The discrepancy appears to be outside the errors involved in the present work, which are perhaps 10–20% in the overall rate coefficient ($k_{ex} + k_{acc}$). A reasonable inference is that the mechanism described by reactions 1–5 is correct as far as it goes but is incomplete. We hope that additional studies will clarify the matter and will lead to estimates of the individual rate constants k_{-1} and k_2 for the reactions of thallium(II) with iron(III) and iron(II), respectively.

Acknowledgment.—We thank F. Silkworth for assistance in some of the experiments and N. Sutin for helpful discussions. B. W. wishes to acknowledge the hospitality of Brookhaven National Laboratory during his stay as a Research Associate.

CONTRIBUTION FROM THE ARCO CHEMICAL COMPANY,
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Lability and Stereochemistry of Dioxobis(2,4-pentanedionato)molybdenum(VI)

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Received December 29, 1970

It is possible for the octahedral complex dioxobis(2,4-pentanedionato)molybdenum(VI) to exist in two geometrical configurations. In one, the complex would contain the two oxo groups in a cis configuration, in the other they would be in a trans arrangement (Figure 1).

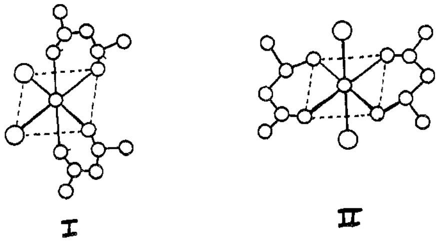

Figure 1.—(I) Cis isomer and (II) trans isomer.

The spectral properties characterizing these two alternative structures were discussed by Moore and Rice,[1] who concluded on the basis of infrared and nuclear magnetic resonance evidence that structure I was the correct assignment. We have verified this structure for the crystalline solid form of the compound by a complete three-dimensional X-ray diffraction study,[2] the main features of which are (a) the Mo–O bonds are shortest (1.69 Å) for the oxo ligands, (b) the two oxo ligands are mutually cis with an O–Mo–O angle of 105°, and (c) the Mo–O bonds to the two 2,4-pentanedionato oxygen atoms which are trans to the oxo ligands are longer (2.19 Å) than for the other two Mo–O bonds (1.98 Å). However, the variable-temperature nuclear magnetic resonance spectra (Figure 2) are indicative of considerable intramolecular lability in solution. We have observed the two methyl resonances ($\Delta\nu_{AB}$ = 2.35 Hz in benzene at 29° and $\Delta\nu_{AB}$ = 1.12 Hz in chloroform at 12°) and single ring proton resonance which Moore and Rice[1] claim characterize the cis configuration, but in addition, we have found that as the temperature is raised, the methyl resonances broaden and coalesce to a single line ($T_c(C_6H_6 \text{ soln}) = 313°K$; $T_c(CHCl_3 \text{ soln}) = 290.7°K$), while the ring proton resonance remains sharp.

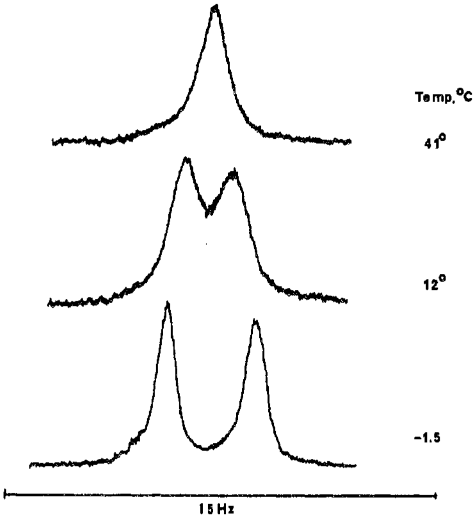

Figure 2.—The 100-MHz nmr spectra of dioxobis(2,4-pentanedionato)molybdenum(VI) in chloroform solution.

The stereochemistry of the complex permits two explanations of this observation: (a) the cis isomer, which possesses a twofold C_2 rotation axis and consequently has two nonequivalent sets of methyl groups, may be capable of rapid configurational changes which exchange the methyl groups between the nonequivalent sites; or (b) the cis isomer could be involved in a rapid equilibration with the trans isomer, which possesses magnetically equivalent methyl groups.

