Industry, Tsukuba, Japan, during the summer of 1991. In addition, we thank Professor Kenneth G. Caulton for his intellectual input and support of J.A.S. during that program. We are grateful to the U.S. National Science Foundation (Grant CHE 9103915) and the Agency of Industrial Science and Technology of Japan for generous support of our research.

Supplementary Material Available: Tables of crystal data, fractional coordinates and thermal parameters, and bond distances and angles for *cis*-1 (9 pages). Ordering information is given on any current masthead page.

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Oxidative Addition of N-Substituted Amides to Molybdenum(II) Involving N–H Bond Cleavage To Give (η^2-*N*-Acylamido-*N*,*O*)hydridomolybdenum(II) Complexes: X-ray Molecular Structure of the Seven-Coordinate Complex $[\overline{MoH\{N(CO}CH_3)CH_3\}\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]$

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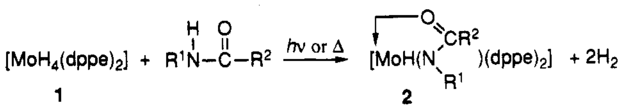
Summary: Photochemical or thermal reaction of $[MoH_4(dppe)_2]$ with *N*-alkylamides R^1NHCOR^2 (R^1, R^2: Me, Me; Ph, Me; Me, H; Ph, H; $(CH_2)_3$; Ph, Ph) in benzene or toluene yielded $[MoH\{N(R^1)COR^2\text{-}N,O\}(dppe)_2]$ as a result of the oxidative addition involving amide N–H bond cleavage (dppe = $Ph_2PCH_2CH_2PPh_2$). The resulting *N*-acylamido complexes have been characterized by means of NMR and IR spectroscopy as well as with an X-ray crystal structure study for R^1, R^2 = Me, Me. Some reactions of the *N*-acylamido complexes, including the oxidation of MeOH to yield a formaldehyde-coordinated complex, are also described.

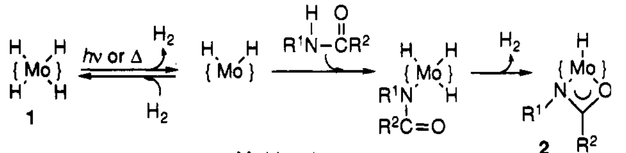
An investigation of the interaction between organotransition metals and organic nitrogen compounds such as amines, amides, and amino acids is intriguing in view of its relevance to biological systems. Among the nitrogen compounds, organic amides are especially important in this respect since they constitute a fundamental component of protein. In contrast to the fairly rich chemistry of transition-metal amido or imido complexes which are synthesized by the reaction of alkali-metal salts of amines with the transition-metal complexes,[1] examples of a direct oxidative addition of the N–H bond of unfunctionalized amines or amides to the transition-metal complexes are surprisingly few.[2] While several examples of the oxidative addition of a highly polarized N–H bond of a cyclic imide such as succinic and phthalic imides have been reported,[3] there has been only one precedent for the oxidative addition of simple amides involving N–H bond cleavage, where (acylamido)hydridoruthenium(II) and -iron(II) complexes are isolated and characterized.[4,5] Here we report the reaction of organic amides with molybdenum polyhydrides to give oxidative-addition products involving nitrogen–hydrogen bond cleavage. Molybdenum is especially important among the transition metals because it is one of the essential metals in biological activity.

Scheme I



$R^1,R^2 = CH_3,CH_3$ (**a**); C_6H_5,CH_3 (**b**); CH_3,H (**c**); C_6H_5,H (**d**); $(CH_2)_3$ (**e**); C_6H_5,C_6H_5 (**f**)

Scheme II



{ Mo } = $Mo(dppe)_2$

Irradiation for 3–5 h with a 100-W high-pressure mercury lamp at room temperature of a yellow benzene solu-

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[†] Yokohama National University.

[‡] Tokyo Institute of Technology.

(1) See for example: (a) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750. (b) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.

