Bidentate Cyclic Imido Complexes of Molybdenum(II). Preparation, Solution Behaviour and X-Ray Crystal Structure†

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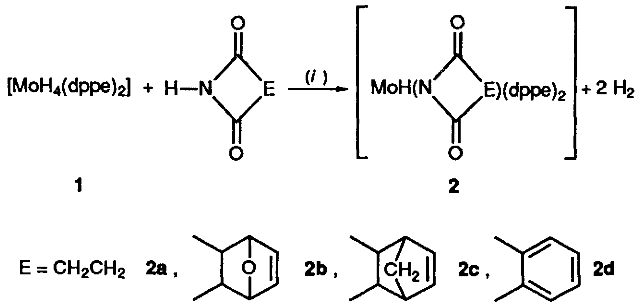
The complex $[MoH_4(dppe)_2]$ **1** (dppe = $Ph_2PCH_2CH_2PPh_2$) in benzene or toluene reacted photochemically or thermally with organic cyclic imides, $HNC(O)EC(O)$ [E = CH_2CH_2 **a**, $CHCH(O)CH{=}CHCHCH$ **b**, $CHCH(CH_2)CH{=}CHCHCH$ **c**, C_6H_4-1,2 **d**] to afford $[MoH\{NC(O)EC(O)\}(dppe)_2]$ **2**. NMR spectral study of the seven-co-ordinate complexes **2** showed that they have a fluxional pentagonal-bipyramidal structure in solution. The X-ray crystal structure of **2a** [monoclinic, space group $P2_1/a$ with $a = 14.949(3)$, $b = 28.691(13)$, $c = 12.503(3)$ Å, $\beta = 103.22(17)°$, $Z = 4$ and $R = 0.0615$] showed that the succinimido ligand is co-ordinated to the metal in a bidentate manner *via* nitrogen and oxygen atoms yielding a four-membered metallocycle.

Organic cyclic imides such as succinimide and phthalimide are known to act as weak acids giving rise to a ready displacement of the NH proton with alkali metals. Since it has been shown that $[MoH_4(dppe)_2]$ **1** (dppe = $Ph_2PCH_2CH_2PPh_2$) is easily protonated with organic acids such as acetic acid to give a cationic hydridoacetato complex,[1] it is of interest to examine whether cyclic imides react with **1** in a similar manner. Complex **1** however did not show any indication of reaction with succinimide in benzene at room temperature, but reacted at the elevated temperature or under irradiation using a high-pressure mercury lamp to give a hydrido(succinimido) complex in which the succinimido ligand co-ordinates in a bidentate manner *via* the nitrogen and an oxygen atom. Since complex **1** is known to release 1 equivalent of H_2 on photolysis or thermolysis to give the 16-electron reactive intermediate $[MoH_2(dppe)_2]$.[2] It is conceivable that the above reaction proceeds *via* direct attack of succinimide on this intermediate as is postulated in the case of the reactions of **1** with methacrylic[3] and allylic esters,[4] allylic carbonates,[5] and carbon dioxide.[6]

There are several examples of transition-metal complexes of cyclic imides such as succinimide, phthalimide, *etc.*[7–10] Most have been shown to have unidentate imido ligands, with the exception of a ruthenium complex which appears to have a bidentate imido ligand on spectral evidence.[9] Only one, however, has been structurally characterized.[11]

Here we report photochemical and thermal reactions of complex **1** with the cyclic imides $HNC(O)EC(O)$, such as succinimide (E = CH_2CH_2, **a**), Diels–Alder adducts of maleimide with furan and cyclopentadiene [E = $CHCH(O)CH{=}CHCHCH$, **b**, and $CHCH(CH_2)CH{=}CHCHCH$, **c**, respectively], and phthalimide (E = C_6H_4-1,2, **d**) to yield the new hydridoimido complexes $[MoH\{NC(O)EC(O)\text{-}N,O\}(dppe)_2]$ **2a**–**2d** and the structural characterization of the complex **2a** in solution and in the solid state. A preliminary account of this study has been communicated.[12]



Scheme 1 (*i*) *h*ν or heat, benzene or toluene

Results and Discussion

(*a*) *Preparation of Hydrido(imido-*N,O*) Complexes.*—Irradiation of a Pyrex flask containing a yellow solution of $[MoH_4(dppe)_2]$ **1** and succinimide in benzene *in vacuo* using a 100 W high-pressure mercury lamp at room temperature for 3 h afforded a dark red solution. The reaction was accompanied by the evolution of *ca.* 2 equivalents of H_2. Wine-coloured prisms of bis[1,2-bis(diphenylphosphino)ethane]hydrido(succinimido-*N,O*)molybdenum(II) **2a** were isolated from the resulting solution in 72% yield (Scheme 1, E = CH_2CH_2; Table 1, run 1). No reaction took place without light irradiation at room temperature (Table 1, run 2). Similar results were obtained when **1** and succinimide were heated in toluene in the dark at 110 °C (Table 1, run 3). Good prismatic crystals of $[MoH\{NC(O)CH_2CH_2C(O)\}(dppe)_2]\cdot C_6H_6$ **2a**·C_6H_6 were obtained by recrystallization from benzene–hexane in which benzene (1 mol) was included as a crystallization solvent.

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† *Supplementary data available* (No. SUP 56809, 4 pp.): NMR spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Nomenclature: Although the use of 'amido ligand' may be more appropriate for the series of complexes reported, 'imido ligand' has been used throughout since it is easier to represent the complexes by conventional nomenclature.

