Carbene Complexes. Part 17.[1] Crystal Structure of *trans*-Tetracarbonylbis(1,3-dimethylimidazolidin-2-ylidene)molybdenum(0), *trans*-[Mo(CO)$_4$-{CN(Me)CH$_2$CH$_2$NMe}$_2$], Structural Comparison with the *cis* Isomer, and a Kinetic Study of the *trans*→*cis* Isomerisation

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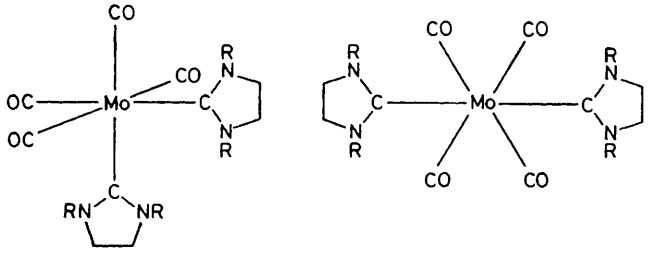
Crystals of the title compound are monoclinic, space group $C2/m$, with a = 14.706(5), b = 7.866(3), c = 8.132(3) Å, and β = 114.40(2). The molecule lies on a site of $2/m$ symmetry with *both* the carbene ligands in the crystallographic mirror plane (*i.e* they are *not* orthogonal). The structure was refined by full-matrix least squares to an R value of 0.027 for 87 variables (including isotropic hydrogen atoms) and 1 661 data. The Mo–C$_{carb.}$ distance of 2.232(2) Å is *ca.* 0.06 Å shorter than in the *cis* isomer. The Mo–CO length of 2.001(2) Å compares with the Mo–CO (*trans* CO) and Mo–CO (*trans* carbene) lengths of 2.028(3) and 1.980(3) Å respectively in the *cis* isomer. The activation energy (70.4 ± 2 kJ mol^{-1}, or 74.7 ± 0.7 kJ mol^{-1} for the ethyl homologues) for the *trans*→*cis* isomerisation was measured in diethyl phthalate by differential scanning calorimetry, using digital data logging equipment and a computer program. The reaction is first order and the negative activation entropy is attributed to interaction with solvent molecules in the transition state.

In Part 9 [2] we described *inter alia* (*a*) the synthesis and characterisation of *cis*- and *trans*-dicarbenetetracarbonylmolybdenum(0) complexes (1) and (2) {abbreviated as *cis*- and *trans*-[Mo(CO)$_4$(L^R)$_2$]}, (*b*) the thermal isomerisation of the *trans* into the thermodynamically favoured



(1a) R = Me
(1b) R = Et

(2a) R = Me
(2b) R = Et

cis isomers [*i.e.*, (2)→(1)], (*c*) the photochemical reverse transformation, and (*d*) the crystal structure of *cis*-[Mo(CO)$_4$(L^{Me})$_2$], (1a). We now report on (*e*) the molecular structure of *trans*-[Mo(CO)$_4$(L^{Me})$_2$], (2a), and (*f*) the kinetics of the *trans*→*cis* isomerisation.

RESULTS AND DISCUSSION

The Molecular Structure of trans-[Mo(CO)$_4$(L^{Me})$_2$], (2a), *and Comparisons with the cis Isomer*, (1a).—Although the molecular structures of numerous monocarbenemetal complexes are now well established (refs. 1 and 2 and bibliography cited therein), our earlier paper [2] was the first to describe that of a dicarbenemetal complex, and, incidentally, the first carbenemolybdenum(0) complex. The structure of the first *trans*-dicarbenemetal complex (2a) is of interest for the following reasons. Firstly, steric effects are less likely to influence the relative conformation of the two carbene ligands in the *trans* complex (2a) than in the *cis* analogue (1a). Secondly, a prediction has been made that the two carbene ligands be orthogonal, based on simple extended Hückel calculations; namely, in a *trans*-dicarbenemetal complex the C$_{carb.}$–M–C$_{carb.}$ moiety was regarded as preferentially pseudo-allenic.[3] Finally, we are able to compare the *cis*- and *trans*-isomers (1a) and (2a); previously, we did this for the platinum(II) complexes *cis*- and *trans*-[PtCl$_2$(L^{Ph})(PEt$_3$)].[4]

The molecular configuration of *trans*-[Mo(CO)$_4$(L^{Me})$_2$], (2a), is illustrated in Figure 1 and, for comparison, of the *cis* isomer, (1a), in Figure 2; the Figures also show the atom-numbering schemes. Details of the molecular geometry are in Table 1.

