# Syntheses, Structures, and Reactions of $\eta^2$-*N*-Acylamido-*N*,*O* Hydrido Complexes of Molybdenum(II) and Tungsten(II)

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The *N*-acylamido complexes $[MH\{N(R^1)COR^2\text{-}N,O\}(dppe)_2]$ (M = Mo, W; $R^1/R^2$ = Me/Me, Ph/Me, Me/H, Ph/H, $(CH_2)_3$, Ph/Ph; dppe = $Ph_2PCH_2CH_2PPh_2$) were synthesized by photochemical or thermal reactions of $[MoH_4(dppe)_2]$ or *trans*-$[W(N_2)_2(dppe)_2]$ with *N*-alkylamides $R^1NHCOR^2$. An X-ray study of $[MoH\{N(CH_3)COCH_3\text{-}N,O\}(dppe)_2]$ revealed a distorted-pentagonal-bipyramidal configuration with two phosphorus atoms, the nitrogen and the oxygen atoms of the amide, and a hydride lying in the equatorial plane. These complexes reacted with methanol or ethanol in toluene at ambient temperature to give the novel alkoxo hydrido complexes $[MH_2(OR)_2(dppe)_2]$ (R = Me, Et). The reactions apparently proceeded via a coordinatively unsaturated 16e intermediate, which is formed upon release of the *N*-acylamido ligand. The reactions between the amido complexes and catechols yielded the chelated catecholato complexes $[MH_2(catecholato\text{-}O,O')(dppe)_2]$ (catecholato = $O_2C_6H_4$, $O_2C_6H_3$(4-Me), $O_2C_6H_3$(4-Bu$^t$), $O_2C_6H_3$(4-COOEt), and $O_2C_{10}H_6$). The structures of catecholato complexes, determined by single-crystal X-ray diffraction studies, exhibit distorted-dodecahedral geometry.

## Introduction

The field of organomolybdenum chemistry has grown rapidly over the last few years, partly because of biological interest. Inter alia, studying interactions between molybdenum complexes and nitrogen compounds is important in its relevance to nitrogenase models.[1] Our continuing interest in the chemistry of molybdenum polyhydrides[2] prompted us to investigate the reaction of $MoH_4(dppe)_2$ (**1**; dppe = $Ph_2PCH_2CH_2PPh_2$), which is kinetically a very reactive species and undergoes a wide variety of transformations,[3] with *N*-alkylamides. We have found that the photochemical or thermal reaction yielded $[MoH\{N(R^1)COR^2\text{-}N,O\}(dppe)_2]$ (**2**) as a result of the oxidative addition which involves amide N−H bond cleavage. Very few examples of a direct oxidative addition of an N−H bond of unfunctionalized amides to the transition-metal complexes are known, and this reaction is intriguing.[4] Here we report the synthesis and spectroscopic and crystallographic characterization of these complexes. We also describe in detail the reactions of a (*N*-acylamido)-hydridomolybdenum complex with aliphatic alcohols and catechol derivatives, together with structural analyses for some catecholato complexes. Further, we have tried to extend this work to tungsten complexes. A preliminary account of some of this work has already appeared.[5]

## Results and Discussion

**Synthesis and Spectroscopic Characterization of Hydrido(*N*-acylamido-*N*,*O*)molybdenum (2) and -tungsten (3) Complexes.** Most complexes containing a nitrogen−metal bond are prepared by a simple metathesis reaction between a transition-metal halide and an alkali-metal salt of an amine. The strongly basic conditions required restrict the flexibility of this approach. We have now found a convenient synthetic route to (*N*-acylamido)hydridomolybdenum complexes, in which the reaction proceeds under neutral conditions.

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

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**Table 1. Preparations of Complexes [MH{N($R^1$)CO$R^2$-*N,O*}(dppe)$_2$] (M = Mo (2), W (3))**

| compd | substrate: complex/amt, mmol | substrate: amide ($R^1$, $R^2$)/amt, mmol | solvent/amt, mL | conditions | yield, % |
|---|---|---|---|---|---|
| **2a** | {Mo}$H_4$$^a$/0.27 | $CH_3$, $CH_3$/0.27 | benzene/27 | 20 °C, *hν*, 3 h | 26 |
| **2a** | {Mo}$H_4$$^a$/1.40 | $CH_3$, $CH_3$/1.84 | toluene/40 | 110 °C, 3 h | 50 |
| **2b** | {Mo}$H_4$$^a$/0.38 | Ph, $CH_3$/0.44 | benzene/30 | 20 °C, *hν*, 3 h | 31 |
| **2b** | {Mo}$H_4$$^a$/0.71 | Ph, $CH_3$/0.78 | toluene/20 | 110 °C, 3*h* | 58 |
| **2c** | {Mo}$H_4$$^a$/0.27 | $CH_3$, H/0.27 | benzene/27 | 20 °C, *hν*, 3 h | 36 |
| **2c** | {Mo}$H_4$$^a$/0.54 | $CH_3$, H/0.53 | toluene/20 | 110 °C, 5 h | 28 |
| **2d** | {Mo}$H_4$$^a$/0.72 | Ph, H/0.93 | benzene/70 | 20 °C, *hν*, 5 h | 44 |
| **2d** | {Mo}$H_4$$^a$/0.72 | Ph, H/1.02 | toluene/20 | 110 °C, 3 h | 40 |
| **2e** | {Mo}$H_4$$^a$/0.23 | $-(CH_2)_3-$/0.23 | benzene/23 | 20 °C, *hν*, 3 h | 52 |
| **2e** | {Mo}$H_4$$^a$/0.36 | $-(CH_2)_3-$/0.36 | toluene/18 | 110 °C, 5 h | 47 |
| **2f** | {Mo}$H_4$$^a$/0.43 | Ph, Ph/0.44 | benzene/30 | 20 °C, *hν*, 3 h | 36 |
| **2f** | {Mo}$H_4$$^a$/0.67 | Ph, Ph/0.73 | toluene/20 | 110 °C, 3 h | 37 |
| **3a** | {W}$(N_2)_2$$^b$/1.43 | $CH_3$, $CH_3$/2.90 | toluene/50 | 110 °C, 6 h | 11 |
| **3b** | {W}$(N_2)_2$$^b$/1.32 | Ph, $CH_3$/2.60 | benzene/50 | 50 °C, 6 h/80 °C, 0.5 h | 12 |

[a] {Mo}$H_4$ = [Mo$H_4$(dppe)$_2$]. [b] {W}$(N_2)_2$ = *trans*-[W$(N_2)_2$(dppe)$_2$].

**Table 2. IR and Analytical Data for [MH{N($R^1$)CO$R^2$-*N,O*}(dppe)$_2$] (M = Mo (2), W (3))**

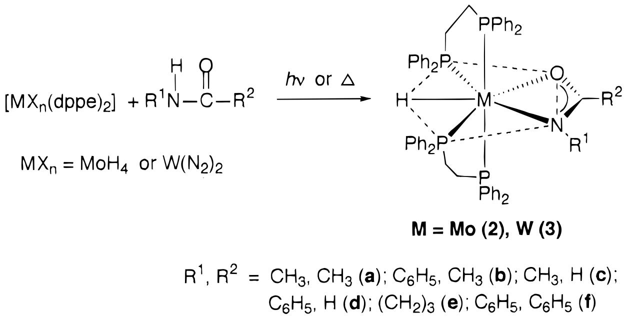
| compd | IR$^a$/cm$^{-1}$: ν(M−H) | IR$^a$/cm$^{-1}$: ν(C−O) | elemental anal.$^b$: C, % | elemental anal.$^b$: H, % | elemental anal.$^b$: N, % |
|---|---|---|---|---|---|
| **2a** | 1810 (vw) | 1560 (s) | 67.94 (68.32) | 5.81 (5.84) | 1.52 (1.45) |
| **3a** | 1893 (w) | 1580 (s) | *d* | | |
| **2b** | 1880 (vw) | 1530 (s) | 69.28 (70.10) | 6.22 (5.58) | 1.31 (1.36) |
| **3b** | 1951 (w) | 1580 (s) | *d* | | |
| **2c** | 1810 (w) | 1580 (s) | 67.38 (68.14) | 5.69 (5.61) | 1.12 (1.47) |
| **2d** | 1880 (w) | 1540 (s) | 68.81 (69.89) | 6.10 (5.47) | 1.19 (1.38) |
| **2e** | *c* | 1560 (s) | 69.59 (68.71) | 5.80 (5.77) | 2.02 (1.43) |
| **2f** | *c* | 1530 (s) | 70.82 (71.62) | 6.08 (5.46) | 1.50 (1.29) |

[a] KBr disk. [b] Calculated values in parentheses. [c] Not discernible. [d] Not performed.