Table 1 Reactions of [$MoH_4(dppe)_2$] **1** with organic cyclic imides HNC(O)EC(O)

		Cyclic imide				Product (% of **1**)	
Run	Complex (mmol)	E	Amount (mmol)	Solvent (cm^3)	Conditions[s]	Complex[b]	H_2[c]
1	0.53	CH_2CH_2	0.61	Benzene 50	20 °C, 3 h, *hν*	72	187
2	0.10	CH_2CH_2	0.12	Toluene 12	20 °C, 12 h	No reaction	
3	0.26	CH_2CH_2	0.32	Toluene 25	110 °C, 3 h	60	176
4[d]	0.08	CH_2CH_2	0.067	Benzene 8	20 °C, 2 h, *hν*	33	113[e]
5	0.70	CHCH(O)CH=CHCHCH	0.63	Benzene 60	20 °C, 5 h, *hν*	53	147
6	0.20	CHCH(O)CH=CHCHCH	0.18	Toluene 20	110 °C, 5 h	3	139
7	0.33	CHCH(CH_2)CH=CHCHCH	0.32	Benzene 30	20 °C, 5 h, *hν*	15	134
8	0.51	CHCH(CH_2)CH=CHCHCH	0.88	Toluene 26	110 °C, 5 h	38	141
9	0.37	C_6H_4-1,2	0.43	Benzene 35	20 °C, 5 h, *hν*[f]	42	194

[a] Irradiation using a 100 W high-pressure mercury lamp through a Pyrex glass. [b] Isolated yield based on the starting complex. [c] Determined by GLC. [d] Complex *trans*-[$Mo(N_2)_2(dppe)_2$] **3** was used in the place of **1**. [e] Yield of N_2. [f] A 400 W high-pressure mercury lamp was used in the place of the 100 W lamp.

Table 2 Infrared spectral data (cm^{-1}) for [MoH(imido-*N*,*O*)$(dppe)_2$] **2a**–**2d** *

Complex	ν(Mo–H)	ν(>C=O)	ν(>C=O→Mo)
2a	1800w	1730m, 1700s	1540s
2b	1800vw	1700s	1540s
2c	1880w	1700s	1535s
2d	1800vw	1705s	1560s

* As KBr disks.

Complex **2a**·C_6H_6 released the crystallization solvent when heated *in vacuo* at 180 °C for 1 h. Photoreaction of *trans*-[$Mo(N_2)_2(dppe)_2$] **3** with succinimide in benzene under irradiation also afforded **2a** (Table 1, run 4).

Interestingly, complex **2** was obtained also, though in low yield, by a similar treatment of **1** with *N*-allyloxy- or *N*-hydroxysuccinimide. In the former reaction the formation of propene in addition to H_2 was observed, although the fate of the oxygen atom in these reactions has not yet been clarified.

The reaction of complex **1** with other cyclic imides such as the Diels–Alder adducts of maleimide, HNC(O)EC(O), proceeded similarly photochemically or thermally to give corresponding hydrido(imido-*N*,*O*) complexes [MoH{NC(O)EC(O)}$(dppe)_2$] **2b** and **2c** (Scheme 1; Table 1, runs 5–8). Although the furan adduct **b** used consisted solely of the *exo* isomer, the cyclopentadiene adduct was a mixture of the *endo* and *exo* isomers (6.5:1.0) as is judged from its ^1H and ^{13}C NMR spectra. Both complexes **2b** and **2c** obtained here were, however, found to contain the imido ligand with only one isomer on the basis of NMR spectra, possibly the *endo* isomer because of steric reasons. Phthalimide, in the place of succinimide, also reacted similarly upon irradiation to give the analogous hydrido(phthalimido-*N*,*O*) complex **2d** (Table 1, run 9).

Since the tetrahydrido complex **1** is known to release 1 equivalent of H_2 upon irradiadtion,[2,13] the initial stage of the present reaction may be co-ordination of imide to the co-ordinatively unsaturated dihydrido intermediate through its carbonyl oxygen, followed by oxidative addition of imido NH group concerted with the release of another mole of H_2. An experiment to confirm this mechanism by using deuterium-labelled imide was unsuccessful due to the easy scrambling of the deuterium over the succinimide framework during the reaction. A radical mechanism involving attack of the imido radical on the metal cannot be ruled out.

(*b*) *Physical Properties and IR Spectra of Hydrido*(*imido*-N,O) *Complexes* **2**.—The hydridoimido complexes **2a**–**2d** are fairly stable to air for at least a few days in the solid state, but easily deteriorate in solution. Complexes **2a**–**2c** are readily soluble in benzene or tetrahydrofuran (thf), soluble in toluene, and insoluble in Et_2O or hexane. Complex **2d** is only slightly soluble in benzene, toluene and thf and insoluble in the other common organic solvents. In chloroform, they are soluble but deteriorate slowly even under anaerobic conditions. Complexes **2a**–**2d** melt at 240–280 °C with decomposition in the absence of air (see Experimental section).

In the IR spectra (Table 2) of complexes **2a**–**2d**, ν(Mo–H) was observed at around 1800 cm^{-1}, *cf.* the parent complex **1** (1810w and 1740m cm^{-1}). In addition, they showed two strong bands at *ca.* 1700 and 1540 cm^{-1} which may be assignable to the carbonyl stretching of the imido ligand, the lower-frequency band to the carbonyl group co-ordinated to the metal and the higher one to the free carbonyl. The free imide shows two bands in the 1700–1800 cm^{-1} region. Thus, ν(>C=O) of the co-ordinated carbonyl group is shifted to lower frequency by about 160 cm^{-1} from that of the free imide. This evidence together with the fact that the IR spectrum of **2** shows no band due to an imide NH group suggests that these complexes have a MoH(imido-*N*,*O*) skeleton in the solid state.

(*c*) *NMR Spectra of Hydrido*(*imido*-N,O) *Complexes* **2**.—In the ^1H NMR spectrum of complex **2a** at room temperature a hydride signal was observed at δ −6.62 as a triplet of triplets assignable to a A_2K_2X spin system ($A = P_{eq}, K = P_{ax}, X = H$). This, together with the *J* values (Table 3), resembles those observed for the related seven-co-ordinate carboxylato complexes [$MoH(O_2CR)(dppe)_2$] **4** (R = H, Me, Et, CMe_3, OMe or OEt) which were assigned a pentagonal-bipyramidal geometry,[4,5] suggesting a structural similarity between complexes **2a** and **4**.