The suggestion that in *trans*-dicarbenemetal complexes the C$_{carb.}$ moiety may be expected to have a preference for a mutually perpendicular arrangement of the two carbene ligands [3] is confounded. In this case, (2a), both carbene ligands lie in the crystallographic mirror plane and are related by a centre of symmetry, *i.e.*, they are constrained to be perfectly parallel, see Figure 1.

The Mo–C$_{carb.}$ lengths in the *trans* isomer (2a) of 2.232(2) Å are *ca.* 0.06 Å shorter than those in the *cis* isomer (1a) [2.293(3) Å] [2] reflecting again the poor π-acceptor character of the carbene ligand relative to CO. The Mo–CO lengths of 2.001(2) Å in the *trans* isomer are *ca.* 0.03 Å shorter than the mutually *trans* Mo–CO distances in the *cis* compound [2.032(3) and 2.024(3) Å] where steric effects bend these CO groups away from the carbene ligands by *ca.* 6.4° from their ideal positions, Figure 2. The intramolecular non-bonded interactions causing this effect are C(1) · · · H(111) 2.69(4), C(1) · · · H(141) 2.79(5), C(2) · · · H(131) 2.66(4), and C(2) · · · H(121) 2.72(4) Å, all of which are within experimental error at the limit of the currently accepted value of the van der Waals contact of 2.8 Å.[5] The magnitude of the Mo–CO lengthening is unlikely to be due to steric effects alone; for both isomers each of the mutually

trans CO groups has two carbene and two CO ligands in *cis* positions and only the arrangement of these *cis* ligands with respect to each other differs.

The Mo–CO lengths in the *trans* isomer (2a) are *ca.* 0.02 Å longer than the Mo–CO (*trans* carbene) distances of 1.979(3) and 1.981(3) Å in the *cis*-dicarbene complex (2a).

The angle C(1)–Mo–C(1′) in the *trans* dicarbene complex (2a) opens to 93.4° while the supplementary angle C(1)–Mo–C(1‴) closes to 86.6° to minimise the non-bonded interactions C(1″) · · · H(51) 2.55(4) and C(1) · · · H(61) 2.58(4) Å, Figure 1. There are no other non-bonded interactions. This compares with the case of the *cis* isomer (1a), where each of the carbene carbons is involved in such interactions: C(5) · · · H(131) 2.64(4), C(6) · · · H(111) 2.69(4) Å as well as the carbonyl carbon atoms C(3) · · · H(121) 2.62(4), C(4) · · · H(141) 2.67(4) Å, and those already discussed for C(1) and C(2) above.

