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Kinetics of Displacement of Dimethyl Sulfoxide from *cis*-Dichlorobis(dimethyl sulfoxide)platinum(II) by Amines in Dimethoxyethane

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The kinetics of the reaction *cis*-[Pt(Me_2SO)$_2Cl_2$] + am → *cis*-[Pt(Me_2SO)(am)Cl_2] + Me_2SO (Me_2SO = dimethyl sulfoxide; am = pyridine, a substituted pyridine, or a diazine) have been studied in 1,2-dimethoxyethane at 25 °C. The second-order rate constant, k_2, is sensitive to the basicity of the entering nucleophile, α (the slope of the plot of log k_2 against pK_a of amH$^+$) = 0.41, and to steric hindrance. These reactivity relationships are compared to those for the corresponding chelated disulfoxide complexes [Pt(*meso*-pse)Cl_2] and [Pt(*rac*-pse)Cl_2] (pse = 1,2-bis(phenylsulfinyl)ethane). The displacement of the monodentate sulfoxide is some 10^2 times more facile than ring opening and slightly less sensitive to steric hindrance than the less congested *meso*-disulfoxide isomer.

Introduction

In a recent paper[3] we reported the kinetics of the opening of the chelate rings of the isomeric [Pt(*meso*-pse)Cl_2] and [Pt(*rac*-pse)Cl_2] species by pyridines in 1,2-dimethoxyethane solution. Here it is shown that the ring-opening process was very much faster than the subsequent displacement of the ligand and that the two isomers differed markedly in their sensitivity to steric hindrance (the racemic isomer being the more sensitive). It has long been known from preparative chemistry[4] that one of the two dimethyl sulfoxides in *cis*-[Pt(Me_2SO)$_2Cl_2$] can be readily displaced by amines, even in polar solvents, whereas a single dimethyl sulfoxide can only be replaced with difficulty. In both cases the observations have been discussed in terms of stereoelectronic repulsion between the two cis sulfoxide ligands.

It was of interest to us to examine the extent to which the reactivity of the chelated disulfoxide differed from that of a corresponding bis(sulfoxide) complex, and we now report the kinetics of the displacement of dimethyl sulfoxide from *cis*-[Pt(Me_2SO)$_2Cl_2$] by pyridines and diazines under conditions identical with those used for the ring opening reaction.[3]

Experimental Section

Materials. *cis*-Dichloro(dimethyl sulfoxide)platinum(II) was prepared from K_2PtCl_4 and dimethyl sulfoxide by the method of Wayland et al.[5]

***cis*-Dichloro(dimethyl sulfoxide)(pyridine)platinum(II).** To a suspension of *cis*-[Pt(Me_2SO)$_2Cl_2$] (0.506 g; 1.2 mmol) in the minimum amount of water (20 cm^3) was added pyridine (0.095 g; 1.2 mmol) with stirring, and the resulting solution was heated on a steam bath for 3 h. The pale yellow precipitate which formed was filtered off, washed with water, ethanol, and ether, and then dried under vacuum.

***cis*-Dichloro(dimethyl sulfoxide)(2-methylpyridine)platinum(II), *cis*-dichloro(dimethyl sulfoxide)(pyridazine)platinum(II),** and ***cis*-dichloro(dimethyl sulfoxide)(pyrimidine)platinum(II)** were prepared in a similar way.

***trans*-Dichloro(dimethyl sulfoxide)(4-cyanopyridine)platinum(II).** To a suspension of *cis*-[Pt(Me_2SO)$_2Cl_2$] (0.211 g; 0.5 mmol) in 1,2-dimethoxyethane (25 cm^3) was added a solution of 4-cyanopyridine in the same solvent (5 cm^3) at room temperature. The pale yellow microcrystalline precipitate that separated from the solution resulting after stirring for 0.5 h was filtered off, washed with dimethoxyethane, and dried under vacuum.

The same product was obtained by reaction of equimolar amounts of reagents suspended in a water–methanol mixture (80:20 v:v).