The photochemical reaction of Mo$H_4$(dppe)$_2$ with *N*-alkylamides in benzene yielded [MoH{N($R^1$)CO$R^2$-*N,O*}(dppe)$_2$] as a result of the oxidative addition involving amide N−H bond cleavage. The closely related phenylamide complex [MoH{N(COH)$C_6H_5$}-(P$Me_3$)$_5$] has been synthesized by the reaction of phenyl isocyanate with [Mo$H_2$(P$Me_3$)$_5$],[6] but to our knowledge this is the first example of the direct oxidative addition of an amide N−H group to a group 6 transition-metal complex. Further, though 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,[7] there are only two precedents for the oxidative addition of simple amides.[4] Preparative, IR, and analytical data for the complexes are compiled in Tables 1 and 2.

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 26% (for **a**, photoreaction) to 58% (for **b**, thermal reaction), and the amount of $H_2$ evolved was estimated to be roughly twice the yield of **2**. In the thermal reaction of *N*-phenylformamide (**d**), the known *cis*-[Mo(CO)$_2$(dppe)$_2$] was observed in addition to **2d**, suggesting that the concurrent insertion reaction of **1** into the formyl C−H bond takes place. A larger ratio of **d**/**1** afforded a higher yield of this carbonyl complex, and the formation of aniline (14%) was observed when **d**/**1** was 1.31. The formation of a carbonyl complex by the reaction of a molybdenum(0) complex with *N,N*-dimethylformamide has been reported.[8]

**Scheme 1**



The analogous tungsten complex [WH{N($R^1$)CO$R^2$-*N,O*}(dppe)$_2$] (**3**) were prepared similarly, although *trans*-[W$(N_2)_2$(dppe)$_2$] was used instead of [W$H_4$(dppe)$_2$] because the dinitrogen complex is more reactive than the tetrahydride in the synthesis of hydrido(malonato)-tungsten complexes.[2e] However, the yield of complex **3** was less than that of **2**, possibly due to the low reactivity of *trans*-[W$(N_2)_2$(dppe)$_2$]. The related tungsten carbamoyl hydrido complex [WH{$\eta^2$-C(O)N$(CH_3)_2$}(dppe)$_2$], in which carbon and oxygen ligate to tungsten, was prepared from the reaction of *trans*-[W$(N_2)_2$(dppe)$_2$] with *N,N*-dimethylformamide.[9]

The reaction of **2** with acetic acid in benzene at ambient temperature gave *N*-phenylbenzamide and [MoH($O_2CCH_3$-*O,O′*)(dppe)$_2$], which has already been synthesized by the photoreaction of **1** with allyl acetate.[2c]

As shown in Table 2, the amide I band in the IR spectra of **2** and **3** shifts to lower frequency by about

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(6) Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 695.

(7) (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.; Matsuda, N.; Tamura, N.; Ito, T. *J. Chem. Soc., Dalton Trans.* **1991**, 1135.

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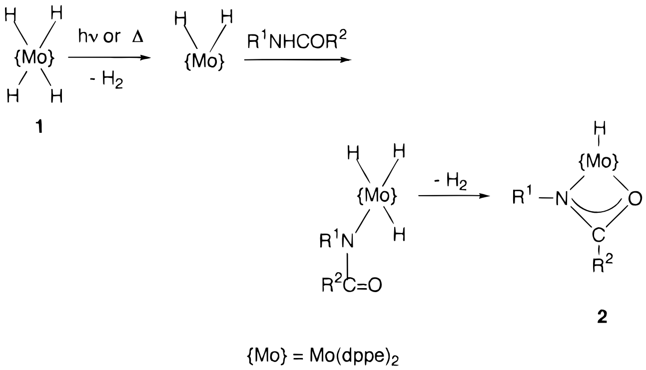
(9) (a) Ishida, T.; Mizobe, Y.; Tanase, T.; Hidai, M. *J. Organomet. Chem.* **1991**, *409*, 355. (b) Ishida, T.; Mizobe, Y.; Tanase, T.; Hidai, M. *Chem. Lett.* **1988**, 441.

**Table 3. $^1H$ and $^{13}C$ NMR Data for $[MH\{N(R^1)COR^2\text{-}N,O\}(dppe)_2]$ (M = Mo (2), W (3))**

| compd | $^1H$ NMR[a] | $^{13}C$ NMR[b] |
|---|---|---|
| **2a** | −4.92 (dddd, Mo*H*, $J_{HP}$ = 17.7, 35.4, 59.8, 79.3 Hz, 1H), 0.66 (s, $OCCH_3$, 3H), 1.85 (s, $NCH_3$, 3H) | 169.6 ($OCCH_3$), 34.3 ($NCH_3$), 18.9 ($OCCH_3$) |
| **3a** | −3.58 (m, W*H*, 1H), 0.62 (s, $OCCH_3$, 3H), 1.92 (s, $NCH_3$, 3H) | 168.7 ($OCCH_3$), 34.2 ($NCH_3$), 19.4 ($OCCH_3$) |
| **2b** | −5.46 (dddd, Mo*H*, $J_{HP}$ = 15.4, 29.1, 56.4, 90.6 Hz, 1H), 1.23 (s, $OCCH_3$, 3H), 7 (m, $NC_6H_5$, 5H) | 170.1 ($OCCH_3$), 21.7 ($OCCH_3$) |
| **3b** | −3.57 (dddd, W*H*, $J_{HP}$ = 12.0, 22.4, 54.8, 96.0 Hz, 1H), 1.23 (s, $OCCH_3$, 3H), 7 (m, $NC_6H_5$, 5H) | 169.5 ($OCCH_3$), 22.2 ($OCCH_3$) |
| **2c** | −5.11 (dddd, Mo*H*, $J_{HP}$ = 16.5, 36.6, 56.8, 81.8 Hz, 1H), 1.80 (s, $NCH_3$, 3H) | 161.1 (OCH) |
| **2d** | −5.53 (dddd, Mo*H*, $J_{HP}$ = 15.0, 26.5, 57.7, 90.6 Hz, 1H), 7.46 (s, OC*H*, 1H), 7 (m, $NC_6H_5$, 5H) | 162.2 (OCH) |
| **2e** | −5.05 (dddd, Mo*H*, $J_{HP}$ = 20.1, 32.4, 61.0, 76.9 Hz, 1H), 1−3 (m, $NCH_2CH_2CH_2$, 6H) | 175.9 ($NCOCH_2$) |
| **2f** | −4.58 (dddd, Mo*H*, $J_{HP}$ = 14.1, 38.9, 50.4, 89.3 Hz, 1H), 7 (m, $NC_6H_5$, $OCC_6H_5$, 10H) | 165.2 ($OCC_6H_5$) |

[a] Conditions: $C_6D_6$, in ppm, 293 K, 270 MHz, TMS reference. [b] Conditions: $C_6D_6$, in ppm, 293 K, 67.8 MHz, TMS reference.

