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SOLID-STATE STUDIES OF α- AND β-[Mo_2Cl_4(dppe)$_2$]—KINETICS OF THE α → β ISOMERIZATION REACTION AND SOLID-STATE ^{31}P AND ^{13}C NMR SPECTRA

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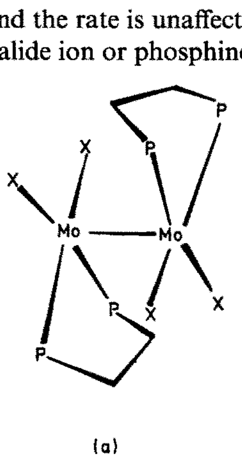
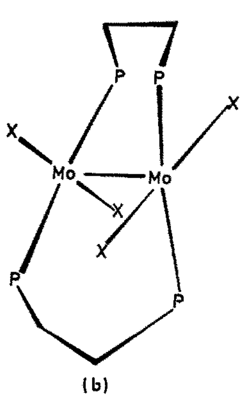
Abstract—We have investigated the reaction in which the chelated (α) form of [Mo_2Cl_4(dppe)$_2$] isomerizes to the bridged (β) form in the solid state. The kinetic parameters for the solid-state reaction ($E_a = 335 \pm 30$ kJ mol^{-1}, $\Delta S^{\ddagger} = 340 \pm 30$ J K^{-1}) are substantially different from those measured for the isomerization in solution ($E_a = 121 \pm 5$ kJ mol^{-1}, $\Delta S^{\ddagger} = 16.2 \pm 0.8$ J K^{-1}). The ^{31}P and ^{13}C solid-state NMR spectra of the two isomers are presented and discussed. Of particular note is the ^{31}P NMR spectrum of the β-isomer which is broad at room temperature and sharpens markedly on cooling. This temperature dependence is interpreted as being due to paramagnetism caused by the presence of the low-lying $^3\delta\delta^*$ state, which has significant population at room temperature.

Complexes of the quadruply-bonded Mo_2 unit with bidentate phosphines exist in two isomeric forms:[1] a chelated (α) isomer[2] in which each phosphine chelates one of the molybdenum atoms, and a bridged (β) isomer[3] in which the phosphines bridge the Mo_2 unit. The structures are illustrated schematically below (**a** and **b**). It is now well established that the α-isomer of $Mo_2X_4(\overset{\frown}{P\,P})_2$ spontaneously isomerizes to the appropriate β-isomer in non-aqueous solvents.[2,4–6] The reaction has been studied for a variety of phosphines and for X = Cl and Br. In each case the reaction follows first-order kinetics and the rate is unaffected by the addition of excess halide ion or phosphine.



(a)



(b)

When we first reported[4] the α → β isomerization reaction we suggested that the mechanism of the reaction involved the dissociation of one end of the diphosphine molecule from Mo(1) of the α structure, followed by attack by the free phosphorus on Mo(2). Agaskar and Cotton showed,[3] however, that the isomerization reaction proceeds cleanly in the solid state, thus eliminating the possibility of any form of dissociation, and suggested a mechanism involving the "flip" of an Mo_2 unit within the essentially static P_4X_4 "cage". Subsequent work by Cotton and co-workers[7,8] has shown that the "flip" mechanism must also be operating in solution. Cayton and Chisholm have recently investigated the flip mechanism theoretically, using Fenske–Hall calculations, and have concluded that the process is symmetry allowed.[9]

We have now studied the kinetics of the solid-state isomerization of Mo_2Cl_4(dppe)$_2$ and in this paper we present kinetic data for the solid-state process and compare them with those for the solution reaction. We also present comparative data for the solution phase isomerization of a number of other $Mo_2X_4(\overset{\frown}{P\,P})_2$ complexes.

