CHEMISTRY LETTERS, pp. 1299-1302, 1990.

Structural Characterization of the Transition-metal Imido Complex Coordinated in a Bidentate Fashion. Preparation and the Molecular Structure of Seven-Coordinate Hydrido(succinimido-N,O)-bis[1,2-bis(dipehnylphosphino)ethane]molybdenum(II)

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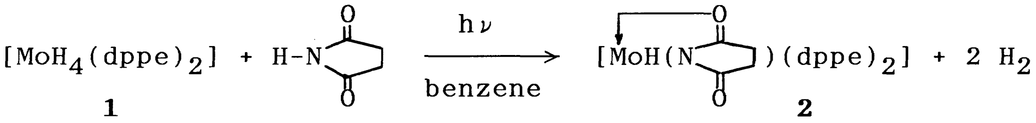
The photoreaction of $[MoH_4(dppe)_2]$ with succinimide gave $[MoH(succinimido\text{-}\underline{N},\underline{O})(dppe)_2]$, which was characterized spectroscopically as well as X-ray crystallographically to have the imido ligand coordinated to the metal bidentately *via* nitrogen and oxygen atoms constructing four membered metallacycle.

There have been several examples of the formation of the transition-metal imido complex *via* the oxidative addition of cyclic imides such as succinimide, phthalimide, *etc*., involving nitrogen-hydrogen bond cleavage.$^{1-4)}$ Most of them have been shown to have the unidentately coordinated imido ligand on the basis of their spectral evidence with an exception of ruthenium complex $[RuH(imido\text{-}\underline{N},\underline{O})(PPh_3)_3]$ which has reportedly bidentate imido ligand.$^{3)}$ None of them, however, has been structurally characterized.$^{5)}$

In the course of our studies on the photoreaction of molybdenum tetrahydride, $[MoH_4(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) (**1**), with various substrates including methacrylic and allylic esters,$^{6,7)}$ allylic carbonates,$^{8)}$ and carbon dioxide,$^{9)}$ we found that the reaction of **1** with succinimide under irradiation gave hydrido(succinimido)molybdenum(II) complex (**2**), in which the imido ligand is coordinated in a bidentate fashion through its nitrogen atom and one of two carbonyl oxygen atoms. Here we report preparation and the structural characterization of **2**.

Irradiation of the Pyrex flask containing a yellow solution of **1** (0.528 mmol) and succinimide (0.660 mmol) in benzene (50 cm^3) *in vacuo* with a 100-W high-pressure mercury lamp at room temperature for 2 h afforded dark red solution. The reaction was accompanied by the evolution of 187 mol% of H_2. Wine-red prisms of hydrido(succinimido-*N*,*O*)bis[1,2-

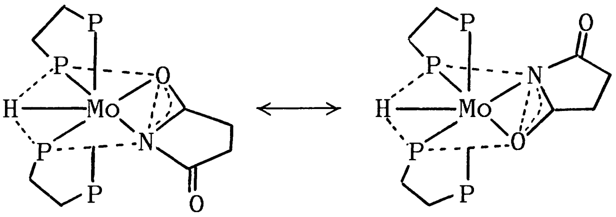
bis(diphenylphosphino)ethane]molybdenum(II) (**2**)[10] were isolated from the resulting solution in 66% yield.

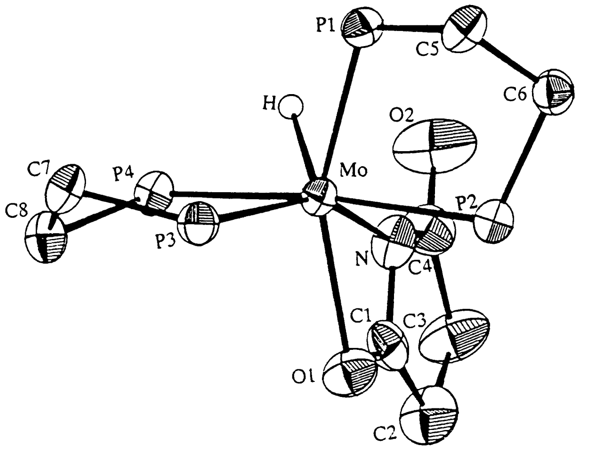


The similar results were obtained when the reaction was carried out in toluene heated at 110 °C in the dark. Interestingly, complex **2** was obtained also, though in low yield, by a similar treatment of **1** with N-allyloxy- or N-hydroxysuccinimide. In the former reaction, accompanying formation of propene in addition to H_2 was observed, although the fate of the oxygen atom in these reactions is uncertain.

