Syntheses and Spectroscopic Properties of Substituted Phthalimido Complexes of Molybdenum(II)

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$[MoH_2(OMe)_2(dppe)_2]$ reacts with a series of phthalimide derivatives, each of which contains an electron-donor, an electron-acceptor, or redox-active center, to give the corresponding (substituted phthalimido)hydrido complexes in good yields. Investigation of spectroscopic properties suggests that some of these complexes have a polarized structure in a polar solvent.

Today, intriguing organometallic complexes are beginning to emerge as the new materials for nonlinear optical (NLO) devices, liquid crystals, receptor molecules, semiconducting materials, and superconducting charge-transfer (CT) complexes.[1] Incorporation of metals into the organic material systems can be expected to give new aspects of chemistry and to introduce many new variables. These compounds contain a wide variety of functionalized groups such as electron-donor, electron-acceptor, redox-active center, or asymmetrical framework in their structures. Occasionally, great difficulties arise in the synthesis of the complexes of these types because the most common route to them involves reactions of highly reactive organometallic reagents or intermediates, and sensitive functionalities are usually incompatible with such procedures. A strategy devised to overcome this problem is to develop a highly selective reaction under relatively mild conditions.

Previously we showed that 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, CHCH(O)CH=CHCHCH, CHCH(CH_2)CH=CHCHCH, C_6H_4-1,2] to afford novel (cyclic imido)hydridomolybdenum complexes, [MoH{NC(O)EC(O)}$(dppe)_2$] (**2**) as a result of the oxidative addition involving imide N–H bond cleavage (Scheme 1).[2,3]

Their structures, which were characterized by spectroscopic methods as well as by X-ray crystallography, showed that the imido ligands are coordinated to the metal in a bidentate manner via the nitrogen and the oxygen atoms, yielding a four-membered metallacycle. Furthermore, this methodology was extended recently to the synthesis of analogous (*N*-acylamido-*N,O*)hydrido complexes of molybdenum **3** and tungsten **4**.[4,5]

Particularly the phthalimido complex, in which the aromatic ring can interact with the metal center through its π-electron system, is of considerable interest for us since the phthalimido group is a commonly encountered building block in the synthesis of organic materials.[6]

We wished to extend this work to prepare functionalized phthalimido complexes. However, this reaction (Scheme 1) was found to be inapplicable to the synthesis of a complex that contains a sensitive substituent. For example, the reaction of **1** with 4-nitrophthalimide requires elevated temperature or photolysis, conditions, under which the hydrides of **1** readily attack the nitro group leading to the formation of 4-aminophthalimide. We have developed a way to overcome this limitation, and report here the synthesis and spectroscopic properties of a wide range of substituted phthalimido complexes of molybdenum(II).

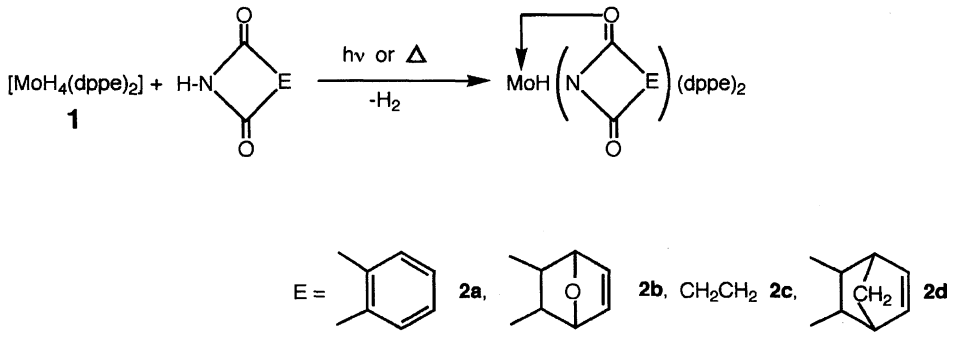
Results and Discussion

During our study of the reactivity of (*N*-acylamido-*N,O*)-hydrido complexes of molybdenum(II) (**3**), we observed that treatment of these complexes with methanol gave a novel dihydridodimethoxo complex **5** (Scheme 2).[5]