Although the hydride signals of complexes **2c** and **2d** were similar to that of **2a**, a more complicated pattern was observed for **2b**: the signal consisted of 14 symmetrical peaks assignable to an ABKMX ($A,B = P_{eq}$; $K,M = P_{ax}$; $X = H$) spin system in which the proton couples with four magnetically inequivalent phosphorus nuclei (Table 3). This spectral discrepancy may be related to the conformational isomerism of the complex which will be discussed in a later section.

^{31}P-{^1H} NMR spectra consistent with the ^1H NMR results were obtained for complexes **2a**–**2d** at 25 °C. Thus, a pair of triplets was observed for **2a** and **2d** which may be assigned to an A_2K_2 spin system (Fig. 1 and Table 4), whereas a complex pattern consisting of two blocks of signals was observed for

Table 3 Proton NMR spectral data for [MoH(imido-*N,O*)(dppe)$_2$] **2a**–**2d** *

Complex	δ(MoH)	^2J(H–P$_{eq}$)/Hz		^2J(H–P$_{ax}$)/Hz		δ (imido ligand)
2a	−6.62(tt)	51.9	51.9	37.2	37.2	1.35(CH$_2$)
2b	−6.66(dddd)	66.5	48.2	39.1	27.5	1.59, 1.76 (COCH); 4.43, 4.99 (CCHC); 6.50 (CH=)
2c	−6.57(tt)	56.8	56.8	36.0	36.0	1.82, 2.45 (CH$_2$); 2.72, 2.83 (COCH); 4.88, 5.25 (CCHC); 6.23 (CH=)
2d	−6.16(tt)	53.3	53.3	36.0	36.0	*ca.* 7(Ph)

* At 270 MHz, room temperature, in C_6D_6. Values downfield positive from the internal reference SiMe$_4$.

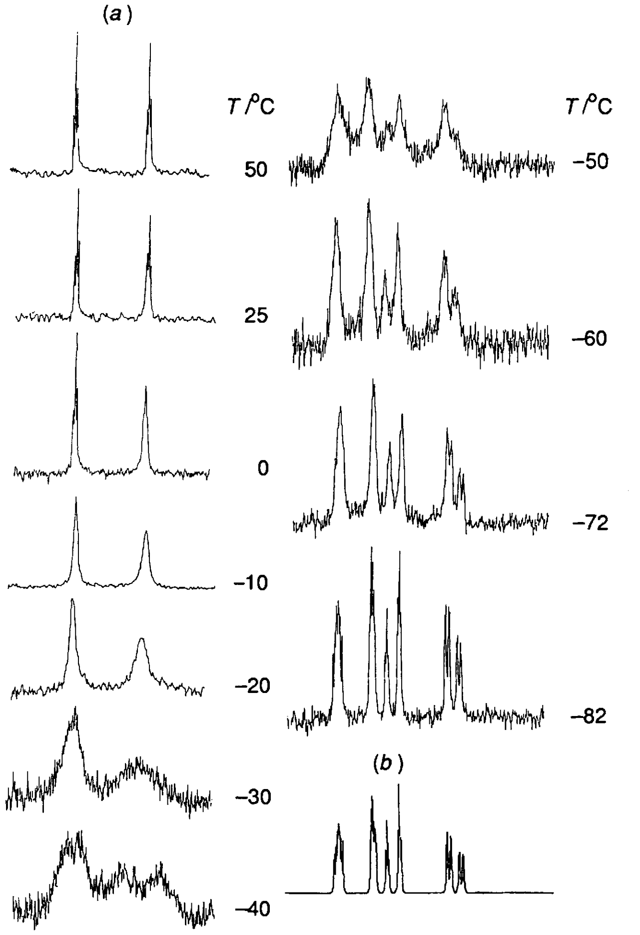


Fig. 1 Temperature-dependent ^{31}P-{^{1}H} NMR spectra of [MoH{NC(O)(CH$_2$)$_2$C(O)}(dppe)$_2$] **2a** in C_4H_8O–C_4D_8O (*a*) and the computer-simulated line shape (*b*)

complexes **2b** and **2c**: two partially overlapped triplets at lower field and an AB quartet at higher field split into triplets. The overall signal pattern may be assigned to an ABKM spin system (Table 4 and Fig. 2).

The ^{31}P NMR spectrum of complex **2a** was found to be temperature dependent suggesting its fluxional behaviour. On lowering the temperature of **2a** in thf, the signal gradually broadened and coalesced at about −30 °C. At −82 °C the hyperfine structure appeared which may be assigned to an ABKM spin system on the basis of a computer simulation (Fig. 1 and Table 4).

The ^{13}C-{^{1}H} NMR spectrum of complex **2a** at room temperature showed a singlet at δ 192.3 assignable to imido C=O together with a singlet at δ 30.9 due to imido CH$_2$. On the other hand, each signal of the spectra of **2b** and **2c** consisted of two sets of signals except for a bridging CH$_2$ of **2c** reflecting the unsymmetrical structure of the complex (Table 5).

These spectral features may be rationalized as follows. Two triplets of A_2K_2 in the ^{31}P NMR spectrum at room temperature, similar to those observed for the hydridocarboxylato complexes **4**[4,5] or for [MoH(O$_2$CR)(PMe$_3$)$_4$] and [MoH{NPhC(O)H}-(PMe$_3$)$_4$],[14] suggests that complex **2a** in solution is exchanging within the NMR time-scale between **I** and **II** in Scheme 2. Thus an interconversion between **I** and **II** which is taking place at higher temperatures slows down on lowering the temperature and finally froze at the intermediate conformation **III** or **III′** which is energetically most favourable, *i.e.* the sterically least demanding conformation. This structurally frozen conformation corresponds to that observed for the solid-state structure determined by X-ray analysis (see below). In the case of complexes **2b** and **2c** which carry bulky substituents on the imido ligand, interconversion between **I** and **II** may be hindered and the sterically least-demanding conformation predominant even at room temperature, giving rise to the observation of a ^{31}P NMR pattern at room temperature similar to those of **2a** at −82 °C. The phthalimido complex **2d** which is sterically less bulky than **2b** and **2c** has a similar conformation to that of **2a**.