**Scheme 2**



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, imply N−H bond cleavage and a mode of coordination in which amide forms a four-membered chelate ring, as shown above. The Mo−H stretching bands of complexes **2** were observed at 1810−1880 $cm^{-1}$, values typical of ν(Mo−H) for $[MoHX(dppe)_2]$-type complexes.[2] In the $^1H$ NMR spectra of complex **2** (Table 3), hydride signals appeared at around δ −5, with a multiplicity corresponding to an ACKMX spin system. These signals are consistent with the four isolated signals in $^{31}P\{^1H\}$ NMR spectra, each being split into a doublet of doublets of doublets (ACKM spin system). In the $^{13}C$ NMR spectra of **2**, the resonances attributable to the carbonyl carbons were observed in the range δ 165−175.

A possible mechanism for the formation of complex **2** is illustrated in Scheme 2.

The mechanism involves the initial evolution of 1 mol of $H_2$ from the molybdenum complex upon irradiation or heating to generate the 16-electron reactive intermediate $[MoH_2(dppe)_2]$, followed by oxidative addition of a N−H bond to molybdenum to give a trihydrido species, which subsequently rearranges to the final product with evolution of a further 1 mol of $H_2$. The photoreaction of **1** is known to give the coordinatively unsaturated 14-electron species with evolution of 2 mol of $H_2$, and a pathway which involves direct N−H bond oxidative addition to this intermediary 14-electron $Mo(dppe)_2$ is also possible. Similar reaction paths involving C−O, C−H, or N−H bond cleavage have been considered for the reaction of **1** with allyl carboxylates and allyl alkyl carbonates, alkyl malonates, or cyclic imides, respectively.[2] An alternative pathway which involves initial protonolysis of **1** with amide may also be possible.[4a] However, this appears to be less likely for the following reasons: (a) the acidity of the amides used here is not high enough and (b) the amide concentration influences neither the reaction rate nor the yield of product.

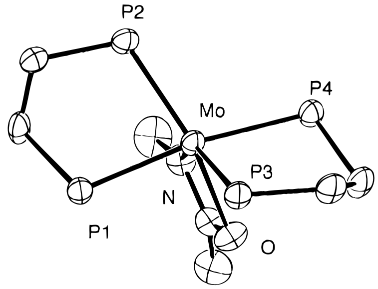


**Figure 1.** ORTEP drawing of the molecular structure of **2a**, with the atom-numbering scheme.

**Table 4. Interatomic Distances (Å) and Angles (deg) for 2a**

| | | | |
|---|---|---|---|
| Distances | | | |
| 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) |
| Angles | | | |
| 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) |

*trans*-$[W(N_2)_2(dppe)_2]$ affords a coordinatively unsaturated reactive W(0) dinitrogen intermediate in a similar manner as **1**, and it supposedly adds the amide N−H bond to give **3**.

**Crystal Structure Determination of Complex 2a.** Complex **2a** has been fully characterized by an X-ray diffraction study. Details of the crystal structure determination have already been published.[5] Some important features of the structure will be described here (see Figure 1 and Table 4).

The complex may be regarded as having a distorted-pentagonal-bipyramidal structure with two phosphorus atoms of dppe, the nitrogen and the oxygen atoms of the amide, and a hydride comprising the equatorial plane. 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 and confirms the planarity of the $MoN\{(COCH_3)CH_3\}$ moiety. The C−O bond distance in **2a** is 1.29(2) Å, which is significantly longer than the corresponding bond distance of free *N*-methylacetamide (1.225 Å), and the C(1)−N bond distance is 1.35(2) Å, which is slightly shorter than that of the free amide (1.386 Å). The Mo−N distance of 2.25(1) Å is slightly shorter than the Mo−N σ-bond distance (2.32 Å) reported for $[Mo(CO)_3(\text{diethylenetriamine})]$,[10] and the

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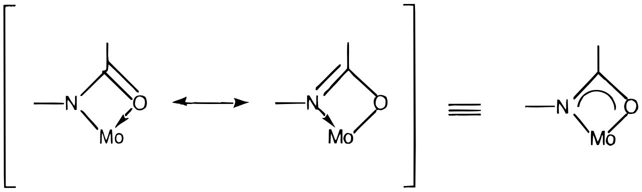
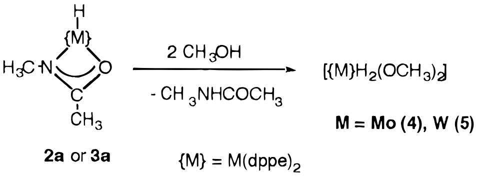
[10] Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *4*, 314.

Mo−O distance (2.24(1) Å) is also shorter than those of the related complex $[MoH(O_2COEt\text{-}O,O')(dppe)_2]$ (2.271(2) and 2.333(3) Å).[2b] These data and the long C−O distance and the short Mo−N distance in **2a** suggest the following resonance forms of the $\eta^2$-amide:



**Reactions of 2a and 3a with ROH (R = Me, Et, Pr$^i$).** In the course of working up complexes **2** and **3**, we observed that they were highly susceptible to electrophiles such as alcohols, suggesting that they can be used to synthesize a variety of new molybdenum or tungsten organometallic complexes. In addition to their novel reactivity, the potential of metal alkoxides in catalysis[11] led us to study in detail the reaction of **2a** or **3a** with a variety of alcohols.

When **2a** was treated with methanol at ambient temperature for 12 h, the moderately air-sensitive yellowish dihydridodimethoxomolybdenum complex $[MoH_2(OMe)_2(dppe)_2]$ (**4**) was formed quantitatively, together with the corresponding organic amide. Since the tetrahydrido complex **1** does not react with methanol, the amide of **2a** seems to play a crucial role in the reaction. Treatment of the tungsten complex **3a** with methanol gave the analogous $[WH_2(OMe)_2(dppe)_2]$ (**5**) in 34% yield.



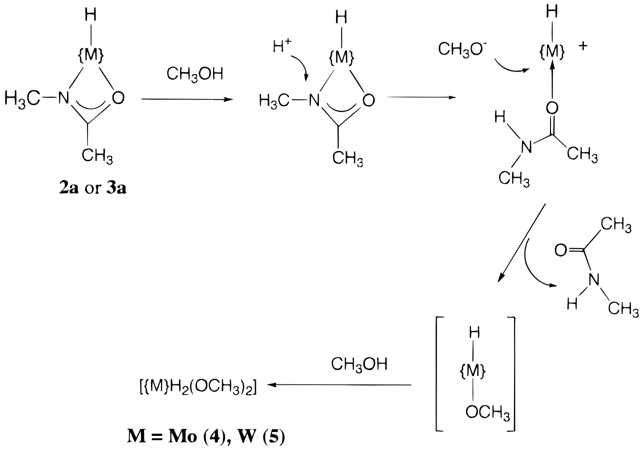
(1)

We observed that **4** gradually changes into the formaldehyde complex $[MoH_2(\eta^2\text{-}CH_2O)(dppe)_2]$[12] in benzene, the conversion being significantly retarded in toluene. A related $\eta^2$-formaldehyde complex of tungsten $[W(PMe_3)_4(\eta^2\text{-}CH_2O)H_2]$ has been prepared by Green and co-workers.[13] At 180 °C, **4** decomposes quantitatively to *trans*-$[Mo(CO)_2(dppe)_2]$.[14]

$$\underset{\mathbf{4}}{[MoH_2(OMe)_2(dppe)_2]} \xrightarrow[-H_2]{\Delta} trans\text{-}[Mo(CO)_2(dppe)_2] \qquad (2)$$

The elemental analysis of complex **4** supports the formulation given. The hydride resonances are coupled magnetically to the phosphorus atoms, and quintet signals appear at $\delta$ −2.29 ($^2J_{HP}$ = 34.6 Hz) for **4**. This coupling constant is much smaller than that of $[MoH_2Cl_2(dppe)_2]$ ($^2J_{HP}$ = 48 Hz).[15] The quintet hydride resonance of complex **4** indicates that the four phosphorus atoms are equivalent at this temperature due to fluxionality.[16] Similar behavior is sometimes observed for related eight-coordinate complexes.[17] The $^1$H NMR spectrum of tungsten complex **5** displays a broadened multiplet resonance at around $\delta$ −1.1 assignable to the hydride, at a lower field than that of **4** by about 1.2 ppm. A similar observation was made for the amido complexes, as described previously. The NMR data support a *cis* arrangement of the hydrides in complex **4**, which was substantiated by the similar features observed in analogous hydrido catecholato complexes, whose structures were fully confirmed by single-crystal X-ray analyses (*vide infra*).