Neither the α- nor β-isomers of Mo_2Cl_4(dppe)$_2$ are sufficiently soluble for solution NMR spectra to be obtained. As an exploratory use of solid-state NMR applied to metal–metal bonded complexes, we have obtained the solid-state ^{13}C and ^{31}P NMR

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spectra of both the α- and β-isomers (the latter at both room temperature and at −80°C) and of the free dppe ligand.

EXPERIMENTAL

Preparation of compounds

The ligand 1,2-bis(di-*p*-tolyl)ethane (dptpe) was prepared by standard procedures from tris-*p*-tolylphosphine and 1,2-dichloroethane. α- and β-$[Mo_2Cl_4(dppe)_2]$, α-$[Mo_2Br_4(dppe)_2]$, α-$[Mo_2Cl_4(R\text{-dppp})_2]$, α-$[Mo_2Cl_4(dppp)_2]$ and α-$[Mo_2Cl_4(dppte)_2]$ were prepared by refluxing degassed methanolic solutions containing the appropriate phosphine and $K_4Mo_2X_8$ in a 2 : 1 mole ratio. All compounds gave satisfactory analyses.

Solid-state NMR spectra

^{31}P and ^{13}C SP/MAS solid-state NMR spectra were measured by the SERC NMR service, University of Durham. The pulse sequence was SXSEQ for all samples except the low-temperature ^{31}P spectrum of β-$[Mo_2Cl_4(dppe)_2]$, where the XPOLWD sequence was used. Chemical shifts are collected in Table 1 and the ^{31}P NMR spectra illustrated in Figs 1 and 4.

Kinetic measurements

The kinetics of the isomerization reactions in solution were followed by monitoring the electronic spectrum of the sample dissolved in dry dichloromethane solution; the solution being contained in an evacuated cell which was thermostated in a water bath. A number of runs were done in the temperature range 15–30°C. The temperature was controlled to within ±0.1°C.

The solid-state reaction is considerably more difficult to follow because of the high temperatures required and because analysis of the extent of reaction is destructive, being accomplished by quenching the sample, dissolving it in CH_2Cl_2 and measuring the absorption spectrum. Furthermore, the sample must be rigorously evacuated to prevent oxidation at the high temperatures used. The procedure adopted was as follows: Several small, narrow glass tubes, fitted with cones, were filled with α-$[Mo_2Cl_4(dppe)_2]$ and evacuated on a vacuum line to at least 10^{-4} torr. After 1 h under evacuation the tubes were sealed using a blow-torch. The tubes were placed in a thermostated oven pre-heated to the chosen temperature. The tubes were removed successively after suitable time intervals, cooled rapidly, broken open and the contents dissolved in CH_2Cl_2 when the spectrum was immediately obtained. In order to eliminate local heating of the sample, we used a fan-assisted oven and hung the tubes from wires in the centre. The tubes were all hung at the same height and the temperature measured at that height also. Three independent samples were analysed for each temperature/time point. By using the weight of each sample and the extinction coefficients of the α- and β-isomers, it was confirmed for each sample that all the α-isomer was converted to the β-form and that there were no by-products. The reaction was repeated at a variety of temperatures between 211 and 250°C. The temperature was accurate to ±1.0°C.

The isomerization reactions were shown to follow first-order kinetics both in solution and in the solid state. The plot of $\ln\{c_\beta/(c_\alpha+c_\beta)\}$ and the Arrhenius plots for the solid state isomerization are shown in Figs 2 and 3 respectively. The kinetic parameters are collected in Table 2.

RESULTS AND DISCUSSION

We begin by discussing the solid-state NMR of the complexes and follow this by discussing the kinetic results for the isomerization reaction.