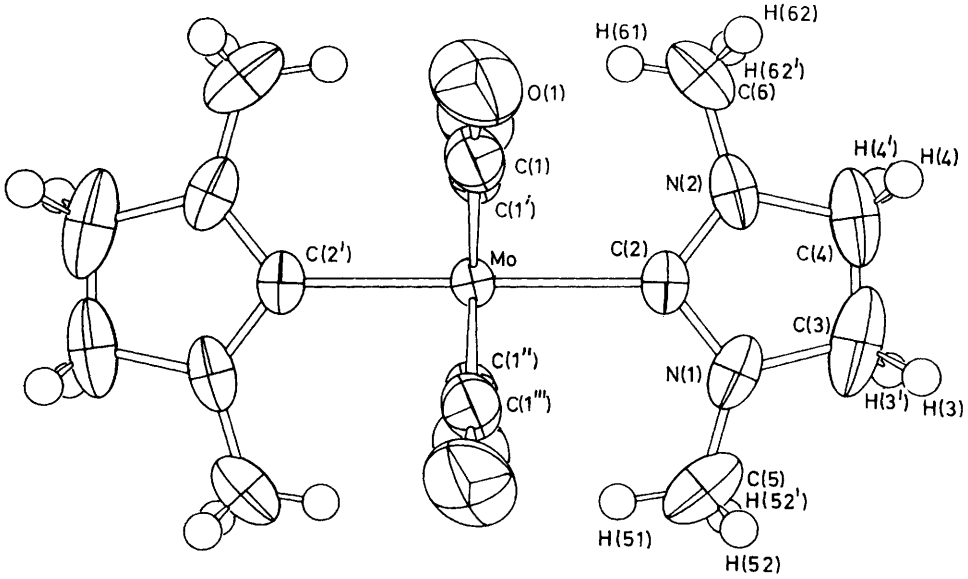


FIGURE 1 Diagram of the molecular structure of *trans*-$[Mo(CO)_4(L^{Me})_2]$, (2a), showing the atom-numbering system used and anisotropic thermal motion (ellipsoids are scaled to enclose 50% probability except for hydrogens which are given a small arbitrary diameter). Superscripts refer to the same co-ordinate transformations as in Table 1

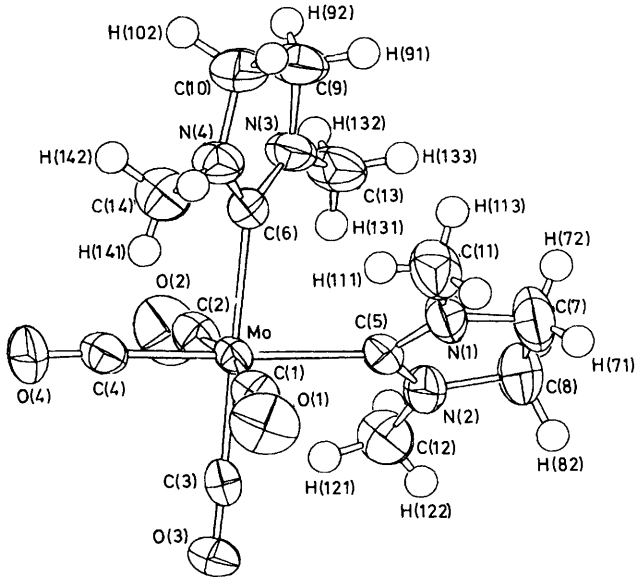


FIGURE 2 Diagram of the molecular structure of *cis*-$[Mo(CO)_4(L^{Me})_2]$, (1a), as for Figure 1

Molecular packing is more efficient for the *trans* isomer (2a), where two molecules occupy a cell volume of 856.6 Å^3 (428.3 Å^3 per molecule), than for the *cis* isomer (1a) where four molecules occupy a cell volume of 1 766.8 Å^3 (441.7 Å per molecule). In each case, however, it is the intramolecular non-bonded interactions which determine the observed conformation.

The geometry of the carbene ligand L^{Me} in the *trans* isomer (2a) agrees well with other structural studies involving this ligand.[6] The bond lengths have not been corrected for the libration about Mo in the crystallographic mirror plane, which is evident from Figure 1.

Kinetics of the Thermal Isomerisation of trans→cis-$[Mo(CO)_4(L^R)_2]$, (2)→(1).—The isomerisation in diethyl phthalate was followed by differential scanning calorimetry (d.s.c.).

The d.s.c. equipment and the data logger together with the appropriate computer program [7] were first tested for reproducibility and accuracy by studying the thermal decomposition of azobisisobutyronitrile; this is known [8] to decompose quantitatively in a first-order process and our results for the activation parameters were in good agreement with the published data.