**Scheme 3**



One possible pathway for the formation of complex **4** is outlined in Scheme 3.

The first step is replacement of amide by methanol, which acts as a proton source, followed by direct oxidative addition of an O−H bond of another molecule of MeOH to the intermediate 16-electron species. There are a few examples of the oxidative addition of alcohols involving O−H cleavage.[18] It is noteworthy that the reaction of complex **2a** with an acid as weak as methanol proceeds at ambient temperature without any forced activation, in view of the fact that irradiation or heating is necessary for the tetrahydride **1** to generate the coordinatively unsaturated reactive intermediate $[MoH_2(dppe)_2]$.[19] *trans*-$[Mo(N_2)_2(dppe)_2]$[20] is also known to be reactive but does not react with methanol at ambient temperature.

The addition of acetic acid (1 equiv) to a toluene solution of **4** resulted in the formation of a seven-coordinate pentagonal-bipyramidal (acetato)hydrido-

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[11] (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 471−474. (b) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

[12] This complex was identified by an NMR tube reaction in $C_6D_6$. $[MoH_2(OCH_2)(dppe)_2]$: $^1$H NMR (270 MHz) $\delta$ −2.99 (qnt, $^2J_{HP}$ = 34.6 Hz, 2H, Mo−*H*), 2.10 (br, 2H, O=C*H*$_2$); $^{13}$C NMR (78.8 MHz) $\delta$ 64.1 (t, O=$CH_2$, $J_{CH}$ = 167.2 Hz); $^{31}P\{^1H\}$ NMR (36.5 MHz, chemical shifts are in ppm with downfield positive from the external benzene solution of $PPh_3$) 71.3 (br, s); $^{13}C\{^1$H off-resonance decoupled$\}$ NMR 64.1 (t, $J_{CH}$ = 167.2 Hz, O=$CH_2$).

[13] Green, M. L. H.; Parkin, G.; Moynihan, K.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1540.

[14] (a) Holden, L. K.; Mawby, A. H.; Smith, D. C.; Whyman, R. *J. Organomet. Chem.* **1973**, *55*, 343. (b) Chatt, J.; Watson, H. R. *J. Chem. Soc.* **1961**, 4980.

[15] Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074.

[16] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 1322.

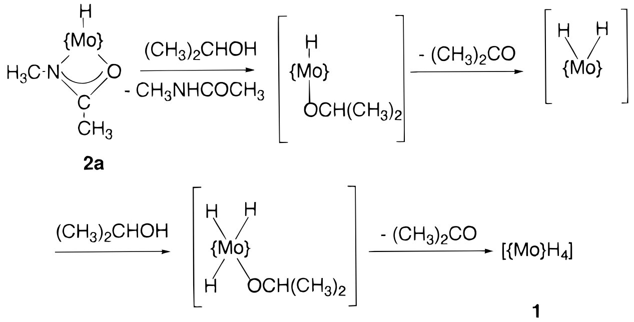
[17] See for example: Hills, A.; Hughes, D. L.; Kashef, N.; Lemos, M. A. N. D. A.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1992**, 1775.

[18] See for example: Osakada, K.; Ohshiro, K.; Yamamoto, A. *Organometallics* **1991**, *10*, 404.

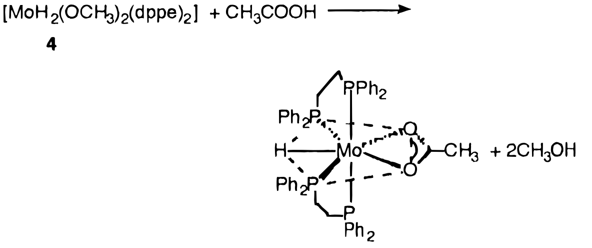
[19] Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; p 278.

[20] Hidai, M.; Tominari, K.; Uchida, Y. *J. Am. Chem. Soc.* **1972**, *94*, 110.

**Scheme 4**

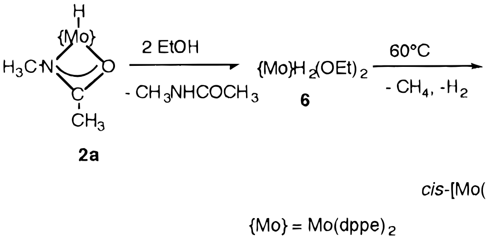


molybdenum complex with evolution of methanol (1.84 mol/mol of **4**). This complex has already been synthesized by the photoreaction of **1** with allyl acetate.[2b,c]



(3)

Complex **2a** reacts with ethanol, as it does with methanol, to give the corresponding diethoxodihydridomolybdenum complex **6**. Complex **6** is much more unstable and decomposes in solution at slightly elevated temperatures to give the carbonyl complex *cis*-[Mo(CO)$_2$(dppe)$_2$][14] with evolution of methane and dihydrogen.



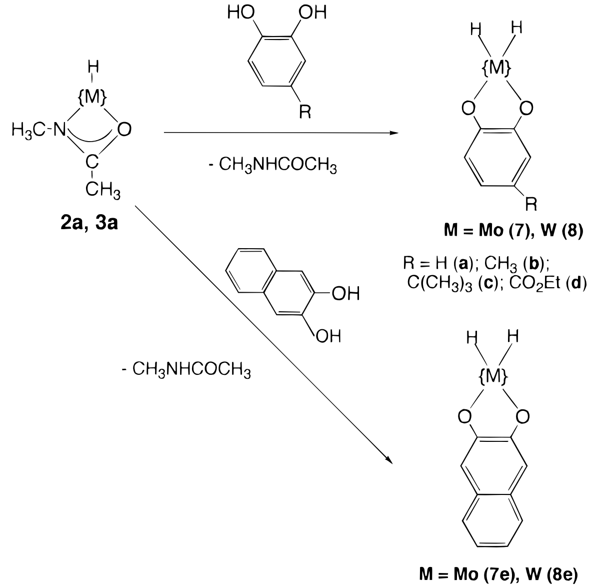
(4)

Repeated attempts to isolate **6** in an analytically pure form were unsuccessful due to its extreme lability.

The tetrahydrido complex **1** was formed quantitatively by treatment of **2a** with 2-propanol at ambient temperature. Formation of acetone was observed by gas chromatography in this reaction, suggesting that the reaction proceeds via a $\beta$-hydrogen elimination process from an isopropoxo intermediate, as shown in Scheme 4.[21]

In contrast, complex **2a** does not react with sterically hindered alcohols such as pinacol and 2-methyl-2-propanol even under prolonged heating in refluxing toluene. dppe, which bears sterically demanding Ph substituents, may prevent the approach of bulky alcohols to the molybdenum atom. These results are in contrast with those of Richards *et al.*, who reported that reaction of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] with the bulky thiols RSH gives the monohydride complexes [MoH(SR)(dppe)$_2$].[22]

**Scheme 5**



Treatment of **2a** with phenol in toluene at ambient temperature gave hydride-free product. However, it could not be characterized owing to its low solubility toward common organic solvents.