(2) See for example: (a) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006. (b) Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309.

(3) (a) Roundhill, D. M. *Inorg. Chem.* **1970**, *9*, 254. (b) Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1978**, *154*, C37. (c) Ikariya, T.; Takizawa, S.; Shirado, M.; Yoshikawa, S. *J. Organomet. Chem.* **1979**, *171*, C47. (d) Yamamoto, T.; Sano, K.; Yamamoto, A. *Chem. Lett.* **1982**, 907. (e) Kurishima, S.; Ito, T. *Chem. Lett.* **1990**, 1299. (f) Kurishima, S.; Matsuda, N.; Tamura, N.; Ito, T. *J. Chem. Soc., Dalton Trans.* **1991**, 1135.

(4) Schaad, D. R.; Landis, C. R. *J. Am. Chem. Soc.* **1990**, *112*, 1628.

(5) While this paper was in preparation, the reaction of NH_2COR (R = CF_3, Ph) with a ruthenium complex to form N-bonded (acylamido)ruthenium complexes was communicated: Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1146.

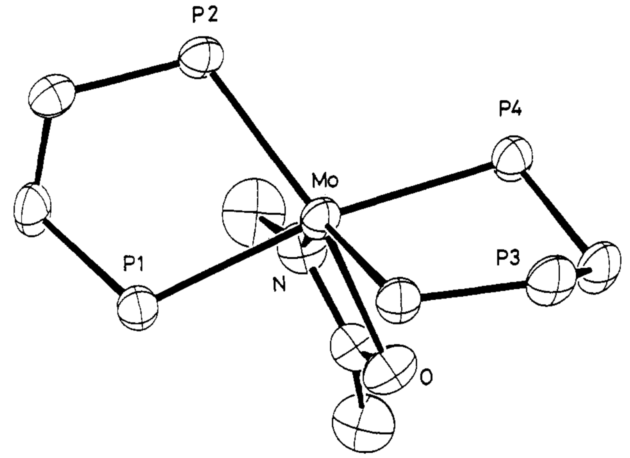
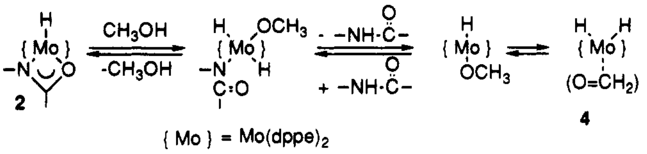


Figure 1. ORTEP drawing of [MoH{N(COCH$_3$)CH$_3$}(dppe)$_2$] (**2a**) showing thermal ellipsoids at 30% probability. Phenyl rings and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo–P(1) = 2.421 (5), Mo–P(2) = 2.421 (5), Mo–P(3) = 2.424 (5), Mo–P(4) = 2.447 (5), Mo–N = 2.25 (1), Mo–O = 2.24 (1), O–C(1) = 1.29 (2), N–C(1) = 1.35 (2), N–C(2) = 1.42 (2), C(1)–C(3) = 1.46 (3); N–Mo–O = 57.9 (4), N–Mo–P(1) = 82.4 (3), N–Mo–P(2) = 93.4 (3), N–Mo–P(3) = 141.5, N–Mo–P(4) = 90.0 (3), O–Mo–P(3) = 83.6 (3), P(2)–Mo–P(3) = 124.8 (2), P(1)–Mo–P(4) = 168.8 (2).