The hydrido(succinimido-N,O) complex **2** is soluble in benzene, toluene, and tetrahydrofuran and melted at 254-7 °C with decomposition. Its IR spectrum (KBr disc) showed ν(Mo-H) at 1800 cm^{-1} as well as medium to strong bands at 1730, 1700, and 1540 cm^{-1} assignable to coordinated (the last band) and uncoordinated (the rest) carbonyl stretching of the imido ligand. The results suggest that the complex **2** possesses imido ligand coordinated to the metal in a bidentate mode via nitrogen and one of two carbonyl oxygens similar to those reported for ruthenium hydride.[3] In the ^1H NMR spectrum of **2** in benzene-d_6, hydride signals were observed at δ -6.57 as a triplet of triplets (J = 51.0 and 38.7 Hz), which is similar to those observed for the related acetato complex, $[MoH(O_2CCH_3)(dppe)_2]$,[7] suggesting the existence of two pairs of phosphorus nuclei each comprising of two equivalent phosphorus atoms. The ^{31}P NMR spectrum consistent with these observations was obtained (two triplets at δ 99.1 and 77.4 ppm downfield from external PPh_3; J = 22.0 Hz). These NMR spectral observations suggest that the complex **2** takes pentagonal bipyramidal configuration as shown below in solution at room temperature, where two carbonyl groups are exchanging rapidly at room temperature within NMR time scale. The mechanism of this exchange process is not clarified yet.

The A_2X_2 pattern of the ^{31}P NMR spectrum of **2** in tetrahydrofuran-d_8 broadened on lowering the temperature and changed to four isolated signals at -60 °C each splitted into doublets of doublets of doublet centered at





Selected Bond Distances (Å)

Mo-P(1)	2.378(3)	Mo-H	1.582
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)-O(1)	1.265(12)
Mo-O(1)	2.354(7)	C(4)-O(2)	1.215(14)
Mo-N	2.282(6)		

Selected Bond Angles (degree)

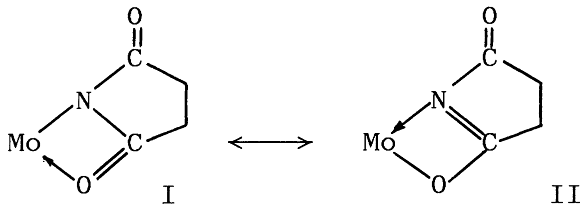
O(1)-Mo-N	57.38(27)
P(3)-Mo-N	153.05(24)
P(1)-Mo-H	68.97
P(3)-Mo-H	115.11
Mo-O(1)-C(1)	91.92(58)
O(1)-C(1)-N	117.53(81)

Fig. 1. ORTEP drawing of $[\mathrm{MoH\{NC(O)(CH_2)_2CO\}(dppe)_2]\cdot C_6D_6}$ (**2**) with the atom-labelling scheme.

δ 76.1, 66.1, 60.5 and 42.4 ppm assignable to the AKMX spin system, which may correspond to the solid state structure of **2** (*vide infra*).

A good prismic crystal of **2** suitable for the X-ray analysis was obtained by crystallization from benzene-$\underline{d}_6$ in which one mole of benzene-$\underline{d}_6$ was included as a crystallization solvent.11) The ORTEP diagram and the atom numbering of the complex **2** are shown in Fig. 1. The complex has a very distorted pentagonal-bipyramidal geometry with P(1), P(2), P(4), a hydrido ligand, and the oxygen atom of succinimido ligand comprising the pentagonal girdle. The hydride ligand, whose location was determined from the Fourier difference map, was found to deviate greatly from the pentagonal plane towards the apical nitrogen atom, which in turn shifted considerably from the apical position towards the plane. 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(4) or P(1), respectively], reflecting the greater *trans* influence of the phosphine ligand than the imido ligand.

Four carbon atoms, two oxygens and a nitrogen atom of the succinimido ligand lie in a plane which also includes a molybdenum atom. C=O bond distance of the coordinated carbonyl group [C(1)-O(1)] is longer than that of the uncoordinated one [C(4)-O(2)] which is similar to the corresponding bond length of free succinimide (1.23 Å). This result suggests a certain degree of contribution of the canonical form II shown below, which is con-



sistent with the smaller N-C(1) bond length as compared with the N-C(4). Mo-O(1) bond distance is similar to the related Mo-O bond reported for the dimethylformamide complex, trans-[Mo(Me_2NCHO)(dppe)$_2$] [2.348(10) Å]$^{12)}$ and for the ethylcarbonato complex, [MoH(O_2COEt)(dppe)$_2$] [2.271(2) and 2.333(3) Å].$^{8)}$

The results described here present, to our knowledge, the first example of the structural characterization of the transition metal imido complex in which the imido ligand coordinated in a bidentate fashion.

We thank the Iwatani Scholarship and Shinsei-shigen-kyokai for the support of this research. We thank Professor K. Osakada and Dr. M. Tanaka of Tokyo Institute of Technology for discussion in the X-ray crystallographic studies and for the elemental analysis, respectively.

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10) Good analytical results (C, H, and N) were obtained for complex **2**.
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(Received May 15, 1990)