Solid-state NMR spectra

^{31}P and ^{13}C MAS solid-state NMR spectra for α- and β-$[Mo_2Cl_4(dppe)_2]$, along with solid-state and solution spectra of the free dppe ligand, are listed in Table 1. The ^{31}P spectra are illustrated in Fig. 1 (room-temperature spectrum of α-[Mo₂

Table 1. Solid-state NMR data for dppe and α- and β-$[Mo_2Cl_4(dppe)_2]$

Compound	^{31}P	^{13}C	
dppe (soln)	−12.57	23.81	(138.0–128.33)
dppe	−12.17	24.60	(140.2–127.94)
α-$[Mo_2Cl_4(dppe)_2]$	40.27, 46.48	19.51, 24.43	(138.42–127.57)
β-$[Mo_2Cl_4(dppe)_2]$ (−80°C)	11.71, 18.26	21.13	(137.70–128.60)

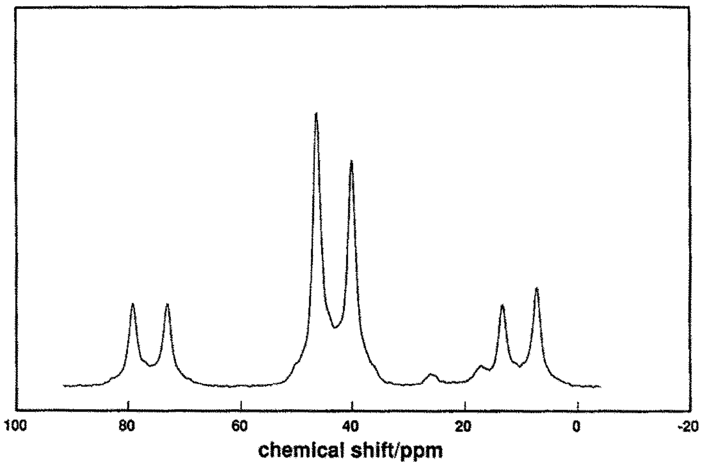

Fig. 1. Solid-state ^{31}P MAS NMR spectrum of α-[$Mo_2Cl_4(dppe)_2$] at room temperature.

$Cl_4(dppe)_2$]) and Fig. 4 (room-temperature and −80°C spectra of β-[$Mo_2Cl_4(dppe)_2$]). The solid-state chemical shifts of the free dppe ligand are essentially the same as those of the molecule in solution, giving us confidence that the solid-state spectra can be used for structural assignments.

The crystal structure of α-[$Mo_2Cl_4(dppe)_2$] has been determined as the THF solvate. The complex crystallizes in the space group $C2/c$, with $Z = 4$ and two phosphorus and two aliphatic carbon atoms in the asymmetric unit. Our spectra are of the complex prepared from $K_4Mo_2Cl_8$ and dppe in ethanol, since the preparation used for the THF adduct leads to a mixture of α- and β-isomers and cannot be used to produce the THF adduct in bulk. The crystal structure of the complex whose spectra we report is therefore not necessarily identical to that reported for the THF solvate. However, both the ^{31}P and ^{13}C NMR spectra are consistent with that structure, showing two ^{31}P and two ^{13}C resonances. The chemical shift difference between the two ^{13}C resonances (5 ppm) seems rather large, however, because although the crystal structure of the THF solvate shows that the two ring carbon atoms are crystallographically inequivalent they are, to all intents and purposes, chemically equivalent. If in our compound the five-membered MoPCCP chelate rings adopt a slightly different conformation, such that one of the carbon atoms is located over the metal–metal bond while the other is on the far side of the metal–metal bond, we can explain the chemical shift difference. The resonance at 19.51 ppm is that of the carbon located over the ring; the other, normal carbon having essentially the same chemical shift (24.6 ppm) as that of the carbons in the free dppe ligand. Additional evidence comes from the fact that the single ^{13}C resonance