The choice of diethyl phthalate as solvent was for the following reasons: (i) the substrate and product had adequate solvent solubility so that a relatively concentrated solution could be used and the reaction mixture remained homogeneous; (ii) the solvent was sufficiently

high boiling, so that the thermal isomerisation was complete before the solvent vapour pressure became too high; and (iii) there was no chemical reaction between solvent and either substrate or product. Among solvents considered but rejected were: (a) a series in which

TABLE 1

Molecular geometry of *trans*-$[Mo(CO)_4\{CN(Me)CH_2CH_2NMe\}_2]$, (2a), and comparative data for the *cis* isomer, (1a) (from ref. 2)

	trans-$[Mo(CO)_4(L^{Me})_2]$	*cis*-$[Mo(CO)_4(L^{Me})_2]$
(*a*) Bond lengths (Å)		
Mo–C(1)	2.001(2) *trans* CO	2.028(3) *trans* CO
		1.980(3) *trans* carbene
Mo–C(2)	2.232(2) *trans* carbene	2.293(3) *trans* CO
C(1)–O(1)	1.136(2)	1.145(4)
C(2)–N(1)	1.333(3)	1.341(3)
C(2)–N(2)	1.341(3)	
N(1)–C(3)	1.458(4)	1.459(4)
N(2)–C(4)	1.432(4)	
N(1)–C(5)	1.421(5)	1.440(4)
N(2)–C(6)	1.426(5)	
C(3)–C(4)	1.468(6)	1.490(4)
C(3)–H(3)	1.12(4)	0.99(2)
C(4)–H(4)	0.93(3)	
C(5)–H(51)	1.00(5)	0.94(2)
C(5)–H(52)	0.84(3)	
C(6)–H(61)	0.89(4)	
C(6)–H(62)	0.85(4)	
(*b*) Angles (°)		
C(1)–Mo–C(1′)	93.4(1)	89.6(1)
C(1)–Mo–C(1″)	180	169.8(1)
C(1)–Mo–C(1‴)	86.6(1)	83.2(1)
C(1)–Mo–C(2)	89.4(1)	91.1(1)
C(1)–Mo–C(2″)	90.6(1)	96.4(1)
C(2)–Mo–C(2″)	180	
Mo–C(1)–O(1)	178.9(2)	172.1(2)
Mo–C(2)–N(1)	127.6(2)	126.7(2)
Mo–C(2)–N(2)	126.7(2)	
N(1)–C(2)–N(2)	105.7(2)	106.5(2)
C(2)–N(1)–C(3)	113.4(3)	113.6(2)
C(2)–N(2)–C(4)	114.4(3)	
C(2)–N(1)–C(5)	127.0(2)	127.6(2)
C(2)–N(2)–C(6)	127.5(2)	
C(3)–N(1)–C(5)	119.6(3)	118.6(3)
C(4)–N(2)–C(6)	118.1(3)	
N(1)–C(3)–C(4)	103.2(3)	102.9(3)
N(2)–C(4)–C(3)	103.3(3)	
N(1)–C(3)–H(3)	114(2)	109(2)
N(2)–C(4)–H(4)	110(2)	
N(1)–C(5)–H(51)	114(3)	111(2)
N(1)–C(5)–H(52)	111(2)	
N(2)–C(6)–H(61)	115(3)	
N(2)–C(6)–H(62)	109(3)	
C(4)–C(3)–H(3)	110(2)	114(2)
C(3)–C(4)–H(4)	116(2)	
H(3)–C(3)–H(3′)	105(4)	107(3)
H(4)–C(4)–H(4′)	102(4)	
H(51)–C(5)–H(52)	109(3)	108(4)
H(52)–C(5)–H(52′)	102(5)	
H(61)–C(6)–H(62)	114(3)	
H(62)–C(6)–H(62′)	94(5)	

The primed atoms correspond to the following co-ordinate transformations: (′) $x, -y, z$; (″) $-x, -y, -z$; (‴) $-x, y, -z$.

solubility of (1) and/or (2) was inadequate [$O(CH_2CH_2OMe)_2$, decahydronaphthalene, 1-bromonaphthalene, and glycerol]; and (b) a number which either caused chemical reaction or were too volatile (*NN*-dimethylformamide, naphthalene, and chlorobenzene). The bis(*NN*′-diethylcarbene) complexes *cis*- and *trans*-$[Mo(CO)_4(L^{Et})_2]$, (1b) and (2b), were examined, as well as the methyl homologues (1a) and (2a), because of their greater solvent solubility; consequently the results for the ethyl compounds (*ca.* 0.05 mol dm^{-3}) are much the more reliable. The data logger and associated computer program were required to monitor the relatively small heat evolution of the output thermogram.