**Reactions of 2a and 3a with Catechol Derivatives.** Complex **2a** reacts with the series of catechol derivatives to give the corresponding chelated catecholato-*O,O′* hydrido complexes **7** in good yield. Although molybdenum catecholate complexes containing oxo ligands are well-known, the analogous complex with a tertiary phosphine is relatively rare.[23,24]

Treatment of **3a** similarly results in the formation of tungsten complexes **8**. The thermal stabilities of these complexes are much higher than those of the corresponding aliphatic dialkoxo complexes, probably due to the absence of the $\beta$-hydrogen atoms in the catecholates. Preparative, analytical, and selected spectroscopic data for the complexes are compiled in Tables 5−7, respectively.

Relatively strong absorption bands at 1256−1293 cm$^{-1}$ ($\nu$(C−O)) in **7** and **8** are observed, typical of catecholato complexes.[25] The anomalously low-field shift of hydride signals in the tungsten complex **8** ($\delta$ 0.14−0.23) is noteworthy. A comparison of the $^1$H NMR spectra of complexes **7a**−**c** reveals substantial similarities in the positions, multiplicities, and coupling constants of the hydride resonances, suggesting that substituents on the aromatic ring of catechol do not influence profoundly the electronic state of the central metal. In contrast to **7a**−**c**, the hydride region of **7d** at 293 K displays a triplet of triplets resonance ($^2J_{HP}$ = 26.5 and 70.2 Hz), which collapses at 323 K into a quintet resonance ($^2J_{HP}$ = 48.0 Hz). In contrast to **4**, the $^{31}$P NMR spectrum of **7a** contains two resonances of equal intensity at $\delta$ 36.4 and 76.3. The chelating catecholate appears to prevent the fluxional behavior

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[21] Bernard, K. A.; Rees, W. M.; Atwood, J. D. *Organometallics* **1986**, *5*, 390.

[22] Richard, A. H.; Hughes, D. L.; Richards, R. L.; Shortman, C. *J. Chem. Soc., Dalton Trans.* **1987**, 1115.

[23] For reviews see: Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

[24] (a) Atovmyan, L. O.; Tkachev, V. V.; Shishova, T. G. *Dokl. Akad. Nauk SSSR* **1972**, 205. (b) Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 1616. (c) Tkachev, V. V.; Atovmyan, L. O. *Koord. Khim.* **1975**, *1*, 845.

[25] Griffith, W. P.; Pumphrey, C. A.; Rainey, T.-A. *J. Chem. Soc., Dalton Trans.* **1986**, 1125.

**Table 5. Preparation of [$MH_2$(Cat)(dppe)$_2$] (Cat = $C_6H_4O_2$ (a), 4-Me$C_6H_3O_2$ (b), 4-Bu$^t$$C_6H_3O_2$ (c), 4-$CO_2$Et$C_6H_3O_2$ (d), and $C_{10}H_6O_2$ (e))**

| compd | catechol/amt, mmol | amt of complex **2a** or **3a**, mmol | amt of toluene, mL | time, h | yield, % |
|---|---|---|---|---|---|
| **7a** (M = Mo) | $C_6H_4(OH)_2$/0.348 | 0.225 | 25 | 5 | 80 |
| **8a** (M = W) | $C_6H_4(OH)_2$/0.144 | 0.133 | 15 | 8 | 47 |
| **7b** (M = Mo) | 4-Me$C_6H_3(OH)_2$/0.196 | 0.193 | 20 | 12 | 69 |
| **8b** (M = W) | 4-Me$C_6H_3(OH)_2$/0.147 | 0.129 | 13 | 48 | 44 |
| **7c** (M = Mo) | 4-Bu$^t$$C_6H_3(OH)_2$/0.285 | 0.150 | 15 | 12 | 79 |
| **8c** (M = W) | 4-Bu$^t$$C_6H_3(OH)_2$/0.1.72 | 0.160 | 16 | 48 | 65 |
| **7d** (M = Mo) | 4-$CO_2$Et$C_6H_3(OH)_2$/0.285 | 0.137 | 15 | 12 | 47 |
| **8d** (M = W) | 4-$CO_2$Et$C_6H_3(OH)_2$/0.154 | 0.151 | 20 | 48 | 53 |
| **7e** (M = Mo) | $C_{10}H_6(OH)_2$/0.214 | 0.202 | 20 | 12 | 83 |
| **8e** (M = W) | $C_{10}H_6(OH)_2$/0.142 | 0.124 | 13 | 8 | 44 |

**Table 6. IR and Analytical Data for [$MoH_2$(Cat)(dppe)$_2$] (M = Mo (7), W (8))**

| | IR[a]/cm$^{-1}$ | | elemental anal.[b] | |
|---|---|---|---|---|
| compd | $\nu$(M−H) | $\nu$(C−O) | C, % | H, % |
| **7a** | 1841 (m) | 1263 (s) | 69.61 (69.46) | 5.43 (5.43) |
| **8a** | 1877 (m) | 1260 (s) | 63.63 (63.86) | 5.04 (4.99) |
| **7b** | 1823 (m) | 1256 (s), 1271 (s) | 70.32 (69.69) | 5.92 (5.55) |
| **8b** | 1882 (m) | 1257 (s), 1273 (s) | 64.67 (64.14) | 5.55 (5.11) |
| **7c** | 1841 (m) | 1264 (s), 1280 (s) | 70.80 (70.32) | 6.27 (5.90) |
| **8c** | 1882 (m) | 1265 (s), 1280 (s) | 64.87 (64.93) | 5.60 (5.45) |
| **7d** | 1828 (m) | 1275 (s), 1293 (s) | 70.80 (70.32) | 6.27 (5.90) |
| **8d** | 1889 (m) | 1276 (s), 1293 (s) | *c* | *c* |
| **7e** | 1838 (m) | 1284 (s) | 70.64 (70.72) | 5.27 (5.36) |
| **8e** | 1884 (m) | 1286 (s) | *c* | *c* |

[a] KBr disk. [b] Calculated values in parentheses. [c] Not performed.

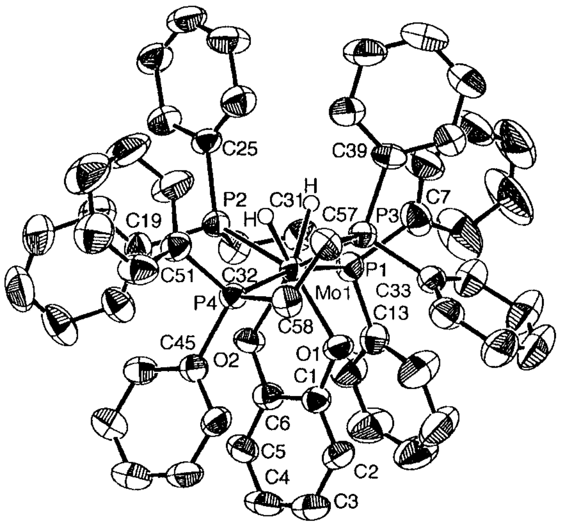

**Figure 2.** ORTEP drawing of the molecular structure of **7a**, with the atom-numbering scheme.

of the molecule, although the hydride signal is a quasi-quintet. The hydride ligands seem to exchange their positions within the complex fast enough to be equivalent on the NMR time scale.

Formation of **7** may be accounted for by a reaction path similar to that considered for the aliphatic alcohols (Scheme 3).