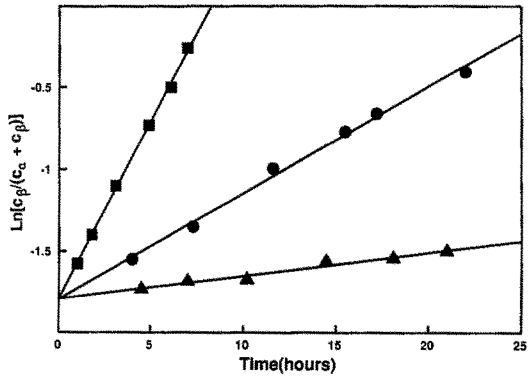

Fig. 2. Plot of $\ln[c_\beta/(c_\alpha - c_\beta)]$ vs time for the solid-state isomerization of α → β-[$Mo_2Cl_4(dppe)_2$] at various temperatures; c_α and c_β are the concentrations of the α- and β-isomers, respectively, in mol dm^{-3}. Squares 234°C; circles 227°C; triangles 218°C.

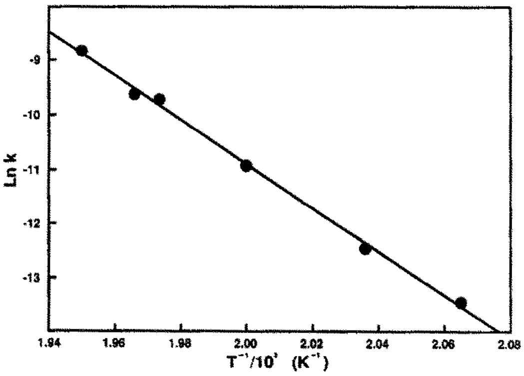

Fig. 3. Arrhenius plot for the solid-state isomerization of α → β-[$Mo_2Cl_4(dppe)_2$].

Table 2. Kinetic parameters for the $\alpha \rightarrow \beta$ isomerization of $[\mathrm{Mo_2Cl_4(\widehat{P\,P})_2}]$ complexes

	$t_{1/2}$ (298)	E_a (kJ mol^{-1})	$\log_{10} A$	$\Delta S^{\ddagger}$ (J K^{-1}mol^{-1})	Ref.
$[\mathrm{Mo_2Cl_4(dppe)_2}]$ solid		335 ± 30	29.7	340	This work
$[\mathrm{Mo_2Cl_4(dppe)_2}]$	19 h	121 ± 5	16.2	57	4
$[\mathrm{Mo_2Cl_4(dptpe)_2}]$	24 h	113 ± 5	14.7	28	4
$[\mathrm{Mo_2Cl_4(}R\mathrm{\text{-}dppp)_2}]$	8 min	107 ± 5	15.9	51	4
$[\mathrm{Mo_2Cl_4(dppp)_2}]$	39 min	96 ± 4	13.3	1	6
$[\mathrm{Mo_2Br_4(dppe)_2}]$	43 min	82 ± 4	10.8	−46	4

of the β-isomer, where both carbon atoms of the six-membered ring are located over the metal–metal bond, is found at 21.13 ppm.

$[\beta\text{-}\mathrm{Mo_2Cl_4(dppe)_2}]$ crystallizes in the space group $P2_1/n$, $Z = 4$ and four phosphorus and four aliphatic carbon atoms in the asymmetric unit. Thus, we should expect to see four ^{31}P and four ^{13}C signals in the solid-state NMR spectra instead of the observed two and one, respectively. In addition, there is disorder in the structure which results in two molecular orientations; 87% of the molecules being in the major and 13% in the minor orientation. First, the spectra either show only the major orientation (i.e. the signals from the molecules in the minor orientation, which will have 10% of the intensity of those of the major orientation molecules, are too weak to be observed) or the molecules in the two orientations have essentially the same chemical shifts. Second, the crystal structure only tells us the *number of crystallographically different* atoms in the molecule, not whether they are sufficiently chemically or magnetically different for the differences in chemical shifts to be observed. The ^{13}C signal is quite broad (FWHH = 300 Hz compared with 150 Hz for the two signals observed in the spectrum of the α-isomer) and the four expected resonances are presumably unresolved under the envelope of the single observed signal.