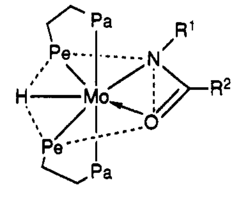
tion containing [MoH$_4$(dppe)$_2$] (**1**; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and an equivalent amount of amides afforded crystalline maroon (η^2-*N*-acylamido-*N*,*O*)hydridomolybdenum(II) complexes **2** accompanied by the evolution of H$_2$ (Scheme I). Similar results were obtained when **1** and amides were heated at 110 °C in toluene for 3–5 h. The yields of **2** ranged from 28% (for **c**, thermal reaction) to 58% (for **b**, thermal reaction), and the amount of evolved H$_2$ could be estimated as roughly twice the yields of **2**.[6] The closely related phenylamide complex [MoH{N(COH)C$_6$H$_5$}(PMe$_3$)$_4$] has been synthesized by the reaction of phenyl isocyanate with [MoH$_2$(PMe$_3$)$_5$],[7] but to our knowledge, this is the first example of the direct oxidative addition of an amide N–H group to the group 6 transition metals.

Since **1** is known to release 1 equiv of H$_2$ upon irradiation or heating to give the coordinatively unsaturated reactive intermediate MoH$_2$(dppe)$_2$,[8] the reaction path for the formation of **2** which involves oxidative addition of a N–H bond to the MoH$_2$(dppe)$_2$ intermediate as shown in Scheme II may be conceivable. Similar reaction paths involving C–O or N–H bond cleavage have been considered for the reaction of **1** with allyl carboxylates,[9] allyl alkyl carbonates,[10] or cyclic imides.[3f]

Scheme III



Complex **2**, which is soluble in benzene, toluene, tetrahydrofuran, and diethyl ether, is moderately stable in the solid state but deteriorates rapidly with air in solution. It reacts with chloroform to give [MoCl{N(COR^2)R^1}(dppe)$_2$]. Complex **2** exhibits spectral properties consistent with the seven-coordinate pentagonal-bipyramidal geometry[11]



The amide I band in the IR spectrum of **2** shifted to lower frequency by about 100 cm^{-1} as compared with this band in the free amide. This, together with the disappearance of the amide II and the ν_{N-H} bands, supports the N–H bond cleavage and the mode of coordination as shown above. In the ^{1}H NMR spectra, hydride signals appeared at around −5 ppm with the multiplicity corresponding to an ACKMX spin system. These signals are consistent with the four isolated signals in ^{31}P{^{1}H} NMR spectra each being split into a doublet of doublets of doublets (ACKM spin system).

A good prismatic single crystal of the *N*-methylacetamido complex **2a** suitable for X-ray analysis was obtained by crystallization from benzene–hexane. An ORTEP drawing around the molybdenum skeleton is shown in Figure 1.[12] Although fairly weak reflection intensities prevented us from defining the hydride ligand, its location was postulated at the site opposite to the nitrogen ligand on the basis of NMR evidence. In fact, there is more than enough room there for the hydride ligand to reside.

The complex is regarded as being in a distorted-pentagonal-bipyramidal configuration with two phosphorus atoms, the nitrogen and the oxygen atoms of the amide ligand, and a hydride ligand comprising the pentagonal girdle. The total of the bond angles around the molybdenum atom (∠P(2)–Mo–P(3) + ∠P(3)–Mo–O + ∠O–Mo–N + ∠N–Mo–P(2)) is 359.7°, which suggests a strictly flat equatorial plane. The nitrogen, oxygen, and three carbon atoms of the amide ligand are in a plane with a C–O bond

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[6] In the thermal reaction of *N*-phenylformamide (**d**), the known *cis*-[Mo(CO)$_2$(dppe)$_2$] (**3**) was observed in addition to **2d**, suggesting that the concurrent insertion reaction of **1** into the formyl C–H bond took place concomitantly. In fact, a higher ratio of **d**/**1** afforded a higher yield of **3** and the formation of aniline (14%) was observed when **d**/**1** = 1.31. The formation of a carbonyl complex by the reaction of a molybdenum(0) complex with *N*,*N*-dimethylformamide has been reported; see: Sato, M.; Tatsumi, T.; Kodama, T.; Hidai, M.; Uchida, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 4447.