**Crystal Structure Determination of Complexes 7a,d and 8a.** Good prismatic single crystals of the catecholato complexes **7a,d** and **8a** suitable for X-ray analysis were obtained by crystallization from toluene−hexane. A summary of the crystallographic data is given in Table 8, and the selected bond lengths and angles are given in Tables 9−11. ORTEP drawings are shown in Figures 2−4. The molecular structures of **7a,d** and **8a**, which are monomeric in the solid state, are well-resolved, and the hydride atoms are clearly identified. Both complexes **7a** and **8a** are chiral, and the correct enantiomorphs were determined by *R* indices (see Table 8).

The crystals belong to the orthorhombic (**7a, 8a**) or to the monoclinic (**7d**) system. The complexes possess distorted-dodecahedral coordination, with the two P atoms and the catecholate in the pseudo-equatorial basal plane and the hydrides and the other two P atoms in the apical sites as shown in Figures 2−4. A number of related hydride complexes with the phosphines have a dodecahedral structure, *e.g.* [$MoH_3$(C≡CBu$^t$)(dppe)$_2$][26] and [$WH_2Cl_2(PMe_2Ph)_4$].[27] The catecholates form symmetrical five-membered chelate rings.

The mean Mo−P distances are 2.480 and 2.484 Å for **7a** and **7d**, respectively, and these distances are close to that found in **1** (2.420 Å).[28]

The bond distances and angles of the molybdenum−catecholato moiety are as expected. The mean Mo−O bond distances are 2.130 and 2.132 Å for **7a** and **7d**, respectively, which are a little longer than that of complex [$MoO_2(O_2C_6H_4)_2$]$^{2-}$ by ca. 0.03 Å,[24c] and these values indicate that a strong electron-withdrawing substituent such as the ethoxycarbonyl group does not influence the length of the Mo−O bond. The mean W−O distance of 2.124 Å in **8a** is very similar to the W−O distance found in [$WH_3(OPh)(PMe_3)_4$] (2.129 Å).[29] The C−O distances of the ligands, which average 1.34 Å in all of the complexes, are typical of chelated fully reduced catecholates, which have C−O lengths of about 1.35 Å with little variation.[30] The C−C bond distances of the catecholate ring average 1.391 Å in **7a** and 1.390 Å in **7d**, which are also comparable to the C−C distances in typical molybdenum−catecholate complexes.[24a,b] The bite angles at the metal formed by the chelating ligand are 76.2° in **7a** and 76.0° in **7d**, and they compare well with the values found in [{$Mo(O_2C_6Cl_4)_3$}$_2$] and [$Mo(O_2C_{14}H_8)_3$] (75−77°).[30b,31] The bite angle O−W−O in **8a** is 75.7°, and this value is slightly smaller than that of **7a**.

In conclusion, the results obtained show that photochemical or thermal reaction of [$MoH_4$(dppe)$_2$] or *trans*-[$W(N_2)_2$(dppe)$_2$] with *N*-alkylamides $R^1$NHCOR$^2$ gives

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(31) Pierpont, C. G.; Buchanan, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 4912.

**Table 7. $^1$H and $^{13}$C NMR Data for [$MH_2$(Cat)(dppe)$_2$] (M = Mo (7), W (8))**

| compd | $^1$H NMR[a] | $^{13}$C NMR[b] |
|---|---|---|
| **7a** | −2.54 (qnt, Mo*H*, $J_{HP}$ = 48.7 Hz, 2H), 6.33 (m, $C_6H_4$, 4H) | 161.9, 114.6, 114.9 ($C_6H_4$) |
| **8a** | 0.23 (qnt, W*H*, $J_{HP}$ = 42.0 Hz, 2H), 6.33 (m, $C_6H_4$, 4H) | 161.0, 114.7, 115.0 ($C_6H_4$) |
| **7b** | −2.60 (qnt, Mo*H*, $J_{HP}$ = 48.5 Hz, 2H), 5.90−6.20 ($C_6H_3$, 3H), 2.31 (s, $C_6H_3CH_3$, 3H) | 161.7, 159.7, 122.1, 116.1, 114.7, 113.9 ($C_6H_3$), 21.5 ($C_6H_5CH_3$) |
| **8b** | 0.16 (qnt, W*H*, $J_{HP}$ = 41.0 Hz, 2H), 5.90−6.20 ($C_6H_3$, 3H), 2.32 (s, $C_6H_3CH_3$, 3H) | 160.9, 158.7, 122.3, 116.1, 114.8, 114.1 ($C_6H_3$), 21.3 ($C_6H_3CH_3$) |
| **7c** | −2.59 (qnt, Mo*H*, $J_{HP}$ = 48.6 Hz, 2H), 6.20 (m, $C_6H_3$, 3H), 1.47 (s, $C(CH_3)_3$, 9H) | 161.0, 159.3, 135.9, 116.6, 113.6, 112.1 ($C_6H_3$), 33.9 ($C(CH_3)_3$), 32.8 ($C(CH_3)_3$) |
| **8c** | 0.16 (qnt, W*H*, $J_{HP}$ = 41.2 Hz, 2H), 6.20 (m, $C_6H_3$, 3H), 1.48 (s, $C(CH_3)_3$, 9H) | 160.1, 158.5, 136.0, 113.7, 112.1, 110.7 ($C_6H_3$), 33.8 ($C(CH_3)_3$), 32.8 ($C(CH_3)_3$) |
| **7d** | −2.66 (tt, Mo*H*, $J_{HP}$ = 26.5, 70.2 Hz, 2H), 1.18 (t, $OCH_2CH_3$, *J* = 7.3 Hz, 3H), 4.4 (m, $OCH_2CH_3$, 2H) | 168.3, 161.5, 119.2, 116.3, 116.0, 114.0 ($C_6H_3$), 161.4 (*C*O), 59.1 ($OCH_2CH_3$), 15.0 ($OCH_2CH_3$) |
| **8d** | 0.2 (br, W*H*, 2H), 1.12 (t, $OCH_2CH_3$, *J* = 7.3 Hz, 3H), 4.4 (m, $OCH_2CH_3$, 2H) | 168.1, 166.8, 119.1, 116.4, 116.0, 114.1 ($C_6H_3$), 160.7 (*C*O), 59.1 ($OCH_2CH_3$), 15.0 ($OCH_2CH_3$) |
| **7e** | −2.67 (qnt, Mo*H*, $J_{HP}$ = 49.2 Hz, 2H) | 163.0, 125.7, 124.3, 119.4, 108.5 ($C_{10}H_6$) |
| **8e** | 0.14 (qnt, W*H*, $J_{HP}$ = 41.2 Hz, 2H) | 163.0, 125.7, 124.4, 119.7, 108.7 ($C_{10}H_6$) |

[a] Conditions: $C_6D_6$, in ppm, 293 K, 270 MHz, TMS reference. [b] Conditions: $C_6D_6$, in ppm, 293 K, 67.8 MHz, TMS reference.