Experimental Section

Since dioxobis(2,4-pentanedionato)molybdenum(VI) appears to be readily hydrolyzed, particularly in solution, all handling was conducted under anhydrous conditions. Samples and solutions for physical measurements were prepared in an argon glove bag. The solvents, benzene and chloroform, were dried by refluxing for at least 12 hr over calcium hydride followed by distillation into bottles equipped with drying tubes. Acetonitrile (line width reference) was dried by refluxing over phosphorus(V) oxide and distilling. Dioxobis(2,4-pentanedionato)molybdenum(VI) was purchased from Research Organic/Inorganic Chemical Corp. and purified by vacuum sublimation. In spite of these precautions, the samples still showed evidence of decomposition; the benzene solution yielded a small yellow-white precipitate, while the chloroform solution which initially was a greenish yellow turned a deep blue after standing for 2 weeks. Proton nmr spectra were recorded with Varian A-60 and HA-100 spectrometers equipped with variable-temperature accessories. Problems of radiofrequency field saturation were encountered at the higher frequency and as a consequence the 60-MHz data are preferred. Temperature calibration was accomplished by measuring the chemical shift difference between the nonequivalent protons of ethylene glycol and methanol. The Varian ethylene glycol calibration was utilized in the case of the benzene solution spectra and the methanol calibration of Van Geet[3] for the chloroform solution spectra.

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TABLE I

NMR AND KINETIC DATA FOR METHYL GROUP EXCHANGE OF DIOXOBIS(2,4-PENTANEDIONATO)MOLYBDENUM(VI) IN C_6H_6 SOLUTION

Temp, °K	$\Delta\nu_{AB}$, Hz	$W_{1/2}$(obsd), Hz A	$W_{1/2}$(obsd), Hz B	CH_3CN $W_{1/2}$(ref), Hz	Av $W_{1/2}$ (cor for inhom), Hz	Intrinsic $W_{1/2}$, Hz	Cor $W_{1/2}$, Hz	τ, sec
287.7	2.8	0.90	0.85	0.45	0.42	0.42	0	
294.2	2.6	0.80	0.85	0.42	0.45	0.39	0.06	
300.2	2.42	1.03	1.05	0.48	0.56	0.38	0.18	0.89
302.2	2.35	1.10	1.10	0.44	0.63	0.35	0.28	0.58
305.7	2.25	1.10	1.20	0.40	0.75	0.33	0.42	0.39
309.2	2.14	. . .	3.28	0.50	2.78	0.31	2.48	0.18
311.2	. . .	3.15		0.45	2.71	0.30	2.41	0.145
317.2	. . .	2.70		0.35	2.35	0.28	2.07	0.11
323.2	. . .	1.95		0.42	1.53	0.24	1.29	0.092
328.2	. . .	1.23		0.50	0.73	0.21	0.52	0.072
333.2	. . .	0.77		0.45	0.32	0.19	0.13	
338.7	. . .	0.60		0.40	0.20	0.15	0.05	
344.7	. . .	0.52		0.39	0.13	0.13	0	

TABLE II

NMR AND KINETIC DATA FOR METHYL GROUP EXCHANGE OF DIOXOBIS(2,4-PENTANEDIONATO)MOLYBDENUM(VI) IN $CHCl_3$ SOLUTION

Temp, °K	$\Delta\nu_{AB}$, Hz	$W_{1/2}$(obsd), Hz A	$W_{1/2}$(obsd), Hz B	CH_3CN $W_{1/2}$(ref), Hz	Av $W_{1/2}$(cor for inhom), Hz	Intrinsic $W_{1/2}$, Hz	Cor $W_{1/2}$, Hz	τ, sec
261.8	1.98	0.95	1.05	0.60	0.40	0.40	. . .	
268.4	1.67	0.98	0.95	0.60	0.37	0.37	. . .	
274.0	1.60	1.03	1.15	0.60	0.49	0.33	0.16	0.96
279.7	1.30	2.40		0.68	1.72	0.29	1.43	0.39
285.2	1.12	2.30		0.65	1.65	0.26	1.39	0.26
290.7	0.7	2.08		0.67	1.41	0.23	1.18	0.20
295.7	. . .	1.65		0.67	0.98	0.20	0.78	0.16
301.6	. . .	1.28		0.67	0.61	0.16	0.45	0.11
306.7	. . .	0.98		0.60	0.38	0.13	0.25	0.07
311.5	. . .	0.85		0.63	0.22	0.10	0.12	0.035
316.5	. . .	0.75		0.63	0.12	0.08	0.04	
320.2	. . .	0.75		0.70	0.05	0.05	. . .	