(*d*) *X-Ray Crystallographic Analysis of Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(*succinimido*-N,O)*molybdenum*(II)–[^{2}H$_6$]*Benzene* (1/1) **2a**·C_6D_6.—A good prismatic crystal of complex **2** suitable for X-ray analysis was obtained by crystallization from C_6D_6 in which C_6D_6 (1 mol) was included as a crystallization solvent. Diagrams of the molecule are shown in Figs. 3 and 4 and selected bond lengths and angles in Table 6.

The incorporated C_6D_6 was found to be disordered over two positions. As shown in Fig. 4, **2a** has a very distorted pentagonal-bipyramidal geometry with P(1), P(2), the oxygen atom of the succinimido ligand, P(4), and a hydrido ligand comprising the pentagonal girdle in accordance with the structure in solution determined by ^{31}P-{^{1}H} NMR spectroscopy at −82 °C.

The hydride ligand, whose location was determined from the Fourier difference map, was found to deviate a little from the pentagonal plane towards the apical nitrogen atom, which in turn was shifted considerably from the apical position towards the plane. The Mo–P bond distances of the mutually *trans* phosphorus atoms [P(2) and P(4)] are longer than those *trans* to the nitrogen or the oxygen atom of the succinimido ligand [P(3) or P(1), respectively], reflecting the greater *trans* influence of the phosphine than of the imido ligand. The situation is similar to those reported for the related bis(dppe) complexes.[5,15]

Four carbon atoms, two oxygens and a nitrogen atom of the succinimido ligand lie in a plane which also includes a molybdenum atom. The carbon–oxygen double-bond distance of the co-ordinated carbonyl group [O(1)–C(1)] is longer than that of the unco-ordinated one [O(2)–C(4)] which is similar to the corresponding bond length of free succinimide (1.23 Å). This suggests a certain contribution from the canonical form **B** which is consistent with the smaller N–C(1) bond length as compared with N–C(4). The planar nature of the succinimido ligand in **2a** may be ascribed to the presence of this resonance structure. The Mo–O(1) bond distance is similar to the Mo–O bond reported for the dimethylformamide complex, *trans*-[Mo(Me$_2$NCHO)-(dppe)$_2$] [2.348(10) Å],[16] and for the ethyl carbonato complex [MoH(O$_2$COEt)(dppe)$_2$] [2.271(2) and 2.333(3) Å].[5]

Table 4 $^{31}P-\{^1H\}$ NMR spectral data for $[MoH(imido-\mathit{N,O})(dppe)_2]$ **2a–2d** [a]

	$\delta(P_{eq})$		$\delta(P_{ax})$							
Complex	P_a	P_b	P_c	P_d	$J(P_aP_b)$	$J(P_aP_c)$	$J(P_aP_d)$	$J(P_bP_c)$	$J(P_bP_d)$	$J(P_cP_d)$
2a	98.1(t)	98.1(t)	77.4(t)	77.4(t)	—	22.0	22.0	22.0	22.0	—
2a [b]	103.2(t)	103.2(t)	82.2(t)	82.2(t)	—	20.5	20.5	20.5	20.5	—
2a [c]	105.4(ddd)	95.5(ddd)	89.1(dt)	71.9(ddd)	32.2	17.6	41.0	17.6	11.7	128.1
2b	99.6(ddd)	97.0(q)	78.0(dt)	72.3(ddd)	17.1	18.1	24.5	17.1	17.1	134.7
2c	95.1(t)	94.8(t)	75.1(dt)	68.8(dt)	—	19.1	19.1	19.1	19.1	140.7
2d	99.3(t)	99.3(t)	76.9(t)	76.9(t)	—	22.0	22.0	22.0	22.0	—

[a] At 36.2 MHz, room temperature, in C_6D_6; δ downfield positive from the external reference PPh_3 (in C_6D_6), *J* in Hz. [b] In $C_4H_8O–C_4D_8O$. [c] At −82 °C in $C_4H_8O–C_4D_8O$.

Table 5 $^{13}C-\{^1H\}$ NMR spectral data for complexes **2a–2d** [a]

Complex	δ(imido ligand)
2a [b]	192.3 (C=O), 30.9 (CH_2)
2b	192.7, 190.1 (C=O); 79.8, 79.6 (C=C*C*C); 51.5 (*C*C=O)
2c	193.5, 192.5 (C=O); 53.2 (CH_2); 50.7, 49.5 (C=C*C*C); 44.9, 43.7 (*C*C=O)
2d	182.6 (C–O)

[a] At 67.5 MHz, room temperature, in C_6D_6; δ downfield positive from the internal reference $SiMe_4$. [b] At 22.5 MHz.

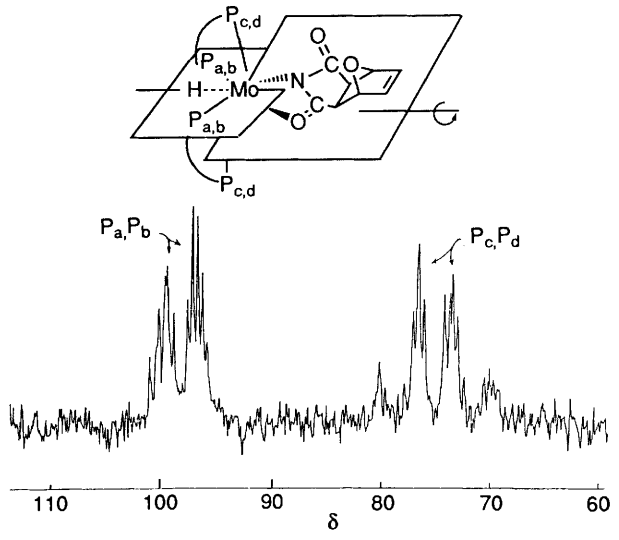
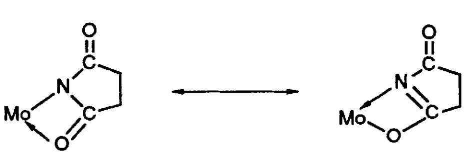
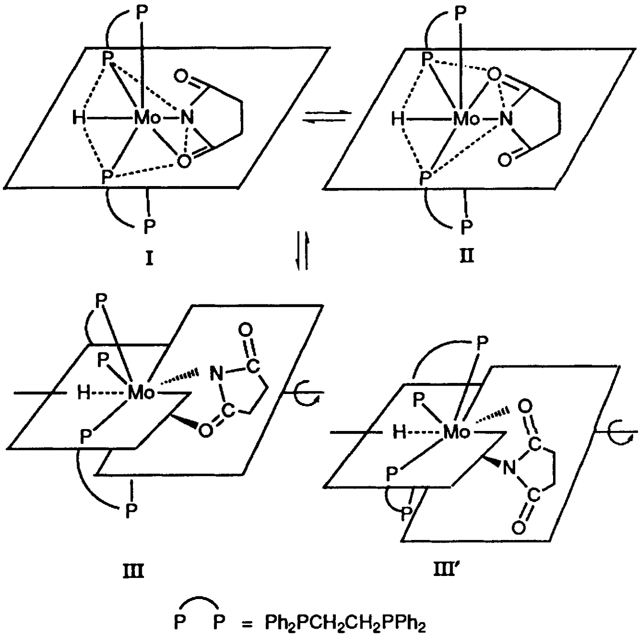