**Table 8. Crystallographic Data for 7a,d and 8a**

| | $C_{58}H_{54}O_2P_4Mo$ (**7a**) | $C_{61}H_{58}O_4P_4Mo$ (**7d**) | $C_{58}H_{54}O_2P_4W$ (**8a**) |
|---|---|---|---|
| fw | 1002.90 | 1074.96 | 1090.81 |
| cryst syst | orthorhombic | monoclinic | orthorhombic |
| space group | $P2_12_12_1$ (No. 19) | $P2_1/n$ (No. 14) | $P2_12_12_1$ (No. 19) |
| *a*, Å | 20.544(5) | 12.23(1) | 20.469(3) |
| *b*, Å | 22.884(4) | 27.37(1) | 22.900(2) |
| *c*, Å | 10.741(6) | 16.18(1) | 10.752(3) |
| *V*, Å$^3$ | 5049(2) | 5402(6) | 5039(1) |
| *Z* | 4 | 4 | 4 |
| $\mu$, cm$^{-1}$ | 4.28 | 4.07 | 24.63 |
| *F*(000) | 2080.00 | 2232.00 | 2208.00 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.319 | 1.322 | 1.437 |
| cryst size, mm | 0.35 × 0.30 × 0.24 | 0.50 × 0.20 × 0.20 | 0.40 × 0.30 × 0.26 |
| 2$\theta$ range, deg | 25.1−29.9 | 29.6−29.9 | 29.8−30.0 |
| scan rate, deg min$^{-1}$ | 16.0 | 32, 16, 8 | 16.0 |
| no. of rflns measd | 4979 | 10220 | 4970 |
| no. of obsd reflns ($I > 3.00\sigma(I)$) | 4046 | 5153 | 4399 |
| final *R* indices[a,b] | R1 = 0.031, wR2 = 0.043 | R1 = 0.046, wR2 = 0.063 | R1 = 0.027, wR2 = 0.034 |
| *R* indices (all data) | R1 = 0.034, wR2 = 0.049 | | R1 = 0.055, wR2 = 0.081 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

**Table 9. Interatomic Distances (Å) and Angles (deg) for 7a**

Distances

| | | | |
|---|---|---|---|
| Mo(1)−P(1) | 2.489(1) | Mo(1)−P(2) | 2.452(1) |
| Mo(1)−P(3) | 2.466(1) | Mo(1)−P(4) | 2.511(2) |
| Mo(1)−O(1) | 2.126(3) | Mo(1)−O(2) | 2.134(4) |
| O(1)−C(1) | 1.336(6) | O(2)−C(6) | 1.345(6) |
| C(1)−C(2) | 1.377(7) | C(2)−C(3) | 1.401(9) |
| C(3)−C(4) | 1.376(10) | C(4)−C(5) | 1.389(8) |
| C(5)−C(6) | 1.393(8) | C(1)−C(6) | 1.410(8) |
| Mo(1)−H(1Ma) | 1.65 | Mo(1)−H(1Mb) | 1.51 |

Angles

| | | | |
|---|---|---|---|
| O(1)−Mo(1)−O(2) | 76.2(1) | O(1)−Mo(1)−P(1) | 91.8(1) |
| O(1)−Mo(1)−P(2) | 148.4(1) | O(1)−Mo(1)−P(3) | 73.9(1) |
| P(1)−Mo(1)−P(2) | 81.53(5) | P(3)−Mo(1)−P(4) | 80.78(5) |
| C(1)−C(2)−C(3) | 120.0(6) | O(1)−C(1)−C(6) | 116.9(5) |
| H(1Ma)−Mo(1)−H(1Mb) | 68.8 | | |

**Table 10. Interatomic Distances (Å) and Angles (deg) for 7d**

Distances

| | | | |
|---|---|---|---|
| Mo(1)−P(1) | 2.468(2) | Mo(1)−P(2) | 2.506(2) |
| Mo(1)−P(3) | 2.508(2) | Mo(1)−P(4) | 2.454(2) |
| Mo(1)−O(1) | 2.127(4) | Mo(1)−O(2) | 2.137(4) |
| O(1)−C(53) | 1.326(7) | O(2)−C(54) | 1.351(8) |
| C(53)−C(54) | 1.391(10) | C(54)−C(55) | 1.401(10) |
| C(55)−C(56) | 1.46(1) | C(56)−C(57) | 1.34(1) |
| C(57)−C(58) | 1.34(1) | C(53)−C(58) | 1.408(9) |
| C(56)−C(59) | 1.45(1) | C(59)−O(3) | 1.29(1) |
| C(59)−O(4) | 1.31(1) | C(60)−O(4) | 1.50(2) |
| Mo(1)−H(0a) | 1.54 | Mo(1)−H(0b) | 1.64 |

Angles

| | | | |
|---|---|---|---|
| O(1)−Mo(1)−O(2) | 76.0(2) | P(2)−Mo(1)−O(2) | 89.1(1) |
| P(1)−Mo(1)−O(2) | 150.5(1) | P(4)−Mo(1)−O(2) | 73.6(1) |
| P(1)−Mo(1)−P(2) | 80.57(5) | P(3)−Mo(1)−P(4) | 80.96(7) |
| C(53)−C(58)−C(57) | 121.6(9) | O(1)−C(53)−C(54) | 117.3(6) |
| O(3)−C(59)−C(56) | 121(1) | H(0a)−Mo(1)−H(0b) | 64.5 |

the seven-coordinate complexes [MH{N($R^1$)CO$R^2$-*N*,*O*}-(dppe)$_2$] (M = Mo (**2**), W (**3**)) as a result of oxidative addition involving amide N−H bond cleavage, and the resulting highly reactive *N*-acylamido complexes **2a** and **3a** react readily with alcohols and catechols to give alkoxo− and catecholato−hydrido complexes. The reactions apparently proceed via a coordinatively unsaturated 16e intermediate, which is formed upon release of the *N*-acylamide. The intriguing chemistries of complexes **2** and **3** are being further developed in our laboratories with special reference to the synthesis of novel molybdenum and tungsten complexes. Further studies on the reactivity of dihydrido dimethoxo complexes such as [$MH_2(OMe)_2$(dppe)$_2$] are also in progress.

## Experimental Section

**General Comments.** 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 *trans*-[$W(N_2)_2$-(dppe)$_2$] were prepared by published procedures.[3,32] UV−

**Table 11. Interatomic Distances (Å) and Angles (deg) for 8a**

| | | | |
|---|---|---|---|
| Distances | | | |
| W(1)−P(1) | 2.482(2) | W(1)−P(2) | 2.452(2) |
| W(1)−P(3) | 2.462(2) | W(1)−P(4) | 2.499(2) |
| W(1)−O(1) | 2.116(4) | W(1)−O(2) | 2.132(5) |
| O(1)−C(53) | 1.348(8) | O(2)−C(58) | 1.332(8) |
| C(53)−C(54) | 1.378(10) | C(54)−C(55) | 1.41(1) |
| C(55)−C(56) | 1.37(1) | C(56)−C(57) | 1.39(1) |
| C(57)−C(58) | 1.39(1) | C(53)−C(58) | 1.42(1) |
| W(1)−H(58) | 1.70 | W(1)−H(59) | 1.80 |
| Angles | | | |
| O(1)−W(1)−O(2) | 75.7(2) | P(1)−W(1)−O(1) | 90.9(1) |
| P(2)−W(1)−O(1) | 147.7(1) | P(3)−W(1)−O(1) | 73.5(1) |
| P(1)−W(1)−P(2) | 81.36(6) | P(3)−W(1)−P(4) | 80.59(6) |
| C(56)−C(57)−C(58) | 120.2(8) | O(1)−C(53)−C(58) | 116.2(6) |
| H(58)−W(1)−H(59) | 70.0 | | |

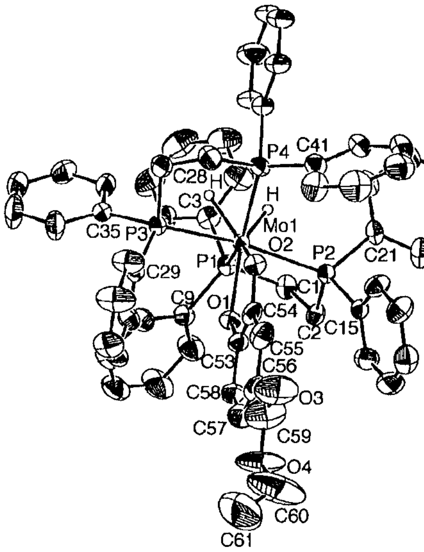

**Figure 3.** ORTEP drawing of the molecular structure of **7d**, with the atom-numbering scheme.

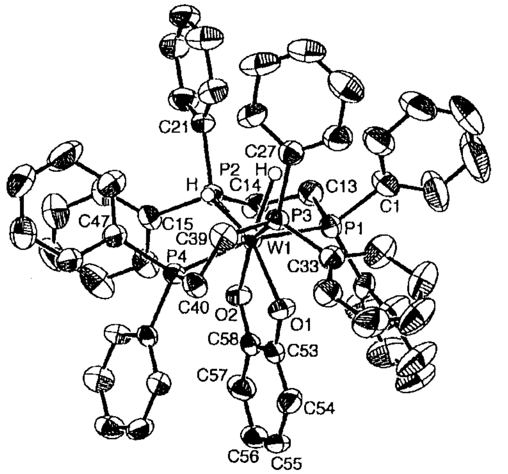

**Figure 4.** ORTEP drawing of the molecular structure of **8a**, with the atom-numbering scheme.

visible light irradiation was performed by using a Riko 400-W high-pressure mercury lamp and a Pyrex glass filter.

