, showing two isosbestic points at 244 and 296 nm (Figure 6[15]). The resulting spectra had maxima at 273 nm ($\epsilon \approx 20\,000$ M^{-1} cm^{-1} on the basis of the complex concentration), indicating the liberation of 2 equiv of enolic Hacac from the complex. The rate increased with an increase in the concentration of water. These observations suggest that the change in the spectra is due to the hydrolysis. Since the complex was stable in the presence of excess Hacac, the reversed formation is rapid. The absorption spectrum of $[Mo(O)_2(acac)_2]$ in CH_3CN at the moment of preparation is presumed to have two maxima at 317 nm (ϵ = 7100 M^{-1} cm^{-1}) and 206 nm (ϵ = 10 150 M^{-1} cm^{-1}) (Figure 6[15]). Values in ref 11 may correspond to those at ca. 20 min after the preparation.

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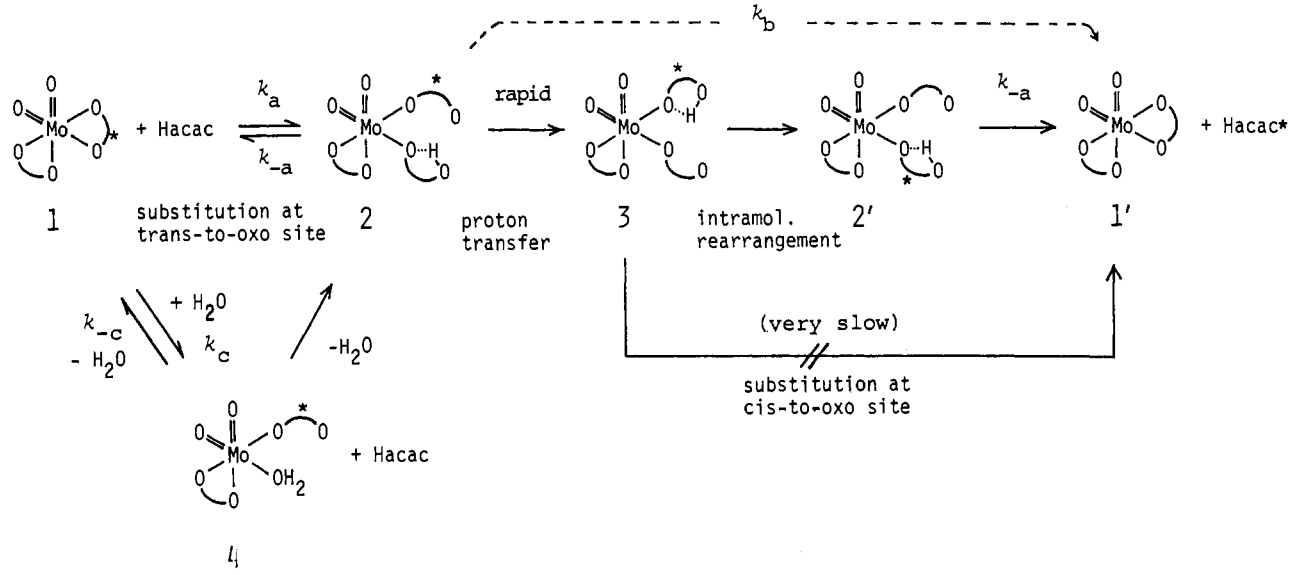

Figure 4. Plausible mechanism of ligand isotopic exchange of *cis*-$[Mo(O)_2(acac)_2]$ in Hacac.

rate of the present exchange may be due to a small value of the factor $k_b/(k_{-a} + k_b)$. k_b should be therefore sufficiently small compared with k_{-a}, and eq 5 can be reduced to the form

$$k_1 = k_a k_b / k_{-a} \quad (6)$$

Significant deuterium isotope effect suggests a participation of protons in the mechanism. Proton transfer from the incoming Hacac to the unidentate $acac^-$ in intermediate **2** to give **3** should be necessary for completing the exchange. Eigen et al. discussed that the proton exchange between Hacac (enol form) and solvent water proceeds at a rate of 2×10^{-2} s^{-1}.[25] In the present system the process from **2** to **3** could be slow enough to determine k_b. However, such a rate-determining step would have given a great k^H/k^D to k_b. Since k_a and k_{-a} may be little influenced by deuteriation of Hacac or H_2O, the deuterium isotope effects on k_1 and k_2 are substantially determined by k_b^H/k_b^D. We prefer to reckon that the observed k^H/k^D values (1.9 and 1.5) are not great enough to assign the proton-transfer process to the rate-controlling step.[7]