The pyridines were purified by distillation as previously reported.[3] The diazines (Aldrich pure chemicals) were used as purchased. 1,2-Dimethoxyethane was first refluxed over $LiAlH_4$, distilled in a stream of dry nitrogen, and then redistilled from potassium in the presence of benzophenone. Analytical and infrared data are collected in Table I. Infrared spectra of the solid samples as KBr pellets or Nujol mulls were measured with a Perkin-Elmer 621 recording spectrophotometer.

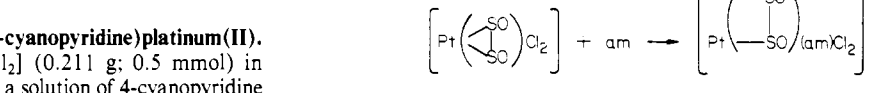
Kinetics. Reactions were started by mixing known volumes of freshly prepared solutions of the complex and the heterocyclic base that had been brought to the reaction temperature separately and were followed in the thermostated cell of a Perkin-Elmer 575 spectrophotometer, either by scanning the spectrum over the range 400–280 nm or by measuring the rate of decrease of absorbance at about 295 or 350 nm (the actual wavelength used depended upon the entering amine). All kinetics were carried out in the presence of a sufficient excess of amine to ensure pseudo-first-order conditions and complete conversion of the substrate.

Results and Discussion

With the exception of that with 4-cyanopyridine, all of the reactions are characterized by an decrease in absorbance over the wavelength range 400–280 nm. This process is followed by a much slower change, characterized by an increase in absorbance which does not interfere with the quantitative study of the first stage. These changes are very similar to those observed in the reactions involving the chelated disulfoxide. At the end of the first stage the spectrum corresponds very closely to that of an authentic sample of *cis*-[Pt(Me_2SO)(am)Cl_2]. No appreciable cis–trans isomerization was observed, and it is concluded that the first reaction is

cis-[Pt(Me_2SO)$_2Cl_2$] + am → *cis*-[Pt(Me_2SO)(am)Cl_2] + Me_2SO

which is directly analogous to the ring opening of the chelating disulfoxide



A mechanism in which the rate-determining step is the temporary displacement of the chloride can be ruled out for the reasons discussed in the previous work.[3]

The spectrophotometric changes obey a first-order rate law, and plots of ln ($A_t - A_\infty$) against time (where A_t and A_∞ are the absorbances at time t and after 8 half-lives respectively) are linear. Plots of k_{obsd} (the slopes of these plots) against [am] are linear and pass through the origin. The second-order rate constants obtained from a linear least-squares analysis of the slope of the k_{obsd} vs. [am] plots are collected in Table II together with the corresponding k_2 values for the ring-opening reactions of the chelated disulfoxide complexes taken from ref 3. The absence of the nucleophile-independent solvolytic

(1) University of Venice.
(2) University College, London.
(3) Cattalini, L.; Marangoni, G.; Michelon, G.; Paolucci, G.; Tobe, M. L. *Inorg. Chem.* **1981**, *20*, 71.
(4) Braddock, P. D.; Romeo, R.; Tobe, M. L. *Inorg. Chem.* **1974**, *13*, 1170.
(5) Price, J. H.; Williamson, A. N.; Schramm, R. F.; Wayland, B. B. *Inorg. Chem.* **1972**, *11*, 1280.

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Table I. Analytical[a] and IR Data for the Complexes

complexes	% C	% H	% N	% S	% Cl	ν_{S-O}, cm^{-1}	ν_{Pt-Cl}, cm^{-1}
cis-[$Pt(Me_2SO)(py)Cl_2$]	19.8 (19.9)	2.60 (2.60)	3.30 (3.31)	7.55 (7.58)	17.1 (16.8)	1150	348, 320
cis-[$Pt(Me_2SO)$(2-Me-py)Cl_2]	22.0 (22.0)	3.04 (2.97)	3.13 (3.20)	7.30 (7.32)	16.1 (16.2)	1132	346, 320
cis-[$Pt(Me_2SO)$(pyridazine)Cl_2]	16.9 (17.0)	2.36 (2.36)	6.55 (6.60)	7.42 (7.55)	16.8 (16.7)	1125	342, 318
cis-[$Pt(Me_2SO)$(pyrimidine)Cl_2]	16.8 (17.0)	2.38 (2.36)	6.56 (6.60)	7.52 (7.55)	17.2 (16.7)	1140	345, 320
trans-[$Pt(Me_2SO)$(4-CN-py)Cl_2]	21.2 (21.4)	2.32 (2.23)	6.15 (6.25)	7.17 (7.14)	15.7 (15.8)	1140	350

[a] Calculated values in parentheses.