**Synthesis of the *N*-Acylamido Complexes.** A typical procedure is as follows. A Pyrex Schlenk flask containing a yellow solution of complex **1** (0.24 g, 0.27 mmol) and $CH_3NHCOCH_3$ (21 μL, 0.27 mmol) dissolved in benzene (27 mL) was irradiated by light under vacuum at ambient temperature for 3 h to give a red solution. The release of $H_2$ (0.77 mol per mol of **1**) was observed. Removal of the solvent from the solution by a trap-to-trap method left a reddish brown solid that was dissolved in benzene (3 mL). To the resulting solution was added hexane (15 mL), and cooling the solution at 6 °C for 12 h gave a yellow precipitate of unreacted **1**. From the supernatant solution, the solvent was evaporated to dryness under reduced pressure, and washing the residue with hexane gave **2a** in 26% yield. Similar results were obtained when **1** reacted with $CH_3NHCOCH_3$ at 110 °C in toluene for 5 h. These procedures are also applicable to the syntheses of the other molybdenum or the tungsten complexes. Experiments listed in Table 1 were carried out under essentially the same conditions. Complexes **2** and **3** are soluble in benzene, toluene, THF, and diethyl ether and are moderately stable to air in the solid state but deteriorate rapidly with air in solution. Analytical data and spectroscopic properties of complexes **2** and **3** are given in Tables 2 and 3.

**Synthesis of the Alkoxo Complexes. [MoH$_2$(OMe)$_2$(dppe)$_2$] (4).** A suspension of **2a** (0.3057 g, 0.45 mmol) in 20 mL of methanol was stirred at ambient temperature for 12 h, during which time the dark red complex **2a** changed to a yellowish powder. The supernatant solution was removed with a bridge filter, and the residue thus obtained was washed successively with methanol, hexane, and diethyl ether. The resulting yellowish solid was dried under vacuum. Anal. Found: C, 67.07; H, 5.93. Calcd for $C_{54}H_{56}O_2P_4$: C, 67.78; H, 5.90. IR (KBr disk): $\nu$(*methyl* C−H) 2805 cm$^{-1}$, $\nu$(Mo−H) 1800 cm$^{-1}$, $\nu$(C−O) 1095 cm$^{-1}$. $^1H$ NMR (270 MHz, $C_6D_5CD_3$): $\delta$ 3.10 (s, OC$H_3$, 6H), −2.29 (qnt, $^2J_{HP}$ = 34.6, 2H, Mo−$H$). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): $\delta$ 71.3 (br, s). The analogous tungsten complex [WH$_2$(OMe)$_2$(dppe)$_2$] (**5**) is obtained when complex **3a** reacts with methanol at ambient temperature for 48 h (34%). The resulting complexes **4** and **5**, which are soluble in benzene and toluene, are moderately stable under an inert atmosphere in the solid state. IR (KBr disk): $\nu$(*methyl* C−H) 2825 cm$^{-1}$, $\nu$(W−H) 1860 cm$^{-1}$. $^1H$ NMR (270 MHz, $C_6D_5CD_3$): $\delta$ 3.05 (s, OC$H_3$, 6H), −1.08 (br, m, 2H, W−$H$).

**[MoH$_2$(OEt)$_2$(dppe)$_2$] (6).** A suspension of **2a** (0.0851 g, 0.09 mmol) in 10 mL of ethanol was stirred at ambient temperature for 96 h, during which time the dark red complex **2a** changed to a yellowish powder. The supernatant solution was removed with a bridge filter and the residue thus obtained was washed successively with ethanol and pentane. The resulting yellowish solid was dried under vacuum. Complex **6** is soluble in benzene and toluene but insoluble in hexane and diethyl ether. IR (KBr disk): $\nu$(Mo−H) 1805 cm$^{-1}$. $^1H$ NMR (270 MHz, $C_6D_6$): $\delta$ 3.40 (q, $J$ = 6.72 Hz, 4H, OC$H_2$CH$_3$), 0.95 (t, 6H, OCH$_2$C$H_3$), −3.66 (qnt, $^2J_{HP}$ = 29.9 Hz, 2H, Mo−$H$).

When this reaction was carried out at 60 °C, the carbonyl complex *cis*-[Mo(CO)$_2$(dppe)$_2$][14] was obtained (62%).

**Reaction of 2a with 2-Propanol.** A suspension of **2a** (0.1481 g, 0.15 mmol) in 15 mL of 2-propanol was stirred under reduced pressure at ambient temperature for 96 h, during which time the dark red complex **2a** changed to a yellowish powder. The solvent was removed under vacuum, and the residue was washed successively with hexane and diethyl ether. The resulting light yellow product was dried under vacuum. It was spectroscopically identical with [MoH$_4$(dppe)$_2$] (**1**; 71%).

**Synthesis of Catecholato Complexes.** A typical procedure is as follows. A solution containing **2a** and catechol in toluene was stirred at ambient temperature under the conditions given in Table 5. During the stirring, the solution changed from dark red to black. The solvent was evaporated from the resulting solution to dryness under reduced pressure. The residue was washed successively with methanol and hexane and dried under vacuum. These procedures are also applicable to the syntheses of the other molybdenum or tungsten complexes. Preparations, analytical data, and se-

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(32) Archer, L. C.; George, T. A.; Nobel, M. E. *J. Chem. Educ.* **1981**, *58*, 727.

lected spectroscopic data for all complexes are compiled in Tables 5−7, respectively. Complexes **7** and **8** are soluble in benzene, toluene, and THF but insoluble in hexane. Although the complexes decompose in solution immediately under air, the solids can be handled briefly in air.

**X-ray Crystallographic Study of 7a,d and 8a.** Crystals of complex **7a,d** and **8a** suitable for X-ray crystallography were grown in toluene−hexane at 10 °C, and crystals thus obtained were mounted on a glass fiber. Measurements were made on a Rigaku AFC7R (for **7a** and **7d**) or a Rigaku AFC5R (for **8a**) diffractometer by using Mo Kα radiation ($\lambda = 0.710\ 69$ Å) for data collection. The unit-cell parameters were determined by least-squares fitting of 25 reflections for **7a**, of 16 reflections for **7d**, and of 24 reflections for **8a** with ranges $25.09° \le 2\theta \le 29.89°$, $29.57° \le 2\theta \le 29.90°$, and $29.81° \le 2\theta \le 29.99°$, respectively. The parameters used during the collection of diffraction data are given in Table 8. The structure was solved and refined by using Fourier techniques.[33] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

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**Supporting Information Available:** Tables of fractional atomic coordinates, anisotropic thermal factors, and all bond distances and angles for **7a,d** and **8a** (51 pages). Ordering information is given on any current masthead page.

OM9603124

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[33] Beurskens, P. T.; Admiraal, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1992.