The most interesting feature of the ^{31}P spectrum of the β-isomer is its broadness at room temperature and subsequent sharpening on cooling to −80°C. It is very unlikely that the complex could be showing fluxional behaviour in the solid state and we suggest that the broadness is due to the slight paramagnetism inherent in the staggered structure. This is due to the thermally accessible $^3\delta\delta^*$ state, which can be very close to the ground state in energy.

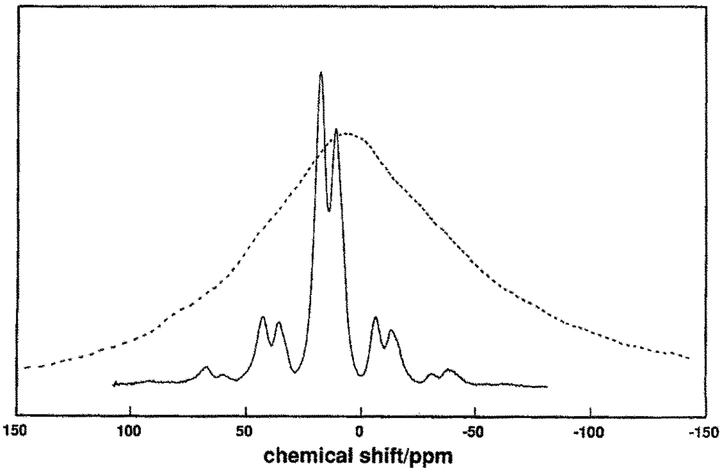

Fig. 4. Solid-state ^{31}P MAS NMR spectra of β-$[\mathrm{Mo_2Cl_4(dppe)_2}]$ at room temperature (dashed line) and at −80°C (full line).

Paramagnetism has been directly detected by Hopkins *et al.*[10] in β-[Mo_2Cl_4(dmpe)$_2$], where the molecule adopts a configuration which is almost eclipsed. The dmpe complex, which has a torsion angle of 40°, has μ_{eff} and $\mu_B = 0.8$ at room temperature, decreasing to 0.4 at −80°C. Although the torsion angle is smaller in β-[Mo_2Cl_4(dppe)$_2$] (30°, measured through the smallest angle), and thus the $^3\delta\delta^*$ state will be at higher energy than in the dmpe complex, it is likely that it is sufficiently thermally accessible to give the observed broadening of the ^{31}P spectrum. The only other (solution) ^{31}P NMR spectrum of a staggered dimolybdenum diphosphine complex which has been published[11] is of Mo_2I_4(dppe)$_2$. This also was anomalously broad at room temperature, sharpening up at −80°C. Although the broadening is this case could well be due to fluxional processes, it is also possible that the broadening has its origin in the paramagnetism of the complex.

Kinetic studies of the α → β isomerization reaction

Kinetic parameters for the solution isomerization of a number of diphosphine complexes and the solid-state isomerization of [Mo_2Cl_4(dppe)$_2$] are collected in Table 2.

The activation energies for the solution isomerization reactions fall within the relatively narrow range of 80–125 kJ mol^{-1}. The isomerization of α-[Mo_2Cl_4(dppe)$_2$], which contains the unsubstituted dppe ligand, requires the largest energy of activation. Substitution on the ring backbone to give *R*-dppp, replacement of the phenyl groups by *p*-tolyl groups or of chloride by bromide all lower the activation energy. *S,S*-dppb, with two methyl substituents, gives only β-[Mo_2Cl_4(*S,S*-dppb)$_2$]; the α-isomer, if it is formed at all, must isomerize with a half-life of seconds even at room temperature. The same is true of β-[Mo_2Cl_4(*R*-phenphos)$_2$], in which the phosphine backbone has been substituted with a phenyl group. The three-carbon backbone phosphine, dppp, also results in the α → β isomerization having a lower activation energy. These results are all consistent with the "internal flip" mechanism, with the hypothesis that the energy of the transition state is roughly the same in all cases and the activation energy largely depends upon the relative energy of the α-isomer. Thus, adding substitutents to the phosphine backbone, or replacing chloride by the bulkier bromide, congests the area of space above the Mo—Mo bond and leads to a less energetically stable α-isomer, thus reducing the energy required to achieve the transition state geometry.