The activation energy values for the isomerisation of $[Mo(CO)_4(L^{Me})_2]$ are somewhat spread (Table 2), but do give an order of magnitude idea of the activation energy; the spread is due to the lower solubility of this compound leading to less accurate results. The activation energies for the more soluble compound, $[Mo(CO)_4(L^{Et})_2]$, show good reproducibility. Each of these activation energies was obtained from a single run using *ca.* 0.2 mg of sample

TABLE 2

Thermal isomerisation of *cis*-$[Mo(CO)_4(L^R)_2]$ to the *trans* isomer *

Complex	Heating rate/ K min^{-1}	$S^‡$/J K^{-1} mol^{-1}	E_a/kJ mol^{-1}	A/s^{-1}
$[Mo(CO)_4(L^{Me})_2]$	5.0	−80.9	68.5	1×10^7
$[Mo(CO)_4(L^{Me})_2]$	10.0	−62.6	72.4	9×10^7
$[Mo(CO)_4(L^{Et})_2]$	5.0	−58.5	74.2	3×10^8
$[Mo(CO)_4(L^{Et})_2]$	10.0	−24.1	74.2	9×10^9
$[Mo(CO)_4(L^{Et})_2]$	10.0	−40.2	75.2	3×10^8

* All isomerisations were carried out in diethyl phthalate.

and each run yielded between 40 and 50 rate constants with a very high correlation coefficient (0.998—0.999) for a straight-line Arrhenius plot assuming first-order kinetics. Another salient feature of the results is the activation entropy, $S^‡$; the values are somewhat spread but are consistently negative and of the order of -50 ± 30 J K^{-1} mol^{-1}. These values indicate an associative transition state for the isomerisation. We propose that the negative values of the activation entropy are due to interaction with the solvent in the transition state.

EXPERIMENTAL

The complexes *cis*-$[Mo(CO)_4(L^R)_2]$, (1), were prepared and purified as described previously.[2]

Crystal Data for trans-$[Mo(CO)_4(L^{Me})_2]$, (2a).—$C_{14}H_{20}MoN_4O_4$, $M = 404.28$, Monoclinic, $a = 14.706(5)$, $b = 7.866(3)$, $c = 8.132(3)$ Å, $\beta = 114.40(2)°$, $U = 856.6$ Å^3, $D_m = 1.56$ g cm^{-3}, $Z = 2$, $D_c = 1.567$ g cm^{-3}, $F(000) = 824$, space group $C2/m$ (C_{2h}^3), Mo-K_α radiation, $\lambda = 0.710\ 7$ Å, μ(Mo-K_α) = 7.53 cm^{-1}.

Cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections having 2θ values between 30 and 40° on a Philips PW 1100/20 automatic four-circle diffractometer using Mo-K_α radiation ($\lambda = 0.710\ 7$ Å) with a graphite crystal monochromator. The irregularly shaped crystal used had a maximum dimension of 0.2 mm and was mounted in a general orientation. Intensity data were collected by the θ—2θ continuous scan technique using a θ scan speed of 1.2° min^{-1} and a scan width in θ of $(0.80 + 0.34 \tan\theta)°$ where the second term allows for the separation of $K_{\alpha 1}$ and $K_{\alpha 2}$ reflections. Stationary background counts of 10-s duration were made at each extreme of the scan range. Intensities of three standard reflections were monitored every 2 h to check crystal and electronic stability. No significant crystal degradation was

observed. Intensities were collected for reflections with 2θ (Mo-K_α) values between 3 and 70°. Of the 3 657 reflections measured, 2 995 (82%), for which $I \geqslant 3\sigma(I)$, were accepted as being significantly above background. After sorting and averaging, only the unique 1 661 were used in subsequent calculations.