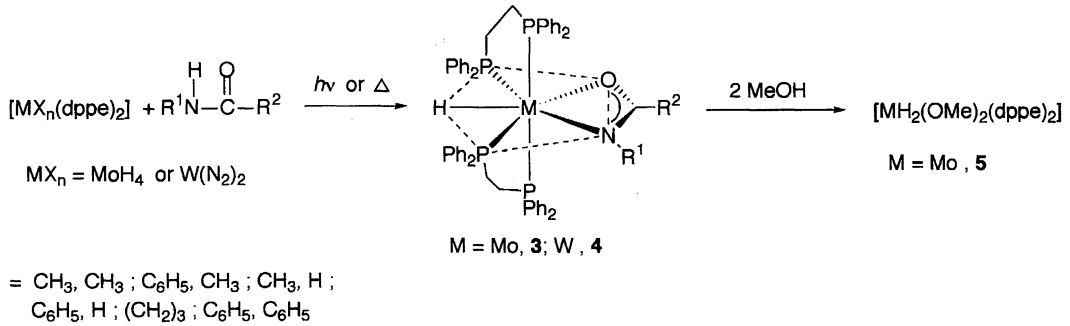
It has been found that complex **5** reacts with a variety of HX compounds (X = CH_3CO_2, $CH(COOEt)_2$, $N(CH_3)COCH_3$, $O_2(C_6H_4$-1,2)) to form the hydrido species. It is noteworthy that the reaction of **5** with phthalimide proceeds at ambient temperature without any forced conditions to produce the phthalimido complex **2a** in good yield. Consequently, complex **5** seems to be a potential precursor of a series of substituted phthalimido complexes.

The reaction of **5** with 4-nitrophthalimide in toluene at −20 °C gives the dark green, hydrido(imido) complex **6**, as shown in Eq. 1.

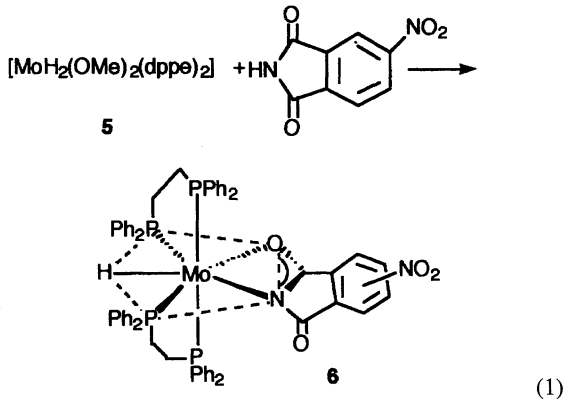
Complex **1** or *trans*-$[Mo(N_2)_2(dppe)_2]$ (**7**), which is also known to be an excellent starting material for the synthesis of a series of organomolybdenum complexes,[7] does not react with 4-nitrophthalimide at this temperature at all.



Scheme 1.



Scheme 2.



(1)

At slightly elevated temperature (0 °C), the reactions between the imide and these complexes (**1** and **7**) proceed, but they attack the nitro group instead of the imide N–H bond, leading to the formation of 4-aminophthalimide. Thus, complex **5** behaves differently in this respect. It seemed strange at first sight that complex **7** can reduce a nitro group to an amino group since it does not bear a hydride as a ligand. We observed that **7** also reduces nitrobenzene to aniline in good yields.[8] *Ortho*-hydrogens of the phenyl groups in dppe ligands might be playing a role of hydrogen source, though there is no solid evidence yet to support this.

Complex **6** is very sensitive to air and moisture, and undergoes slow thermal decomposition in solution at room temperature.