Results and Discussion

Our results are suggestive of the recent studies on structurally similar dihalobis(2,4-pentanedionato)-titanium(IV) complexes reported by Fay and Lowry.[4] The presence of an appreciable concentration of the trans isomer below the coalescence temperature was eliminated by low-temperature spectra. However, the existence of a rapidly isomerizing cis–trans mixture may not be excluded on the basis of chemical shift data.[5,6] On the other hand, there is little or no evidence to support this second concurrent equilibration. In lieu of contrary proof, only an interchange of methyl groups between nonequivalent environments of the cis isomers was assumed to occur. The mean residence lifetimes, τ, for the methyl groups in their respective environments were obtained by a method[7] which compares experimental and theoretical $W_{1/2}$'s, the line widths at half-height. The experimental line widths were corrected for all factors other than exchange (field inhomogeneity, intrinsic line width, etc.) which may contribute to broadening. The theoretical widths were computed from the Gutowsky–Holm[8] equation for a given $\Delta\nu_{AB}$ and τ, simplified by the assumptions that $P_A = P_B$ and $T_2^{-1} = 0$. These kinetic data are given in Tables I and II. It is to be noted that the magnitudes, determined at the limits of slow and rapid exchange, of intrinsic widths drastically affect the kinetic data, especially here where the chemical shift differences are so small.

The activation energies, E_A, were obtained from a least-squares analysis of ln k *vs.* $1/T$ plots, where $k = {}^1/_2\,\tau$ is the first-order rate constant for exchange. The enthalpies and entropies of activation were obtained by least-squares analysis of the slopes and intercepts of ln (k/T) *vs.* $1/T$ plots. The results of these analyses are listed in Table III.

TABLE III

Benzene soln	Chloroform soln
E_A = 17.0 kcal/mol	E_A = 13.0 kcal/mol
$\Delta H^\ddagger$ = 16.4 kcal/mol	$\Delta H^\ddagger$ = 12.4 kcal/mol
$\Delta S^\ddagger$ = 4.4 cal/deg mol	$\Delta S^\ddagger$ = 14 cal/deg mol
$\sigma(E_A, \Delta H^\ddagger)$ = 2.4 kcal/mol	$\sigma(E_A, \Delta H^\ddagger)$ = 1.0 kcal/mol
$\sigma(\Delta S^\ddagger)$ = 8 cal/deg mol	$\sigma(\Delta S^\ddagger)$ = 4 cal/deg mol

The activation energies observed in the two solvents, benzene and chloroform, do not agree, 17 *vs.* 13 kcal/mol. The latter value, as suggested by the large entropy of activation, seems to be the least reliable of the two. This is a consequence of the small chemical shift difference, which seriously limits the determination of the kinetic parameters. Nevertheless, both activation energies are found to be significantly larger than those observed by Fay and Lowry[4] in the titanium(IV) complexes.

Sufficient experimental data are not available to permit a definitive statement on the mechanism of these stereochemical rearrangments. However, it is useful to comment briefly on the four processes which could result in methyl group interchange: (a) dissociation of

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(6) T. J. Pinnavaia, *et al.*, *Inorg. Chem.*, **9**, 993 (1970).

(7) K. C. Ramey, D. J. Louick, P. W. Whitehurst, W. B. Wise, R. Mukhjerjee, and R. M. Moriarty, *J. Org. Magn. Resonance*, **3**, 201 (1971).

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an oxo ion to give a five-coordinate intermediate, (b) rupture of one Mo–O bond to give a five-coordinate intermediate possessing one monodentate pentanedionato ligand, (c) complete dissociation of one pentanedionato ligand, and (d) twist mechanisms which exchange methyl groups without metal–ligand bond breaking.