Fig. 2 $^{31}P-\{^1H\}$ NMR spectrum of complex **2b** at 22 °C in C_6D_6



A **B**



Scheme 2

The results described here present, to our knowledge, the first example of a cyclic imido complex whose structure has been determined by X-ray analysis, in which the imido ligand is co-ordinated to the metal in a bidentate fashion.

In order to obtain a direct relationship between the solid-state molecular structure and the NMR results described in the preceding section, the solid-state cross-polarization magic angle spinning (CP-MAS) $^{31}P-\{^1H\}$ NMR spectrum of $\mathbf{2a}\cdot C_6H_6$ was investigated. Although the resolution is not good as compared with the solution NMR spectrum, the spectrum consisted of two blocks of relatively broad signals at δ 73.3 and 64.5 with respect to the H_3PO_4 external reference, both of which split into doublets (*J* = 117 and 85 Hz, respectively): the results suggest the fundamental similarity between the spectra taken in the solid state at room temperature and in solution at −82 °C.

Experimental

Most manipulations were carried out under argon or under vacuum using Schlenk-type flasks. Solvents were dried, purified in the usual manner, and stored under an atmosphere of argon. Ultraviolet/visible irradiation was performed by using a Riko 100 W or a 400 W high-pressure mercury lamp and a Pyrex glass filter. Infrared spectra were recorded on a JASCO A202 spectrometer using KBr disks prepared under an inert atmosphere, NMR spectra on JEOL JNM-FX-90Q (22.5 MHz for ^{13}C and 36.2 MHz for ^{31}P), JNM EX-270 (270 MHz for ^1H and 67.5 MHz for ^{13}C) and JNM GX-270 (109.38 MHz for CP-MAS ^{31}P) spectrometers. Gases evolved during the reaction were quantitatively analysed by GLC by means of an internal reference method using a molecular sieve 5A column and a Shimadzu GC-3BT gas chromatograph using argon as carrier gas. Succinimide and phthalimide were used as purchased. The other imides **b** and **c** were prepared by a Diels–Alder addition reaction of maleic anhydride with furan and cyclopentadiene, respectively, followed by treatment with ammonia.[17] The complexes, $[MoH_4(dppe)_2]$ **1** and *trans*-$[Mo(N_2)_2(dppe)_2]$ **3** were prepared according to the reported methods.[18,19]

Physical and analytical data for complexes **2a–2d** are listed in Table 7.

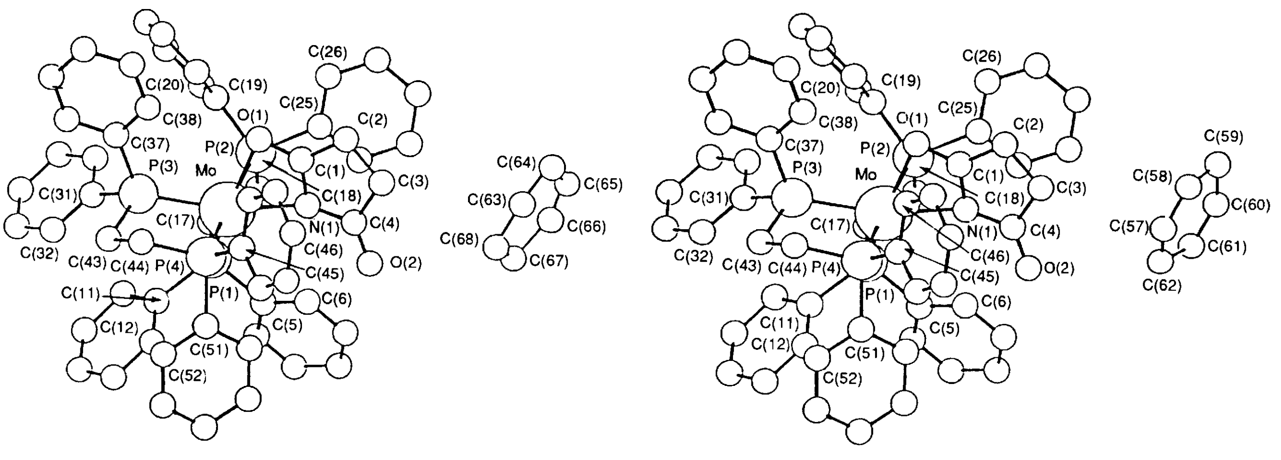


Fig. 3 Molecular structure of $[\mathrm{MoH\{NC(O)(CH_2)_2C(O)\}(dppe)_2]\cdot C_6D_6}$ **2a**·C_6D_6 with the atom-labelling scheme