Similarly, complex **5** reacts with the members of the series of phthalimide derivatives, which contain an electron-donor, an electron-acceptor, or redox-active center, to give the corresponding (substituted phthalimido)hydrido complexes in good yields (Fig. 1) The thermal stability of these complexes is much higher than that of the complex **6**. Because 4-aminophthalimide does not react with **1** to give the corresponding hydrido complex, complex **5** proves useful in the synthesis of substituted phthalimido complexes. Preparative, analytical, and selected spectroscopic data for the complexes are compiled in Tables 1, 2, and 3.

The Mo–H stretching bands of complexes were observed at 1811—1890 cm^{-1}, values characteristic of ν(Mo–H) for [MoHX(dppe)$_2$]-type complexes.[9] As compared with (unsubstituted phthalimido)hydrido complex **2a**, these bands shift to higher frequency. The relatively strong IR absorptions in these complexes at around 1700 cm^{-1} and at around 1560 cm^{-1} are assignable to uncoordinated and coordinated carbonyl stretching bands of the imido ligands, respectively.[3]

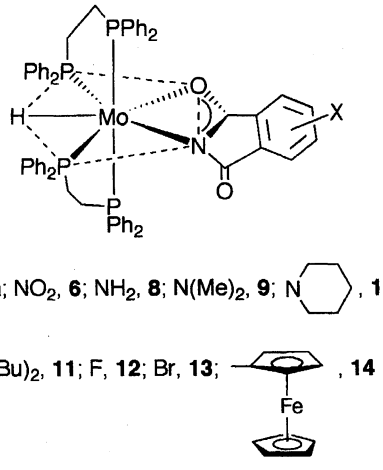


Fig. 1.

Table 1. Preparation of Substituted Phthalimido Complexes

Entry	**5**/mmol	Imide/mmol	Conditions	Solvent/ml	Product (X)	Yield (%)
1	0.247	0.347	−20— −15 °C, 5 h	30	**6** (NO_2)	53
2	0.233	0.240	r.t., 24 h	75	**8** (NH_2)	67
3	0.250	0.250	r.t., 17 h	40	**9** (NMe_2)	68
4	0.254	0.250	r.t., 18 h	40	**10** (Piperidino)	62
5	0.210	0.210	r.t., 20 h	40	**11** (N(*n*-Bu)$_2$)	52
6	0.328	0.320	r.t., 40 h	40	**12** (F)	92
7	0.221	0.220	r.t., 19 h	40	**13** (Br)	92
8	0.210	0.210	r.t., 20 h	30	**14** (Ferrocenyl)	37

Table 2. IR and Analytical Data for Substituted Phthalimido Complexes

	IR[a]/cm^{-1}			Elemental anal.[b]		
Compd	ν(Mo-H)	ν(C=O)	ν(C=O→Mo)	C/%	H/%	N/%
6	1811	1715	1565	[c]	[c]	[c]
		1528, 1329 ($\nu(NO_2)$)				
8	1880	1701	1559	67.88 (68.31)	5.53 (5.16)	2.34 (2.66)
		3354, 3474 ($\nu(NH_2)$)				
9	1883	1701	1564	68.87 (68.76)	5.59 (5.40)	1.97 (2.59)
10	1886	1703	1561	69.28 (69.52)	5.72 (5.56)	2.30 (2.49)
11	1870	1701	1557	69.81 (69.98)	6.29 (6.06)	2.08 (2.40)
12	1889	1715	1567	68.18 (68.12)	5.04 (4.95)	1.01 (1.32)
13	1878	1717	1567	65.17 (64.41)	5.00 (4.68)	1.14 (1.25)
					Br; 6.43 (7.14)	
14	1890	1708	1563	[c]	[c]	[c]
2a[d]	1800	1705	1560			

a) KBr disk. b) Calculated values in parentheses. c) Analytically pure sample was not obtainable. d) Data from Ref. 3.