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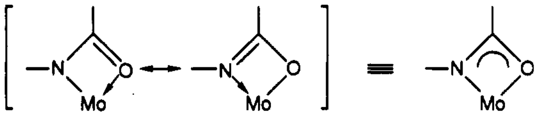
[11] Satisfactory analytical results (C, H, and N) were obtained for complexes **2a**–**f**. Since the spectral data for these complexes are much the same, those for **2a** are quoted here as a typical example: IR (KBr) ν_{Mo-H} = 1810 (vw), ν_{CO} = 1560 (s) cm^{-1}; ^{1}H NMR (270 MHz, C$_6$D$_6$) δ −4.92 (dddd, 1 H, Mo-*H*, J_{H-P_a} = 79.3, 59.8 Hz, J_{H-P_e} = 35.4, 17.7 Hz), 1.85 (s, 3 H, NC*H*$_3$), 0.66 (s, 3 H, CC*H*$_3$); ^{13}C NMR (78.8 MHz, C$_6$D$_6$) δ 169.6 (N*C*=O), 34.3 (N*C*H$_3$), 18.9 (C*C*H$_3$); ^{31}P{^{1}H} NMR (36.5 MHz, C$_6$D$_6$, chemical shifts are in ppm with downfield positive from the external benzene solution of PPh$_3$) four signals with ddd multiplicity at 103.2, 90.2, 76.5, and 73.5 (J_{P-P} = 159.7, 17.6, 17.6, 17.6, 13.2, and 8.8 Hz). Coupling constants were estimated by means of a computer simulation.

[12] Crystals of **2a** are triclinic, space group $P\bar{1}$, with a = 20.102 (12) Å, b = 23.948 (19) Å, c = 10.423 (6) Å, α = 95.56 (6)°, β = 90.03 (5)°, γ = 104.14 (5)°, V = 4841.3 (5.6) Å^3, Z = 4, F(000) = 2008; μ = 4.32 cm^{-1}, D(calcd) = 1.326 g cm^{-3}, Rigaku AFC-5R diffractometer, Mo Kα radiation, (λ = 0.71069 Å), 2θ range 3–45°, 5163 reflections with $F_o > 3\sigma(F_o)$, R = 0.069, and R_w = 0.071. The non-hydrogen atoms were refined anisotropically, and all hydrogen atoms except the hydride were placed at a distance of C–H = 1.00 Å. These hydrogen atoms were included in least-squares calculations without refinement of their parameters.

length of 1.29 (2) Å, which is longer than the corresponding bond length of free *N*-methylacetamide (1.225 Å), and a C(1)–N bond length of 1.35 (2) Å, which is slightly shorter than that of the free ligand (1.386 Å). The Mo–N distance of 2.25 (1) Å for **2a** is shorter than the average value of the σ-donating Mo–N bond distance of 2.33 Å,[13] whereas the Mo–O distance (2.24 (1) Å) is close to those of the related complex [MoH(O_2COEt-*O,O'*)(dppe)$_2$] (2.271 (2) and 2.333 (3) Å).[10] These structural features strongly suggest the following resonance form of the η^2-amide ligand of **2**:



In contrast to the thermal instability of the formamido complexes **2c** and **2d** (**2d** releases aniline, giving [Mo(CO)$_2$(dppe)$_2$] upon heating at 180 °C in vacuo), the rest of the amido complexes **2** are thermally stable both in the solid state and in solution.[14] They are, however, found to be susceptible to the electrophilic attack by organic acids. The reaction of **2f** with acetic acid in benzene at room temperature gave [MoH(O_2CCH_3-*O,O'*)(dppe)$_2$][9] together with *N*-phenylbenzamide, while that of **2b** with hexafluoroacetylacetone under similar conditions afforded [MoH{CH($COCF_3$)$_2$-*O,O'*}(dppe)$_2$] and *N*-phenylacetamide. Methanol reacted with **2** to give the formaldehyde complex [$MoH_2(OCH_2)$(dppe)$_2$][15] (**4**) together with the corresponding amides. A labeling experiment using CH_3OD and CD_3OD[16] revealed that the reaction proceeds as shown in Scheme III, where a β-hydrogen elimination process from the methoxo intermediate is involved. Although the reduction of transition-metal complexes with alcohol has long been known,[17] this result provides a rare example of trapping aldehyde formed by the reaction.[18]

Acknowledgment. T.I. thanks the Iwatani Scholarship and Shinsei-Shigen Kyokai for financial support.