Table II. Second-Order Rate Constants for the Reaction[a]

cis-[$Pt(Me_2SO)_2Cl_2$] + am → *cis*-[$Pt(Me_2SO)$(am)Cl_2] + Me_2SO

am	$pK_a(amH^+)$	k_2,[a] M^{-1} s^{-1}	10^2k_2,[b] M^{-1} s^{-1}	10^2k_2,[c] M^{-1} s^{-1}
4-ethylpyridine	6.08		24.7 ± 0.8	50.9 ± 0.5
4-methylpyridine	6.02	20.5 ± 0.9	23.0 ± 0.5	47.0 ± 3.6
pyridine	5.17	8.33 ± 0.54	7.82 ± 0.32	16.2 ± 0.6
4-chloropyridine	3.84		1.18 ± 0.08	2.72 ± 0.23
pyridazine	2.24	1.02 ± 0.08		
4-cyanopyridine	1.84	0.30 ± 0.01		
pyrimidine	1.30	0.52 ± 0.01		
pyrazine	0.65	0.26 ± 0.01		
3,4-dimethylpyridine	6.44	30.0 ± 2.1	40.5 ± 1.35	73.0 ± 1.6
3,5-dimethylpyridine	6.34	14.7 ± 0.7	19.9 ± 0.6	32.7 ± 0.8
3-methylpyridine	5.68	10.6 ± 1.0	12.6 ± 0.4	24.5 ± 0.3
2,4-dimethylpyridine	6.99	1.21 ± 0.05	1.43 ± 0.13	0.78 ± 0.02
2-methylpyridine	6.10	0.52 ± 0.05	0.43 ± 0.006	0.25 ± 0.007

[a] In 1,2-dimethoxyethane at 25 °C. [b] k_2 values for the ring-opening reactions of the chelated *meso*-disulfoxide complex by amines in 1,2-dimethoxyethane at 25 °C.[3] [c] k_2 values for the ring-opening reactions of the chelated *rac*-disulfoxide complex by amines in 1,2-dimethoxyethane at 25 °C.[3]

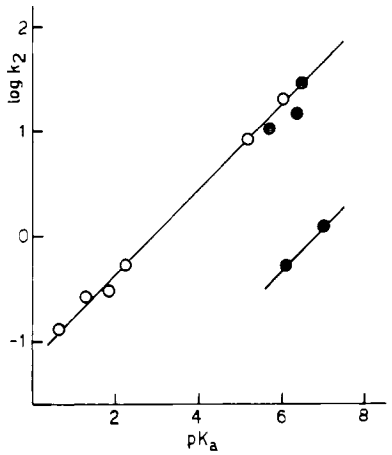
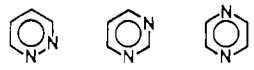


Figure 1. log k_2 for the reaction *cis*-[$Pt(Me_2SO)_2Cl_2$] + am → *cis*-[$Pt(Me_2SO)$(am)Cl_2] + Me_2SO plotted against pK_a of amH^+: open circles, pyridine, para-substituted pyridines, and diazines; hatched circles, meta-substituted pyridines; solid circles, ortho-substituted pyridines.

pathway (represented by an intercept to these plots) is a normal feature of substitutions in the poorly coordinating 1,2-dimethoxyethane.[3,6-8]

In the case of the reaction with 4-cyanopyridine the second spectrophotometric change was relatively fast and prevented a simple first-order analysis of the first stage with use of an experimental infinity value. The rate constant for the first step was calculated by fitting the absorbance–time data by a nonlinear regression analysis with a Gauss–Newton algorithim, implemented on a Tektronix 4052 minicomputer. The plots of log k_2 against the pK_a (in water) of amH^+ are shown in Figure 1. The values for the nucleophiles pyridazine (I), pyrimidine (II), and pyrazine (III) quoted in Table II are the