Table 3. Selected ^{1}H and ^{13}C NMR Data for Substituted Phthalimido Complexes

Compd	^{1}H NMR[a,b]	^{13}C NMR[c]
6	−6.05 (tt, Mo*H*, J_{HP}=34.7, 54.2 Hz, 1H)	
8	−6.21 (dddd, Mo*H*, J_{HP}=35.8, 37.3, 51.8, 55.5 Hz, 1H)	183.6 (*C*=O→Mo), 182.1 (*C*=O)
9	−6.24 (dddd, Mo*H*, J_{HP}=35.4, 37.5, 50.6, 56.5 Hz, 1H), 2.23 (s, NCH_3, 6H)	184.1 (*C*=O→Mo), 182.6 (*C*=O)
10	−6.24 (tt, Mo*H*, J_{HP}=36.6, 53.4 Hz, 1H)	183.4 (*C*=O→Mo), 182.8 (*C*=O)
11	−6.17 (dddd, Mo*H*, J_{HP}=32.8, 40.0, 49.1, 58.7 Hz, 1H)	184.4 (*C*=O→Mo), 182.4 (*C*=O)
12	−6.20 (tt, Mo*H*, J_{HP}=35.7, 54.0 Hz, 1H)	181.1 (*C*=O→Mo), 180.4 (*C*=O)
13	−6.22 (tt, Mo*H*, J_{HP}=35.4, 54.0 Hz, 1H)	181.0 (*C*=O→Mo), 180.5 (*C*=O)
14	−6.23 (tt, Mo*H*, J_{HP}=36.0, 53.4 Hz, 1H), 3.86 (s, FeC_5H_5, 5H)	182.7 (*C*=O→Mo), 182.5 (*C*=O)
2a[d]	−6.16 (tt, Mo*H*, J_{HP}=36.0, 53.3 Hz, 1H)	182.6 (*C*=O)

a) Conditions: C_6D_6 in ppm, 293 K, 270 MHz, TMS reference. b) The resonances attributable to the aromatic ring of phthalimide were observed in the range of δ=6—7 and were obscured by overlapping signals of the dppe ligands and the solvent. c) Conditions: C_6D_6 in ppm, 293 K, 67.8 MHz, TMS reference. d) Data from Ref. 3.

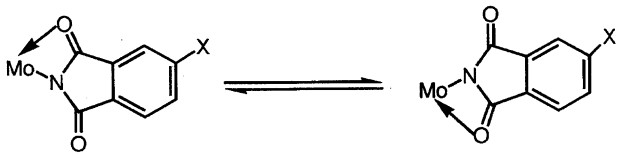
A comparison of these data with the value for (unsubstituted phthalimido)hydrido complex **2a** shows marked propensity. In complexes **8**, **9**, **10**, and **11**, which contain an electron-donating substituent, the uncoordinated ν(C=O) bands are shifted to lower wavenumber from that of the complex **2a**, while those in complexes **6**, **12**, and **13**, which contain an electron-accepting group, are shifted to higher wavenumber. Therefore these shifts seem to reflect the nature of the substituent directly. On the other hand, in coordinated ν(C=O)bands, such regularity could not be observed and the substituents seem not to influence the interaction between the metal and the carbonyl group.

Complex **2a** has been fully characterized by an NMR spectral study and shown to have a fluxional pentagonal bipyramidal structure in solution.[3] The ^{1}H NMR spectra of the new complexes show a multiplet at ca. δ=−6.2 ppm which is assigned to the hydride signal coupled to ^{31}P. A comparison of the hydride resonances of complexes **2a** and **8**—**14** reveals a substantial similarity in the position except for complex **6**, which has a strong electron-accepting nitro group; the resonance is apparently at lower field than that of **2a**. The splitting patterns of these signals are noteworthy. In complexes **6**, **10**, and **12**—**14**, the resonances appear as a triplet of triplets assignable to an A_2K_2X spin system (A=P_{eq}, K=P_{ax}, X=H) in solution at room temperature and the coupling constants are compatible with those of **2a**, whereas in complexes **8**, **9**,

and **11**, the hydride signals appear with the multiplicity corresponding to an ABKLX (A, B=P_{eq}; K, L=P_{ax}; X=H) spin system in which the proton couples with four magnetically inequivalent phosphorus nuclei. This spectral discrepancy may be related to the conformational isomerism of the complexes. In analogy with **2a**, the complexes **6**, **10**, and **12**—**14** seem to possess a fluxional structure involving rapid attachment and detachment of the Mo–O bonds in solution at room temperature (Scheme 3).