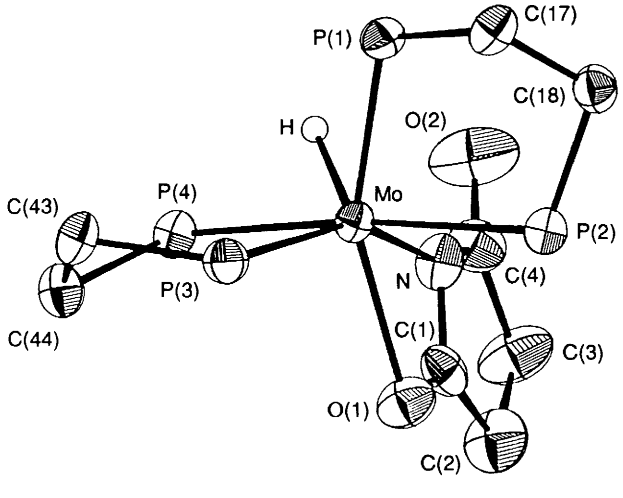


Fig. 4 ORTEP drawing of $[\mathrm{MoH\{NC(O)(CH_2)_2C(O)\}(dppe)_2]\cdot C_6D_6}$ **2a**·C_6D_6 showing thermal ellipsoids at 30% probability. Phenyl rings are omitted for clarity

Table 6 Selected bond lengths (Å) and angles (°) for $[\mathrm{MoH\{NC(O)(CH_2)_2C(O)\}(dppe)_2]\cdot C_6D_6}$ with estimated standard deviations in parentheses

Mo–H	1.582	O(1)–C(1)	1.265(12)
Mo–P(1)	2.378(3)	O(2)–C(4)	1.215(14)
Mo–P(2)	2.510(3)	N–C(1)	1.339(14)
Mo–P(3)	2.394(2)	N–C(4)	1.378(12)
Mo–P(4)	2.453(3)	C(1)–C(2)	1.494(13)
Mo–N	2.282(6)	C(2)–C(3)	1.506(16)
Mo–O(1)	2.354(7)	C(3)–C(4)	1.516(15)
N–Mo–O(1)	57.38(27)	P(2)–Mo–P(4)	172.26(8)
N–Mo–H	74.23	P(3)–Mo–H	115.11
N–Mo–P(1)	117.96(23)	P(3)–Mo–P(4)	79.42(9)
N–Mo–P(3)	153.05(24)	P(4)–Mo–H	56.47
N–Mo–P(4)	86.68(21)	C(1)–O(1)–Mo	91.92(58)
N–Mo–P(2)	87.57(21)	Mo–N–C(1)	93.17(54)
O(1)–Mo–H	124.85	Mo–N–C(4)	157.76(71)
O(1)–Mo–P(1)	155.88(19)	C(1)–N–C(4)	108.23(77)
O(1)–Mo–P(3)	100.28(17)	C(1)–C(1)–N	117.53(81)
O(1)–Mo–P(4)	93.55(19)	O(1)–C(1)–C(2)	128.01(95)
O(1)–Mo–P(2)	78.98(19)	N–C(1)–C(2)	114.46(86)
P(1)–Mo–H	68.97	C(1)–C(2)–C(3)	102.00(88)
P(1)–Mo–P(2)	77.13(9)	C(2)–C(3)–C(4)	104.68(81)
P(1)–Mo–P(3)	88.63(9)	O(2)–C(4)–N	124.67(92)
P(1)–Mo–P(4)	110.19(9)	O(2)–C(4)–C(3)	124.88(94)
P(2)–Mo–H	126.55	N–C(4)–C(3)	110.41(91)
P(2)–Mo–P(3)	103.73(9)		

Table 7 Physical and analytical data for $[\mathrm{MoH(imido\text{-}}N,O\mathrm{)(dppe)_2]}$ **2a**–**2d**

			Analysis (%)[a]		
Complex	Appearance	M.p./°C[b]	C	H	N
2a	Orange powder	254–257	67.3 (67.8)	5.7 (5.5)	1.4 (1.4)
2a·C_6H_6[c]	Wine-coloured prisms	*ca.* 150[d]	69.8 (69.6)	6.0 (5.6)	1.3 (1.3)
2b	Orange powder	241–244	68.0 (68.1)	6.0 (5.2)	1.1 (1.3)
2c	Wine-coloured prisms	258–260	70.3 (69.8)	5.9 (5.4)	1.2 (1.3)
2d	Dark yellow powder	277–279	67.9[e] (69.3)	5.7 (5.1)	1.2 (1.4)

[a] Calculated values in parentheses. [b] With decomposition. [c] Data for benzene solvate, $[\mathrm{MoH\{NC(O)CH_2CH_2C(O)\}(dppe)_2]\cdot C_6H_6}$. [d] Original clear prisms turned turbid at this temperature and changed their shape at about 250 °C. [e] See text.

Preparation of the Complexes $[\mathrm{MoH(imido\text{-}}N,O\mathrm{)(dppe)_2]}$.—(*a*) *Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(*succinimido*-N,O)*molybdenum*(II) **2a**. (*i*) *Photoreaction*. A Pyrex Schlenk flask containing a yellow solution of complex **1** (0.47 g, 0.53 mmol) and succinimide (0.061 g, 0.61 mmol) dissolved in benzene (50 cm^3) was irradiated under vacuum at room temperature for 3 h to give a dark red solution accompanied by the release of H_2 (1.87 mol per mol of **1**). Ethanol (10 cm^3) was added to the resulting solution. Cooling the mixture at 6 °C gave a yellow precipitate (0.082 g) which was removed by filtration. To the supernatant solution was added ethanol (15 cm^3) and cooling the solution at 6 °C gave complex **2a** as wine-coloured microneedles which were filtered off, washed with ethanol and dried *in vacuo* (0.38 g, 0.38 mmol, 72%). Complex **2a** was recrystallized from benzene–hexane (1:2 v/v) to give prisms which contain 1 mol of benzene of crystallization, **2a**·C_6H_6 (0.35 g, 0.32 mmol, 60%).