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slopes of the plots of k_{obsd} against [am] but, so that we could account for the statistical effect of two equivalent nitrogens per molecule, they have been halved for the plot of log k_2 vs. pK_a in Figure 1.[9]

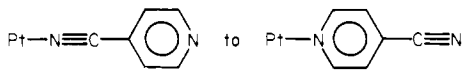
(6) (a) Cattalini, L.; Martelli, M.; Marangoni, G. *Inorg. Chim. Acta* **1968**, *2*, 405. (b) Martelli, M.; Marangoni, G.; Cattalini, L. *Gazz. Chim. Ital.* **1968**, *98*, 1031. (c) Marangoni, G.; Degetto, S.; Celon, E. *Ibid.* **1969**, *99*, 816. (d) Cattalini, L.; Marangoni, G.; Coe, J. S.; Vidali, M.; Martelli, M. *J. Chem. Soc. A* **1971**, 593.

(7) Cattalini, L.; Coe, J. S.; Faraone, F.; Marsala, V.; Rotondo, E. *Inorg. Chim. Acta* **1972**, *6*, 303.

(8) Marangoni, G.; Martelli, M.; Cattalini, L. *Gazz. Chim. Ital.* **1968**, *98*, 1038.

(9) A reviewer has suggested that, in addition to applying the statistical correction to k_2 for the diazine nucleophiles to take account of the two equivalent donor sites, it is also necessary to treat the pK_a of the diazine in a parallel fashion.[10] This would require the correction $pK_a(cor) = pK_a(exptl) - 0.30$ which displaces the data for the diazines significantly to the left of the line defined by the data for the substituted pyridines and places them on a parallel line. The need for the statistical correction for bifunctional amines of the type $NH_2(CH_2)_nNH_2$ is well established in systems where k_2 is essentially independent of the basicity of the amine, and hence any plot is insensitive to the detailed values assigned to $pK_a(amH^+)$,[11,12] but we are unable to produce any statistical thermodynamic argument that allows us to ignore a correction to the experimentally measured basicity. However if we represent a proton-transfer process in water as N–NH + H_2O ⇄ N–N + H_3O^+, the reverse reaction, being diffusion controlled, will not warrant a statistical correction to take account of the bifunctional nature of N–N. While we recognize that kinetic arguments of this sort ought not to affect data relating to equilibrium and that this raises a very serious problem in terms of linear free energy relationships and we hope to study it in more detail in the future, it is only of minor consequence to the main purpose of this paper.

There is a linear relationship between log k_2 and the pK_a of amH^+ for amines with the same extent of steric hindrance, e.g., for 4-substituted pyridines where it is assumed that there is no steric hindrance from the substituent and for 2-methylpyridines where the hindrance is considerable. A small decrease in the expected reactivity is noticed for 3-methyl-substituted pyridines, a common observation in these systems.[3,13,14] The two lines are parallel; the slope $\alpha = 0.41$ is taken as a measure of the ability of the substrate to discriminate between amines of different basicity, and the vertical separation between the lines, $\Delta = 1.68$, is taken as a measure of the steric hindrance of the methyl group in the ortho position. The anomalous behavior of 4-cyanopyridine requires further comment. Attempts to isolate the product of the first stage of this reaction were unsuccessful, and all experiments yielded *trans*-$[Pt(Me_2SO)(4\text{-CN-py})Cl_2]$, which has a spectrum that is identical with that of the reaction mixture at the end of the second stage of the spectrophotometric change. The infrared spectrum of this compound has only one peak that can be assigned to ν_{Pt-Cl}, hence the assignment of a trans configuration, and the ν_{C-N} stretch is unchanged on coordination (ν_{C-N} = 2242 cm^{-1} in the complex and 2240 cm^{-1} in the free ligand). Therefore the ligand is bound to platinum through the heterocyclic nitrogen. The second stage therefore corresponds to a cis–trans isomerization, but we have not yet studied this in detail. We have considered the possibility that initial attack is by way of the nitrile nitrogen and that the cis–trans change and the



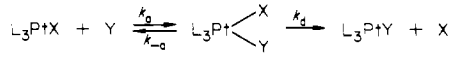
changes are synchronous and connected, but the observation that the reaction between 4-cyano-2,6-dimethylpyridine, where the heterocyclic nitrogen is strongly sterically hindered, and *cis*-$[Pt(Me_2SO)_2Cl_2]$ is immmeasurably slow, indicates that 4-cyanopyridine is attacking through its heterocyclic nitrogen and can be included in the data for the 4-substituted pyridines. The fact that the point lies on the appropriate log k_2 vs. pK_a line supports this conclusion.