Supplementary Material Available: Tables which contain reaction conditions and physical and spectral properties for **1** and **2**, tables of crystal data, bond distances and angles, and fractional coordinates and anisotropic thermal parameters for [MoH{N(COCH$_3$)CH$_3$}(dppe)$_2$] (**2a**), and a figure giving an additional view of **2a** (10 pages). Ordering information is given on any current masthead page.

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[14] The melting points of complexes **2** except **2c** and **2d** are in the range 179–241 °C under a vacuum. These complexes tolerated heating in toluene with reflux for 5 h under a nitrogen atmosphere.

[15] [$MoH_2(OCH_2)$(dppe)$_2$] (**4**): IR (KBr) ν_{Mo-H} = 1800 (br, m), $\nu_{formyl\ C-H}$ = 2800 (m) cm^{-1}; ^1H NMR (270 MHz, C_6D_6) δ −2.99 (quint, 2 H, J_{H-P} = 34.63 Hz); ^{13}C NMR (78.8 MHz, C_6D_6) δ 64.11 (t, O═CH_2, J_{C-H} = 167.2 Hz); $^{31}P\{^1H\}$ NMR (36.5 MHz, C_6D_6, chemical shifts are in ppm with downfield positive from the external benzene solution of PPh_3) 71.3 (br, s).

[16] The reactions were followed by ^1H NMR spectroscopy. When **2b** and CD_3OH were mixed, a hydrido signal assignable to [$MoH_2(OCD_2)$(dppe)$_2$] appeared at first, the intensity of which then gradually decreased. In the reaction between **2b** and CD_3OD, signals due to **2b** and [$MoHD(OCD_2)$(dppe)$_2$], which were observed at the very early stages of the reaction, decreased gradually and disappeared completely after 1 h, leaving signals solely assignable to $N(D)C_6H_5C(O)CH_3$ and [MoD{N(C_6H_5)C(O)CH_3}(dppe)$_2$].

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Synthesis, Structure, and Reactivity of the Four-Coordinate Aryl Complex Ir(CO)(2-mesityl)(dppe), Which Displays an Unusual Aryl to Benzyl Rearrangement

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Summary: The synthesis, structure, and reaction chemistry of Ir(CO)(2-mesityl)(dppe) (**1**; dppe = 1,2-bis(diphenylphosphino)ethane) is described. Complex **1** is prepared from the reaction of 2-mesitylmagnesium bromide and IrBr(CO)(dppe). The molecular structure of **1** in the solid state is that of a nearly square-planar four-coordinate complex with cis phosphine donors, a σ-bound mesityl ligand, and a slight tetrahedral distortion. Complex **1** reacts readily with diphenylsilane and H_2 to yield the respective cis oxidative-addition products IrHY($C_6H_2(CH_3)_3$)(dppe), where Y = Ph_2HSi, H. A unique transformation occurs when **1** is heated in the presence of ethylene at 90 °C in benzene to yield Ir(CO)(η^2-C_2H_4)(3,5-dimethylbenzyl)(dppe). The reaction of **1** with CO generates the acyl complex Ir(CO)$_2$(C(O)mesityl)(dppe).

The reactions of small molecules with four-coordinate d^8 metal centers play a major role in homogeneous catalysis, including hydrogenation, hydroformylation, and hydrosilation.[1] For the study of these reactions mechanistically, iridium complexes such as *trans*-IrCl(CO)(PPh_3)$_2$ (Vaska's complex) have been useful as model systems for elucidating substrate activation via oxidative addition and adduct formation.[2,3] From our laboratory, studies have employed the bis(phosphine) complex IrX-

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