Table 8 Experimental data for the crystallographic analysis of complex **2a**·C_6D_6

Formula	$C_{62}H_{52}D_6MoNO_2P_4$
M	1075.08
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	14.949(3)
b/Å	28.691(13)
c/Å	12.503(3)
α/°	90
β/°	103.22(17)
γ/°	90
U/Å^3	5220(3)
Z	4
F(000)	2248
μ/cm^{-1}	4.09
D_c/g cm^{-3}	2.05
Crystal size/mm	0.1 × 0.1 × 0.1
2θ range/°	3–45
Scan rate/° min^{-1}	8
h, k, l Ranges	$-19 < h < 19, 0 < k < 35, 0 < l < 16$
Unique reflections	6471
Used reflections [$F_0 > 3\sigma(F_0)$]	4007
R	0.0615
R'	0.0619
Weighting scheme parameter g in $w = [\sigma^2(F_0) + g^2(F_0)^2]^{-1}$	0.051

Complex **2a**·C_6H_6 (0.051 g, 0.048 mmol) in a Schlenk flask was heated *in vacuo* at 189 °C for 1 h to remove benzene in the crystal, resulting in a change from wine colour to orange. The [MoH{NC(O)CH$_2$CH$_2$C(O)}(dppe)$_2$] **2a** thus obtained (0.047 g, 0.048 mmol, 100%) was subjected to elemental analysis.

The photoreaction of *trans*-[Mo(N_2)$_2$(dppe)$_2$] **3** (0.077 g, 0.081 mmol) with succinimide (0.0066 g, 0.067 mmol) was carried out similarly to give **2a** (0.027 g, 0.027 mmol, 33%) and N_2 (1.13 mol per mol of **3**).

(*ii*) *Thermal reaction.* A Pyrex Schlenk flask containing a yellow solution of complex **1** (0.23 g, 0.26 mmol) and succinimide (0.031 g, 0.32 mmol) dissolved in toluene (25 cm^3) was heated under vacuum at 110 °C for 3 h to give a dark red solution with accompanying evolution of H_2 (1.76 mol per mol of **1**). Solvent was removed from the solution *in vacuo* to give an orange powder, which was then dissolved in benzene–ethanol (7.5 cm^3 : 10 cm^3). The solution was cooled at 6 °C and a yellow precipitate was removed by filtration. To the supernatant was added ethanol (10 cm^3) and cooling the solution at 6 °C gave complex **2a** (0.15 g, 0.15 mmol, 60%).

(*b*) *Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(7-*oxabicyclo*[2.2.1]*hept*-5-*ene*-2,3-*dicarboximido*-N,O)*molybdenum*(II) **2b**. Benzene (60 cm^3) was added to *exo*-7-oxabicyclo-[2.2.1]hept-5-ene-2,3-dicarboximide (0.10 g, 0.63 mmol) and complex **1** (0.63 g, 0.70 mmol) *in vacuo*, and the mixture was irradiated with stirring at room temperature for 5 h to give a deep red solution with accompanying evolution of H_2 (1.47 mol per mol of **1**). Solvent was evaporated from the solution to give

Table 9 Fractional atomic coordinates for complex **2a**·C_6D_6 with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Mo	0.668 17(5)	0.648 88(2)	0.962 40(6)
P(1)	0.733 8(2)	0.576 86(9)	1.035 4(2)
P(2)	0.547 3(2)	0.615 72(9)	1.050 8(2)
P(3)	0.770 9(2)	0.688 02(9)	1.110 1(2)
P(4)	0.769 8(2)	0.688 08(9)	0.862 1(2)
O(1)	0.551 9(4)	0.705 5(2)	0.914 6(5)
O(2)	0.548 1(6)	0.602 7(3)	0.644 3(6)
N	0.561 3(5)	0.647 4(3)	0.799 7(5)
C(1)	0.520 0(7)	0.686 3(4)	0.822 7(9)
C(2)	0.440 5(7)	0.701 7(4)	0.734 1(8)
C(3)	0.442 8(8)	0.667 0(4)	0.644 4(9)
C(4)	0.521 6(7)	0.634 6(4)	0.693 2(9)
C(5)	0.713 5(6)	0.526 0(3)	0.938 6(8)
C(6)	0.657 4(6)	0.530 6(4)	0.836 8(8)
C(7)	0.639 8(8)	0.493 7(4)	0.765 5(9)
C(8)	0.680 1(8)	0.451 2(4)	0.796 5(11)
C(9)	0.737 0(7)	0.445 9(4)	0.900 8(10)
C(10)	0.754 5(7)	0.482 9(4)	0.970 4(8)
C(11)	0.856 9(6)	0.566 4(3)	1.098 8(8)
C(12)	0.918 7(7)	0.570 7(4)	1.033 1(9)
C(13)	1.012 6(8)	0.560 4(5)	1.074 4(11)
C(14)	1.040 7(8)	0.546 3(4)	1.184 1(11)
C(15)	0.980 3(8)	0.541 2(4)	1.248 9(10)
C(16)	0.886 1(7)	0.552 1(4)	1.207 6(9)
C(17)	0.678 5(6)	0.551 8(4)	1.140 0(8)
C(18)	0.574 1(6)	0.553 9(3)	1.090 7(8)
C(19)	0.531 4(6)	0.643 8(4)	1.179 1(7)
C(20)	0.524 8(7)	0.618 5(4)	1.271 4(8)
C(21)	0.526 2(8)	0.641 8(5)	1.368 3(9)
C(22)	0.529 9(7)	0.690 9(5)	1.373 2(10)
C(23)	0.532 5(7)	0.715 3(4)	1.277 4(9)
C(24)	0.533 5(7)	0.692 1(4)	1.179 8(8)
C(25)	0.430 5(6)	0.612 0(3)	0.963 3(7)
C(26)	0.359 7(7)	0.641 5(4)	0.977 7(9)
C(27)	0.275 8(7)	0.640 1(4)	0.903 0(10)
C(28)	0.261 6(7)	0.609 8(4)	0.812 9(9)
C(29)	0.330 6(7)	0.579 4(4)	0.798 6(8)
C(30)	0.415 7(6)	0.581 9(4)	0.873 2(8)
C(31)	0.824 2(6)	0.665 0(3)	1.248 0(7)
C(32)	0.919 6(7)	0.658 7(4)	1.285 2(8)
C(33)	0.955 4(8)	0.644 1(4)	1.391 9(10)
C(34)	0.898 9(9)	0.634 3(4)	1.461 3(10)
C(35)	0.804 7(9)	0.640 8(4)	1.425 6(9)
C(36)	0.768 3(7)	0.654 7(4)	1.318 7(8)
C(37)	0.737 6(7)	0.746 7(3)	1.155 6(8)
C(38)	0.667 7(7)	0.772 4(4)	1.090 1(8)
C(39)	0.642 2(7)	0.816 2(4)	1.121 1(9)
C(40)	0.687 7(8)	0.835 0(4)	1.219 7(10)
C(41)	0.759 0(8)	0.810 6(4)	1.284 6(9)
C(42)	0.783 8(7)	0.766 3(4)	1.255 3(8)
C(43)	0.875 8(6)	0.708 3(3)	1.066 3(7)
C(44)	0.844 7(7)	0.730 8(4)	0.952 9(8)
C(45)	0.724 5(6)	0.724 2(3)	0.740 0(7)
C(46)	0.659 4(7)	0.758 4(4)	0.745 4(9)
C(47)	0.625 6(8)	0.787 4(4)	0.654 7(10)
C(48)	0.657 2(9)	0.781 9(5)	0.558 7(10)
C(49)	0.719 4(8)	0.747 2(4)	0.551 1(9)
C(50)	0.753 7(8)	0.719 3(4)	0.642 3(9)
C(51)	0.851 9(7)	0.650 2(4)	0.811 8(8)
C(52)	0.945 8(7)	0.658 1(4)	0.840 2(9)
C(53)	1.005 6(8)	0.625 1(5)	0.811 7(10)
C(54)	0.971 0(10)	0.585 7(5)	0.754 3(11)
C(55)	0.877 4(10)	0.579 2(4)	0.720 7(9)
C(56)	0.816 2(7)	0.610 6(4)	0.749 7(8)
C(57)	0.316 1	0.565 1	0.494 2
C(58)	0.232 1	0.577 4	0.492 2
C(59)	0.155 6	0.541 0	0.530 8
C(60)	0.201 8	0.508 9	0.521 6
C(61)	0.280 7	0.483 0	0.547 0
C(62)	0.349 2	0.513 2	0.533 4
C(63)	0.272 3	0.567 8	0.493 7
C(64)	0.184 5	0.561 6	0.506 7
C(65)	0.170 1	0.504 5	0.545 7
C(66)	0.232 3	0.485 8	0.548 9
C(67)	0.333 9	0.495 3	0.542 6
C(68)	0.355 4	0.544 2	0.513 6