The differences between the ring opening of the chelating disulfoxide and the displacement of the first dimethyl sulfoxide are expected to arise mainly from (i) the electronic effects of the change in substituent and (ii) the chelate effect. The most significant observation is that the displacement of a monodentate sulfoxide is some 2 orders of magnitude faster than the opening of the chelate ring. Preliminary studies of the reactions of other *cis*-bis(sulfoxide)dichloroplatinum(II) complexes indicate that there is very little difference in the reactivities of bis(dimethyl sulfoxide) and bis(phenyl methyl sulfoxide) complexes,[15] and so the enhanced reactivity of the bis(sulfoxide) complex over the ring opening of the chelated bis(phenylsulfinyl)ethane species cannot be ascribed to the replacement of phenyl by methyl. We must therefore conclude that the presence of the chelate ring restricts the stretching of the Pt–S bond in the bond-breaking transition state.

In view of the known facts (i) that the trans effect of dimethyl sulfoxide is considerably greater than that of chloride (for example, Elding and Gröning have shown a 10^3-fold enhancement of reactivity in monoanionic complexes[16]), (ii) that the extra cis-labilizing effect of dimethyl sulfoxide over chloride (a factor of 12 when measured under similar conditions[16]) which should affect the other sulfoxide and the chloride equally, and (iii) that a single S-bonded sulfoxide is usually much more difficult to replace than a chloride (all other conditions being equal), the observation that the sulfoxide is replaced in preference to the chloride calls for further discussion. It is now a common observation that, in a nonpolar solvent such as dimethoxyethane, substitution processes that lead to charge separation in the transition state are strongly disfavored, and so it is not too surprising that the neutral amine replaces the neutral sulfoxide in the uncharged substrate. However solvent effects will not explain the observations, based on preparative chemistry, that one of the two sulfoxides in *cis*-$[Pt(Me_2SO)_2Cl_2]$ is replaced by amines in methanol. Thus, a convenient method to prepare *cis*-$[Pt(Me_2SO)(am)Cl_2]$, where am is a cycloalkylamine, was found to be the reaction between *cis*-$[Pt(Me_2SO)_2Cl_2]$ and the amine in methanol.[4] It seems clear that there exists a mutual labilization effect between two cis sulfoxides that cannot be accounted for by any scheme of cis and trans effects that independently involve the leaving group and the other ligands in the complex. In the absence of any novel electronic effect we wish to account for the effect in terms of steric repulsion which must assist the bond-breaking part of the process. The steric effect of two dimethyl sulfoxides as measured by Δ (1.68) in retarding the entry of 2-methyl-substituted pyridines is still reasonably large and is not much smaller than that of [Pt(*meso*-pse)Cl_2] (Δ = 1.80) where the entering group has a choice of the side of the plane where the two phenyl groups are found and the other where the two oxygens stick out (it is not immediately apparent which side would be the most disfavored). The [Pt(*rac*-pse)Cl_2] isomer does not offer this choice and the hindrance in much larger (Δ = 2.31). A search for similar mutual labilization effects in other *cis*-bis(sulfoxide), -bis(thioether), and even -bis(phosphine) or -bis(arsine) complexes would make it possible to further examine this concept of stereoelectronic repulsion (the term is chosen to include the repulsions of lone pairs on adjacent atoms, e.g., on S in thioethers and O in the sulfoxides) in more detail.

If it is accepted that the large difference in the rates of ring opening and the displacement of the monodentate sulfoxide is due to the special requirements of the chelate, it must also be accepted that there is a great deal of disturbance to the Pt–S bond in the rate-determining transition state. This suggests that bond breaking is rate determining, i.e., the bond-making transition state, which precedes the formation of the five-coordinate intermediate and whose Pt–N bond is partially formed while its Pt–S bond is virtually intact, lies at a lower energy than the bond-breaking transition state, which follows the intermediate and whose Pt–N bond is almost fully formed and whose Pt–S bond nearly broken.