Electron-accepting groups tend to make the hydride signal split into a triplet of triplets and these complexes have a fluxional property in solution, although complexes **10** and **14** show a different behavior. On the other hand in the case of complexes **8**, **9**, and **11**, interconversion such as in Scheme 3 is hindered. Contribution of a polar resonance structure **B** of the canonical formula below, in which the amino group pours a certain amount of electron density on the molybdenum atom, may be more important than **A** (Fig. 2).

This sort of contribution may prevent the fluxional behavior of the complexes. It is also necessary to consider steric effects since complex **10** shows an unexpected splitting pattern (triplet of triplets) in spite of electron-donating character of the piperidino group. If the molecule adopts such a polar resonance structure, the aromatic ring of the phthalimido ligand and the C–N–C moiety of the amino group have to be in a plane. However, in the case of complex **10**, they would be sterically forced out of planarity because rotations about the C–N single bonds are prevented and steric repulsion between the ortho hydrogens of the phenyl group and the α-hydrogens in piperidino ring would become evident. The fact that complexes **8**, **9**, and **11** differ from the others in the binding mode of imido ligand can be deduced from a ^{13}C NMR study. As shown in Table 3, the coordinated C=O resonance in **8**, **9**, and **11** is shifted to lower field by about δ=1.5 ppm from that of the uncoordinated one, whereas the magnitudes of this shift are small ($\delta \leq 0.7$ ppm) for the rest of the complexes. In contrast with ^{13}C NMR spectrum of **2a**, which shows a singlet at δ=182.6 assignable to imido



Scheme 3.

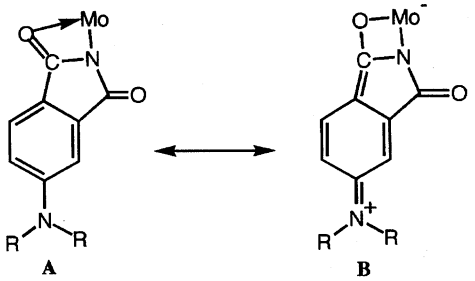


Fig. 2. Canonical formula for the complexes bearing amino group on 4-position of the phthalimido ligand.

Table 4. UV-vis Absorption Spectra for Substituted Phthalimido Complexes

Compd	λ/nm (ε/M^{-1} cm^{-1})		
2a	417 (11340),[a]	700 (533)[a]	
6	413 (12000),[a]	575 (3889)[a]	
8	363 (6000),[a]	414 (5900),[a]	616 (520)[a]
	365 (4800),[b]	486 (1600),[b]	614 (220)[b]
9	380 (7800),[a]	430 (4900),[a]	612 (420)[a]
	381 (11000),[b]	498 (8300),[b]	670 (240)[b]
10	379 (11000),[a]	431 (7300),[a]	660 (510)[a]
	382 (12000),[b]	480 (3700),[b]	660 (430)[b]
12	420 (8300),[a]	689 (620)[a]	
	413 (6500),[b]	698 (390)[b]	
13	425 (7000),[a]	717 (600)[a]	
	421 (3700),[b]	737 (260)[b]	
14	415 (11000),[a]	669 (870)[a]	
	409 (5200),[b]	675 (450)[b]	

a) Solution in toluene. b) Solution in DMF.