Oxo dissociation is not an attractive mechanism because (a) the interchange occurs even in the nonpolar solvent benzene and (b) the Mo–O oxo bonds are probably stronger than those to the 2,4-pentanedionato ligands (see the molecular structure data). Complete dissociation of a pentanedionato ligand requires rupture of two Mo–O bonds. This mechanism, which seems less likely than the one-bond rupture, may be eliminated since the 100-MHz spectra indicate no exchange with excess 2,4-pentanedionato. The pentanedionato signals remain sharp although the resonances of the complex show broadening and coalescence. However, a definite choice between the twist mechanism and the single-bond rupture mechanism cannot be made on the basis of presently available data.

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The Synthesis of Chelating Ligands Incorporating Secondary and Primary Phosphines and Arsines

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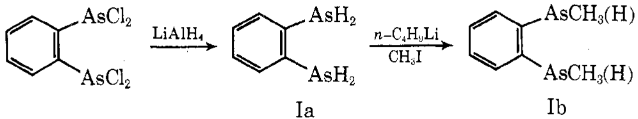
Received March 23, 1971

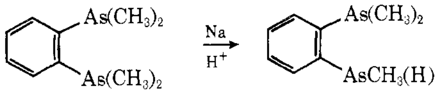
The coordination chemistry of the bis(secondary arsine) ligand (Ib) is potentially interesting because of the similarity of the derived dianion to the intriguing dithiolate systems, the latter ligands behaving as metal-stabilized radicals[1] upon coordination and forming, in some cases, complexes having unusual molecular geometries.[2] The catalytic activity of phosphido complexes[3] and the ability of primary phosphines to form thermally stable polymers[4] are additional topics to be included in a projected study. Accordingly, we have synthesized a number of primary and secondary phosphines and arsines by means of sequences 1–3.

Results and Discussion

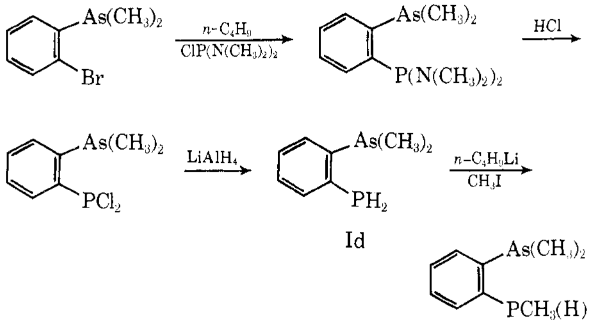
All the derivatives (Ia–e) are air-sensitive and must be prepared and handled in inert atmospheres. The synthetic procedures adopted are fairly standard and call for little comment. The cleavage of a methyl group from *o*-phenylenebis(dimethyl)arsine by sodium in liquid ammonia is somewhat unusual since earlier work[5] would lead one to expect cleavage of the arsenic–phenyl bond by alkali metals; approximately 15–25% of phenyldimethylarsine was detected in the final distillates of this reaction and it is likely that the preferential cleavage is a steric effect.



Ia Ib (1)



Ic (2)



Id Ie (3)

An attempt to cleave selectively the P–CH_3 bond in 1-(dimethylphosphino)-2-(dimethylarsino)benzene using similar conditions led to a mixture of Ie and the secondary arsine–tertiary phosphine derivative which we were unable to separate.

The use of the $-N(CH_3)_2$ blocking group in scheme 3 developed by Burg and Slota[6] and utilized by Wagner and coworkers[7] in the synthesis of *p*-phenylenediphosphines worked well in the present instance although the overall yield of Id (from *o*-bromophenyldimethylarsine) was low.

Pmr Spectra of the Ligands.[8]—Magnetic resonance data for the various ligands are collected in Table I. As an analytical tool pmr spectroscopy has proved invaluable for confirming the purity of the highly air-sensitive ligands; it has, in addition, demonstrated in certain of the molecules magnetic nonequivalence of chemically equivalent protons providing thereby a conclusive demonstration of the identity of the ligand. For example, examination of the 100-MHz spectrum of *o*-phenylene-*As*,*As*,*As'*-trimethyldiarsine reveals the presence of three nonequivalent methyl groups; the doublet centered at τ 8.8 results from the CH_3 group attached to the hydrogen-bearing arsenic atom, the protons of the two methyl groups on the arsenic atom ortho to the asymmetric center are nonequivalent as a result of this asymmetry. From models it can be seen that the methyl groups on the tertiary arsenic are not interchangeable by any symmetry operation and are thus diastereotopic.[9] It has been demon-

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