There is no paradox in the statement that the rate of an associative (A) reaction in which the bond-breaking transition state lies at the maximum of the energy-reaction coordinate diagram is much more sensitive to the proton basicity of the entering amine than the one in which bond formation is the rate-determining step. The A mechanism can be represented as



where L_3PtXY is the five-coordinate intermediate. (For simplification of the discussion it is assumed that this reaction is irreversible; however, the conclusions can be readily extended to the reverse reaction by applying the principle of microscopic reversibility.)

If the concentration of the intermediate is always small, the application of the stationary-state approximation gives

$$-d[L_3PtX]/dt = k_a k_d/(k_{-a} + k_d)[L_3PtX][Y]$$

(10) Benson, S. W. *J. Am. Chem. Soc.* **1958**, *80*, 5151.
(11) Baracco, L.; Cattalini, L.; Coe, J. S.; Rotondo, E. *J. Chem. Soc.* **1971**, 1800.
(12) Cattalini, L.; Orio, A.; Doni, A. *Inorg. Chem.* **1966**, *5*, 1517.
(13) Cattalini, L.; Martelli, M. *J. Am. Chem. Soc.* **1969**, *31*, 312.
(14) Chan, S. C.; Wong, F. T. *Aust. J. Chem.* **1968**, *21*, 2873.
(15) Bonivento, M., unpublished results.
(16) Elding, L. L.; Gröning, O. *Inorg. Chem.* **1978**, *17*, 1872.

i.e., the observed second-order rate constant $k_2 = k_a k_d/(k_{-a} + k_d)$.

The two limiting conditions (i) $k_d \gg k_{-a}$ and (ii) $k_d \ll k_{-a}$ are alternative ways of representing the situations where (i) the bond-making transition state lies highest and (ii) the bond-breaking transition state lies highest. In case i the expression reduces to $k_2 = k_a$ and the influence of chelation on bond breaking would be negligible, while in case ii it reduces to $k_2 = k_a k_d/k_{-a}$. The sensitivity of the rate constant to the pK_a of the entering amine resides mainly in k_{-a}, the rate constant for the dissociation of the amine from the five-coordinate intermediate, rather than in k_a. Thus the strength of binding of the amine to platinum parallels its proton basicity, and this must be reflected in its dissociative lability; i.e., k_{-a} decreases as the proton basicity of the amine increases. In this way k_2 will increase as the proton basicity of the amine increases. k_a may also be sensitive to amine basicity but rarely to the same extent, and there are even cases where k_2 actually decreases as the basicity of a heterocyclic amine increases.[17] The proton basicity is important in that part of the process where the amine moves from its fully bound to its partially bound state and far less important in the longer range interactions where it moves from an unbound state to a partially bonded state.[18]

The difference in the values of α for the reactions of the chelated ($\alpha = 0.58$) and monodentate ($\alpha = 0.41$) sulfoxides probably represents the greater assistance given to the more different bond-breaking step in the chelate complex by the amine when bound to the platinum (i.e., a dependence of k_d[19] upon the nature of the entered amine).

It follows that any discussion of nucleophilicity, which is effectively defined as a measure of k_2 rather than k_a, must take account of the relative importance of the bond-making and bond-breaking aspects of the substitution process. We propose to discuss this problem in a broader context elsewhere.

Acknowledgment. We thank Professor P. Uguagliati for some kinetic computing and the Italian Council of Research, CNR, Rome, for financial support in a bilateral project.

Registry No. *cis*-[Pt(Me_2SO)(py)Cl_2], 20647-45-4; *cis*-[Pt(Me_2SO)(2-Me-py)Cl_2], 61551-15-3; *cis*-[Pt(Me_2SO)(pyridazine)Cl_2], 76479-91-9; *cis*-[Pt(Me_2SO)(pyrimidine)Cl_2], 76479-92-0; *cis*-[Pt(Me_2SO)(4-CN-py)Cl_2], 76479-93-1; *cis*-[Pt(Me_2SO)$_2Cl_2$], 22840-91-1; 4-Me-py, 108-89-4; py, 110-86-1; pyridazine, 289-80-5; 4-CN-py, 100-48-1; pyrimidine, 289-95-2; pyrazine, 290-37-9; 3,4-Me_2-py, 583-58-4; 3,5-Me_2-py, 591-22-0; 3-Me-py, 108-99-6; 2,4-Me_2-py, 108-47-4; 2-Me-py, 109-06-8.