C=O, each signal in the spectra of the substituted phthalimido complexes consisted of two sets of signals, reflecting the unsymmetrical structure of these complexes.

Contrary to our expectation, the hydride signals of complexes **10** and **12** are temperature independent; there was virtually no change in these triplet of triplets signals measured both at room temperature (23 °C) and at −70 °C in toluene-d_8.

UV-vis absorption spectra in toluene and in DMF are recorded for the compounds (Table 4).

In complexes **8**, **9**, and **10**, there are three absorptions around λ=370, 420, and 615 nm, although in complexes **2a**, **6**, **12**, **13**, and **14**, only two bands appear in this region. Replacement of aryl H (**2a**) by NO_2 (**6**) in the phthalimido ligand results in a blue shift of 125 nm in lower energy band and replacement by NH_2 (**8**) or NMe_2 (**9**) resulted in a shift to higher energy by ca. 85 nm in this region. In contrast, replacement by F (**12**) or Br (**13**) does not lead to an appreciable shift of that band. Comparison of the spectra of complexes **8**, **9**, and **10** measured in toluene and in DMF, exhibit a positive solvatochromic behavior associated with a significant dipole moment change between ground and excited states. This result suggests a contribution of the polar resonance structure of these complexes, as previously described.

Experimental

All reactions were carried out under purified argon (except where otherwise indicated) using standard Schlenk techniques. Commercially available reagent grade chemicals were used as such without any further purification. All solvents were dried by standard methods and were stored under argon. [MoH_4(dppe)$_2$] (**1**) and [MoH_2(OMe)$_2$(dppe)$_2$] (**5**) were prepared by published procedures.[5,10] 4-Nitrophthalimide was used as purchased. 4-Aminophthalimide was prepared by catalytic hydrogenation of 4-nitrophthalimide using palladium on activated carbon. The other phthalimides were prepared according to the reported methods.[11—13]

Preparation of the Complex [MoH(4-nitrophthalimido-*N*,*O*)-(dppe)$_2$] (6). In a Schlenk flask, [MoH_2(OMe)$_2$(dppe)$_2$] (**5**) (0.237

g, 0.247 mmol) and 4-nitrophthalimide (0.0470 g, 0.247 mmol) were placed. Toluene (30 ml) was added and the mixture was stirred in the range of −20 to −15 °C for 5 h, during which time the solution changed from yellow to dark green. From the reaction mixture, the solvent was evaporated to dryness under reduced pressure at −10 °C. Then, ether (20 ml) was added at −30 °C and cooling the resultant solution at −15 °C for 12 h gave an off-white precipitate of dppe ligand, which was filtered off. The filtrate was further cooled overnight at −15 °C and impurities were filtered off again. To the resulting solution was added cold hexane (10 ml) and cooling the solution at −15 °C for 72 h gave a dark-green powder of **6** (0.143 g, 53%). Elemental analysis and ^{13}C NMR investigation failed to provide useful information because of the thermal instability of the complex.

Preparation of the Other Complexes. A typical procedure is as follows. In a Schlenk flask, **5** (0.223 g, 0.233 mmol) and 4-aminophthalimide (0.0390 g, 0.240 mmol) were placed. Toluene (75 ml) was added and the mixture was stirred at room temperature for 24 h, during which time the solution changed from yellow to black. From the reaction mixture, the solvent was evaporated to dryness under reduced pressure; then cold ether (20 ml) was added at −40 °C and cooling the resultant solution at −15 °C for 12 h gave a dark red precipitate. The supernatant solution was removed with a bridge filter, and the residue thus obtained was washed with hexane, then extracted with benzene. This benzene solution was further cooled for several days at 6 °C and yellow impurities were filtered off. From the resulting solution, the solvent was removed under vacuum. The dark red powder thus obtained was **8** (0.166 g, 67%). These procedures are also applicable to the syntheses of the other complexes. Preparations, analytical data, and selected spectroscopic data for all complexes are compiled in Tables 1, 2, and 3.

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