The solid-state isomerization of α- to β-[Mo_2Cl_4(dppe)$_2$] is a first-order reaction with an activation energy of 335±30 kJ mol^{-1} and an entropy of activation of 340±30 J K^{-1}. Typical rate plots are shown in Fig. 2 and the Arrhenius plot in Fig. 3. We confirm Cotton *et al.*'s conclusion that the reaction has no side products; by using the extinction coefficients of the α- and β-isomers to calculate concentrations, all the α-isomer was shown to convert to the β-isomer. This must be taken as final proof that the solid state reaction proceeds by the internal flip mechanism.

Why are the kinetic parameters for the solid-state reaction so different from those of the corresponding solution reaction? Perhaps it is not surprising that the activation energy should be very much higher in the solid state than in solution. Cayton and Chisholm's Fenske–Hall calculations, although qualitative, suggest that there should be a substantial activation energy since both the Mo—Mo σ, and particularly π, molecular orbitals increase in energy as the Mo_2 unit is twisted through 45° to the geometry of the transition state. We have performed extended Hückel calculations on the ground and transition state geometries of an $Mo_2Cl_4(PH_3)_4$ unit in order to estimate the activation energy. Perhaps fortuitously, the difference in energy between the two geometries is calculated to be ~400 kJ mol^{-1}, which is reasonably near to the experimental value. The calculation was performed keeping the eight ligands in the same position in both ground and transition states, which is probably appropriate for the solid state. In solution we would expect the molecule to be more flexible, thus allowing the ligator positions to expand in the transition state and so reduce the activation energy.

The increased entropy of activation on going from solution to the solid state is more difficult to explain. The values of the Arrhenius factor obtained for all the solution isomerization reactions fall in the range expected for a unimolecular reaction. The considerably higher value of the Arrhenius factor found for the solid-state isomerization of α-[Mo_2Cl_4(dppe)$_2$] implies a considerable gain in the number of degrees of freedom of the intermediate. This might normally imply a bond-breaking mechanism, but this is clearly ruled out in the present case. The best suggestion that we can offer is that the flips are concerted; that is flipping one molecular unit in the crystal assists in flipping neighbouring units, thus allowing the isomerization to proceed in domains rather than as isolated molecules.

In all the compounds discussed above the back (β → α) isomerization is very much slower than the forward reaction and equilibrium lies substantially on the right. Cotton *et al.* have estimated the equilibrium constant for the α → β isomerization reactions of [$Mo_2Cl_4(dppe)_2$] and [$Mo_2Cl_4(dpdt)_2$] to be of the order 10, at which concentrations the α-isomer is undetectable by absorption spectroscopy in the presence of the β-isomer. In the case of the latter complex they were able to isolate the α-isomer from a solution of the β-isomer by utilizing the differential solubilities of the two isomers in a 1 : 2 mixture of methanol and CH_2Cl_2. Inspection of the ^{31}P solid-state NMR spectrum of β-[$Mo_2Cl_4(dppe)_2$] formed by the solid-state isomerization shows no detectable signal for the α-complex. The signal-to-noise ratio is such that it should be possible to detect at least 5% and probably 1% of the α-isomer. It seems, therefore, that the equilibrium for the solid-state isomerization lies further to the right than that for the solution reaction.

Cotton *et al.*[12] have recently reported a determination of the $^3\delta\delta^*$ energies of a number of quadruply bonded species by following the variation of the ^{31}P chemical shift with temperature.

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