Supplementary Material Available: A table of first-order rate constants (2 pages). Ordering information is given on any current masthead page.

(17) Gosling, R.; Kennedy, B. P.; Tobe, M. L. *Inorg. Chem.* **1977**, *16*, 1744.
(18) Romeo, R.; Tobe, M. L. *Inorg. Chem.* **1974**, *13*, 1991.
(19) We wish to thank one of the reviewers for helping us to focus our attention upon this point.

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The Molybdenum-Molybdenum Triple Bond. 8.[1] Bis(6-methyl-2-pyridyl)methyltetrakis(dimethylamido)dimolybdenum

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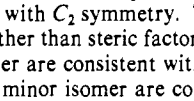
$Mo_2Cl_2(NMe_2)_4$ reacts in hydrocarbon solvents with a suspension of (6-methyl-2-pyridyl)methyllithium to give the title compound which has been obtained as a yellow crystalline solid by recrystallization from hexane solutions. In the solid state, each molybdenum atom is coordinated to two amido nitrogen atoms and the carbon atom of the (6-methyl-2-pyridyl)methyl anion, $-CH_2$pyMe. The halves of the molecule are joined by an unbridged Mo-to-Mo triple bond of distance 2.204 (1) Å and the central $Mo_2N_4C_2$ unit adopts the gauche ethane-like conformation with C_2 symmetry. The pyridine nitrogen is not coordinated to the Mo_2^{6+} center, a fact which is attributed to electronic rather than steric factors. ^{1}H NMR studies show the presence of two isomers in toluene-d_8. The spectra of the major isomer are consistent with the gauche conformation of the molecule found in the solid state; the spectra associated with the minor isomer are consistent with those expected for the anti rotamer. These observations are compared with those reported previously for bis(2-oxy-6-methylpyridine)tetrakis(dimethylamido)dimolybdenum. Crystal data for $Mo_2N_6C_{22}H_{40}$: space group $P2_1/a$; $Z = 4$; a = 22.013 (5), b = 7.974 (2), c = 14.933 (3) Å; β = 96.43 (1)°; V = 2604.7 Å^3; d_{calcd} = 1.480 g/cm^3.

Introduction

As a part of our continuing studies of the coordination chemistry surrounding the dinuclear metal centers $(M{\equiv}M)^{6+}$, where M = Mo and W,[2] we have embarked upon the synthesis and characterization of a series of compounds of general formula $M_2X_4(Y\text{-}L)_2$, where X = R (alkyl), NR_2, and OR and Y-L represents a uninegative and potentially bidentate ligand. We intend to investigate the Lewis acidity of these dimetal centers as a function of X and the donor ligand atom of potentially bidentate ligand Y-L. We report here the preparation of the compound where X = NMe_2 and Y-L is the uninegative ligand



which is derived from deprotonation of 2,6-dimethylpyridine.

Results and Discussion

Synthesis. $Mo_2Cl_2(NMe_2)_4$ in hexane solution reacts slowly with a suspension of (6-methyl-2-pyridyl)methyllithium, $LiCH_2$pyMe, to give brown solutions and a finely divided precipitate of LiCl. Yellow crystals of the air- and moisture-sensitive title compound are obtained by crystallization of the hexane filtrate upon cooling. Analytical, infrared, and ^{1}H NMR data are reported in the Experimental Section.

Solid-State Structure. In the crystalline state, the compound is composed of discrete $Mo_2(NMe_2)_4(CH_2pyMe)_2$ molecules. Final atomic positional parameters are given in Table I, and bond distances and angles are given in Tables II and III ,

(1) Part 7: M. H. Chisholm, D. A. Haitko, J. C. Huffman, and K. Folting, *Inorg. Chem.*, **20**, 171 (1981).
(2) For recent reviews of the chemistry associated with these compounds, see M. H. Chisholm and F. A. Cotton, *Acc. Chem. Res.*, **11**, 356 (1978).

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