The resulting unidentate Hacac at the cis-to-oxo site leaves the coordination sphere either in situ (**3** → **1′**) or after the intramolecular rearrangement from rather inert cis-to-oxo position to labile trans-to-oxo site (**3** → **2′** → **1′**), and k_b may correspond to the rate of the faster route of the two. The site exchange of **1** was observed by the dynamic ^1H NMR technique in acetone, benzene, $CHCl_3$, etc. (k = 1–10 s^{-1} at 25 °C)[10,19] to be faster than the present ligand exchange (Table III). For the site exchange, since the effect of solvent dielectric constant on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values and no influence of Hacac concentration on the site-exchange rate are observed,[19] intramolecular mechanisms[26] are suggested. Therefore, a similar rearrangement process can be involved in the ligand exchange. The presence of a preequilibrium to give **2**, which makes $\Delta S^{\ddagger}$ more negative, may be responsible for the difference in activation parameters between the ligand exchange and the site exchange. Such an explanation can be acceptable for the present system. On the other hand, still no evident data are available for the rate of substitution at the cis-to-oxo position.

$\Delta V^{\ddagger}$ may be helpful for further elucidation of the mechanism.[27] Generally, $\Delta V^{\ddagger}$ consists of both a change in intrinsic volume of the species and a volume change in the solvation sphere. The present complex has not net charge, and we consider in the following discussion that the contribution of the former is important. $\Delta V^{\ddagger}_1$ for k_1 is derived from eq 6 as

$$\Delta V^{\ddagger}_1 = \Delta V^{\ddagger}_a - \Delta V^{\ddagger}_{-a} + \Delta V^{\ddagger}_b \quad (7)$$

where subscripts denote the individual processes in Figure 4, and a similar equation can be written for k_2. Observed $\Delta V^{\ddagger}$ values for both k_1 and k_2 paths were zero within the experimental error. Since the Mo–O bond at the trans-to-oxo site is long, the change in volume accompanied by the substitution should be rather small, as compared with that of the normal Mo–O bond, and may give smaller absolute values to $\Delta V^{\ddagger}_a$ and $\Delta V^{\ddagger}_{-a}$. Furthermore, $\Delta V^{\ddagger}_a$ may be partly cancelled by $-\Delta V^{\ddagger}_{-a}$. Thus, the magnitude of $\Delta V^{\ddagger}_1$ may be determined substantially by $\Delta V^{\ddagger}_b$.

If k_b would reflect the substitution at the cis-to-oxo site, $|\Delta V^{\ddagger}_b|$ might be significantly large, and $|\Delta V^{\ddagger}_1|$ could not be small, except when the substitution has a nature between that of associative and dissociative processes. On the contrary, if k_b would correspond to the rate of the intramolecular rearrangement process, $|\Delta V^{\ddagger}_b|$ might be small. The absolute value of $\Delta V^{\ddagger}_1$ will be also small, irrespective of the nature of the substitution. We thus conclude that the ligand exchange proceeds through a chelate-opening process at the trans-to-oxo site, followed by a rapid proton transfer between two unidentate ligands, $acac^-$ and Hacac, and an exchange of the ligating site of those ligands between the trans-to-oxo and cis-to-oxo position.

Acknowledgment. We thank Dr. N. Fujiwara (Faculty of Medicine, Niigata University) and Prof. Y. Sasaki and Dr. H. Kido (Faculty of Science, Tohoku University) for helpful discussions.

Registry No. *cis*-$[Mo^{VI}(O)_2(acac)_2]$, 21884-95-7; D_2, 7782-39-0.

Supplementary Material Available: Figure 5 (dependence of k_o on the concentration of acetylacetone for the ligand isotopic exchange of *cis*-$[Mo(O)_2(acac)_2]$ in CH_3CN at 25 °C in the presence of various concentrations of water) and Figure 6 (change in UV absorption spectra of *cis*-$[Mo(O)_2(acac)_2]$ in CH_3CN with time at 25 °C) (2 pages). Ordering information is given on any current masthead page.

(25) The rates of deprotonation on keto and enol forms of Hacac to give an enolate ion are 2×10^{-2} and $<1.7 \times 10^{-2}$ s^{-1}, respectively, in aqueous solution, whereas those of the reversed protonation processes are nearly diffusion controlled. Eigen, M. *Angew. Chem.* **1963**, *75*, 489–508.

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