A value of 0.02 was used for the experimental uncertainty factor p.[9,10] Intensities were corrected for Lorentz and polarisation effects but not for absorption or extinction.

The structure was solved and refined in an identical way to the *cis* isomer.[2] On the final cycle of full-matrix least-squares refinement, no parameter shifted by more than 0.02 times its standard deviation. The final value of both R and R' was 0.027 for 87 variables and 1 661 data. The hydrogen atoms were refined with isotropic and the non-hydrogen atoms with anisotropic thermal parameters The standard deviation of an observation of unit weight was 1.13. There were no peaks in the final difference map >0.2 e Å^{-3}. Final atomic fractional co-ordinates are in Table 3. Observed

TABLE 3

Final atomic fractional co-ordinates for complex (2a)

Atom	x/a	y/b	z/c
Mo	0.0	0.0	0.0
C(1)	0.037 1(1)	0.185 1(2)	0.185 1(2)
O(1)	0.057 6(1)	0.292 1(2)	0.287 8(3)
C(2)	0.156 3(1)	0.0	0.021 3(3)
N(1)	0.185 8(2)	0.0	−0.113 1(3)
N(2)	0.240 3(1)	0.0	0.173 8(3)
C(3)	0.294 1(3)	0.0	−0.051 4(7)
C(4)	0.330 4(2)	0.0	0.146 1(7)
C(5)	0.123 9(4)	0.0	−0.301 3(5)
C(6)	0.248 7(2)	0.0	0.354 9(5)
H(3)	0.324(3)	0.113(5)	−0.097(5)
H(4)	0.370(2)	0.092(4)	0.206(5)
H(51)	0.050(4)	0.0	−0.332(7)
H(52)	0.137(2)	0.082(4)	−0.353(5)
H(61)	0.191(3)	0.0	0.365(6)
H(62)	0.289(3)	0.079(5)	0.413(5)

and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22931 (10 pp.).*

Differential Scanning Calorimetry.—These experiments were performed on a Perkin-Elmer model DSC-2 differential scanning calorimeter. The data logging equipment used was either an MBM 2000 series data logger with integral digital voltmeter or an MBM Mini-logger in conjunction with an SE Laboratories type SM212 digital voltmeter. A Facit 4070 tape punch was used as the output device. Computer programs were run on the University of Sussex Computing Centre ICL 1904A series computer.

For the d.s.c. experiments, the two halves of the aluminium sample container were washed in dichloromethane to remove any traces of grease from the sealing surfaces and were then left to dry. A solution (8.5 μl) of the required complex (1a) or (1b) was placed in the lower half of the pan by means of a 10-μl capacity syringe. The lid was cold-welded into place using a hand press. The sample pans, which were handled with forceps to prevent contamination, were not fully filled to their 10 μl capacity to avoid traces of solution either 'creeping' up the sides of the pan, or splashing on to the sealing surfaces. Diethyl phthalate (8.5 μl) in an identical aluminium pan was used as a reference material.

The samples were run over the temperature range 320—420 K at various heating rates but most commonly at 2.5, 5, or 10° min^{-1}. In order to obtain a peak on the thermogram large enough for kinetic analysis, the machine was operated on its most sensitive range, *i.e.*, 0.1 mcal s^{-1}.† The baseline, *i.e.*, the thermogram produced by running a completely reacted sample against an identical reference, was not linear at this sensitivity over large temperature ranges. Accordingly, after a thermogram for the running of the sample under the conditions required had been obtained, the sample was cooled to the starting temperature. It was then re-run under identical conditions, this time to produce the experimental baseline, which was subtracted from the experimental thermogram, to yield the peak for the isomerisation, which was analysed to yield the differential enthalpy dH/dt. From dH/dt, the areas under the peaks, and the peak heights, the rate constants at various temperatures were determined. A computer program was written to analyse the rate constants and temperature and to perform a linear regression (least-squares) analysis on the Arrhenius points, in order to find the slope and intercept of the line of best fit through the Arrhenius points.

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† Throughout this paper: 1 cal = 4.184 J.

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

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