an orange powder, which was recrystallized from benzene–hexane (1:3 v/v) to give complex **2b** (0.39 g, 0.37 mmol, 53%).

Complex **2b** was also obtained when the reaction was carried out without irradiation at 110 °C in toluene *in vacuo*. The yield of the complex was significantly low in this case (Table 1) due to difficulties in working up, suggesting the existence of many side reactions.

(*c*) *Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(*bicyclo*-[2.2.1]*hept*-5-*ene*-2,3-*dicarboximido*-N,O)*molybdenum*(II) **2c**. Complex **1** (0.30 g, 0.33 mmol) and bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide [mixture of *endo* and *exo* isomers (6.5:1.0)] (0.045 g, 0.32 mmol) was dissolved in benzene (30 cm^3) and the mixture irradiated for 5 h. The resulted dark red solution was condensed to *ca.* 10 cm^3 and ethanol (15 cm^3) was added. Cooling the solution at 6 °C gave a yellow precipitate which was removed by filtration. Evaporation of the solvent left an orange solid residue, which was recrystallized from benzene–hexane (2:5 v/v) yielding 0.053 g (0.05 mmol, 15%) of complex **2c**.

The thermal reaction between complex **1** and bicyclo-[2.2.1]hept-5-ene-2,3-dicarboximide was carried out similarly to that described for succinimide and worked up by a similar procedure to that above (see Table 1).

(*d*) *Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(*phthalimido*-N,O)*molybdenum*(II) **2d**. Complex **1** (0.33 g, 0.37 mmol) and phthalimide (0.062 g, 0.43 mmol) in benzene (35 cm^3) was irradiated at room temperature *in vacuo* for 5 h to cause a colour change of the solution from yellow to brown, accompanied by evolution of H_2(1.94 mol per mol of **1**). A dark yellow solid obtained upon evaporation to dryness was recrystallized from benzene–acetone (1:1 v/v) to give a dark yellow powder of complex **2d** (0.16 g, 0.16 mmol, 42%). The poor crystallizability and the poor solubility of the product prevented an analytically pure sample from being obtained (Table 7).

X-Ray Crystallography.—Crystals of complex **2a** suitable for X-ray crystallography were grown in C_6D_6 at room temperature and mounted in a glass capillary tube under argon. The unit-cell parameters were obtained by least-squares refinement of 25 reflections with $19 \leqslant 2\theta \leqslant 22°$. Intensities were collected on a Rigaku AFC-5 four-circle diffractometer by using Mo-Kα radiation ($\lambda = 0.710\,68$ Å). Details of the data collection are summarized in Table 8. Standard reflections, monitored after every 200, showed no decrease in intensity during the measurement.

Calculations were carried out with the program systems SAPI 85[20] on a FACOM A-70 computer. No absorption correction was applied. The structure was solved by common Fourier methods. A full-matrix least-squares refinement procedure was used with anisotropic thermal parameters for the non-hydrogen atoms of the complex and isotropic thermal parameters for the carbon atoms of solvated C_6D_6 and all the hydrogen atoms. The hydride was located from the Fourier difference map. Other hydrogen atoms were placed at a distance of 1.00 Å from the carbon atoms. These hydrogen atoms were included in least-squares calculations without refinement of their parameters. Atomic coordinates are listed in Table 9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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