Templated C–C and C–N Bond Formation

Facilitated by a Molybdenum(VI) Metal Center

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Abstract. Preparation of molybdenum dioxido complexes with novel iminophenolate ligands bearing pendant secondary amide functionalities led to unprecedented C–C and C–N coupling reactions of two α -iminoamides upon coordination. The diastereoselective cyclization to asymmetric imidazolidines occurs at the metal center in two consecutive steps via a mono coupled intermediate. A meaningful mechanism is proposed based on full characterization of intermediate and final molybdenum-containing products by spectroscopic means and by single-crystal X-ray diffraction analyses. This process constitutes the first example of a diastereoselective self-cyclization of two α -iminoamides.

Introduction

Mononuclear dioxidomolybdenum(VI) complexes with a large variety of ligands have been prepared and extensively investigated due to their reactivity in oxygen atom transfer (OAT) reactions. They have proven useful, both as biomimetic models for mononuclear molybdoenzymes and also as highly active oxygenation catalysts of e.g. olefins using oxidants such as hydrogen peroxide or *tert*-butyl hydroperoxide.^{1,2,3} In both cases, various mechanistic studies showed hydrogen bonding to be of crucial importance for the reactivity. Intermolecular H bonding between the incoming oxidant and the oxido ligands of the molybdenum complex is involved in catalytic epoxidation reactions,⁴ while for biomimetic OAT reactions, the work of Borovik highlighted the influence of intramolecular H bonding between the ligand and the oxido group in the stabilization of highly unusual iron and manganese complexes.⁵ In our group, we previously reported Mo complexes coordinated by phenolate ligands bearing donor atoms or hydroxyl group in the side chain in order to influence the hydrogen bonding and thereby gaining information on the OAT process. When Mo dioxido complexes substituted by bidentate Schiff-base ligands with donor sites were used in epoxidation reactions, a difference in reactivity was

observed depending on the nature of the donor atom of the ligand, hence the ability to form weak or strong hydrogen bonds.² More recently, we used Mo and W complexes bearing tetradentate bisphenolate ligands which are able to form intramolecular H bonding, but here no influence on the epoxidation activity could be observed.³

Inspired by the tripodal amidoamine ligands reported by Borovik, we envisioned to introduce similar amide functionalities in our previously used iminophenolate ligands and investigated their coordination behavior towards the molybdenum dioxido core (Figure 1). Herein, we thus report the synthesis of bidentate iminophenolate ligands bearing amide functionalities and their unexpected reactivity as 1,3-dipoles upon coordination at an electron poor, high oxidation state metal center (Mo^{VI} , d^0), involving C–C and C–N bond formation.

Figure 1. Synthesized iminophenolate ligands **HL1–HL3** and their derived complexes of the type $[\text{MoO}_2\text{L}_2]$, showing the desired intramolecular hydrogen bonding.

The coupling behavior of the here investigated ligands is reminiscent of the Huisgen–type [2+3] cycloaddition between an azomethine ylide and a dipolarophile.⁶ Whereas α -iminoesters are extensively used to form dipoles which can undergo cycloaddition reactions with a broad scope of dipolarophiles as well as intermolecular self-cyclization,^{7–9} reports of cycloaddition reactions of α -iminoamides are scarce and require activated alkenes as reaction partners.^{10,11} According to

Grigg and coworkers the acidity of the α -protons has a crucial influence as demonstrated by introducing adjacent electron withdrawing groups (EWG) thereby increasing reactivity.^{8,12} The lower acidity of the amide α -protons in α -iminoamides compared to structurally related carboxylic acid esters¹² is likely the reason why hardly any cycloadditions with α -iminoamides are described in literature. Within this report, a diastereoselective cyclization of the latter at a metal template to form imidazolidine coordinated complexes is presented and a step-wise reaction pathway via a single C-C coupled intermediate of two ligand molecules is demonstrated. Full characterization of intermediate and final complexes including single-crystal X-ray diffraction analyses is provided, allowing to propose a meaningful mechanism for the cyclization sequence at the metal center.

Results and Discussion

Ligand Synthesis. Ligands **HL1–HL3** were prepared according to Scheme 1. In the first step 2-chloroacetylchloride was reacted with 2 equiv of *tert*-butyl or phenyl amine, following a published route.¹³ For the subsequent conversion to the previously described amines **A1** and **A2**,^{14,15} a simple approach, by reaction of N-substituted 2-chloroacetamides with a large excess of aqueous ammonia (35%) in a pressure reactor, was used. In the last step, the resulting primary amines were condensed with the respective aldehydes to the desired iminophenolates.

Ligands **HL1–HL3** were characterized via ¹H, ¹³C NMR and FT-IR spectroscopy as well as EI-MS. Noteworthy is the difference in the shift of the amide NH proton, dependent on the substituent (6.27 ppm in **HL1** and 6.26 ppm in **HL3**, *tert*-butyl amide vs. 8.42 ppm in **HL2**, phenyl amide).

Scheme 1. Three-step synthesis of the iminophenolate amide ligands **HL1–HL3**.

Complex Synthesis. For the synthesis of disubstituted dioxidomolybdenum(VI) complexes of the type $[\text{MoO}_2\text{L}_2]$ well established synthetic protocols using the $[\text{MoO}_2(\text{acac})_2]$ precursor were investigated.¹⁶ Thus, reaction of two equiv of **HL1** and **HL2**, respectively, with $[\text{MoO}_2(\text{acac})_2]$ in dry MeCN under inert conditions led instead of the targeted $[\text{MoO}_2\text{L}_2]$ complexes to compounds **1** and **2** in good yields (Scheme 2). Whereas initial ^1H NMR data suggested the selective formation of the desired disubstituted complexes, HSQC 2D NMR experiments pointed towards a different species with two distinct CH moieties, indicating the formation of a new C–C bond within the synthesis. Unambiguous elucidation of the nature of the obtained complexes **1** and **2** allowed a single-crystal X-ray diffraction analysis of **1**, revealing a mononuclear dioxidomolybdenum complex coordinated by a tetradentate, dianionic adduct, which had formed by C–C coupling of two ligand molecules (Scheme 2). Extended NMR spectroscopy of compounds $[\text{MoO}_2(\text{L1}^{\text{C-C}})]$ (**1**) and $[\text{MoO}_2(\text{L2}^{\text{C-C}})]$ (**2**), where $\text{L1}^{\text{C-C}}$ and $\text{L2}^{\text{C-C}}$ denote dianionic adducts of two **HL1/HL2** ligands, confirms these structures, as resonances for two sets of ligands but only one resonance for a $\text{CH}=\text{N}$ proton are assignable. Coordination of the imine moiety to the electrophilic metal center supposedly led to the activation of the imine carbon

enabling nucleophilic attack by the activated and therefore easily deprotonated α -carbon of another coordinated ligand moiety (vide infra).^{17,18} To test if different conditions would lead to the desired $[\text{MoO}_2\text{L}_2]$ species, a reaction screening was performed, varying solvent and temperature. Whereas the temperature only affected the reaction time, the solvent had a large influence on the reaction product. Anhydrous toluene and acetonitrile led selectively to complexes **1** and **2** but analogous reactions in dry MeOH yielded compounds **3** and **4** as the only products as shown in Scheme 2.

Their HSQC 2D NMR spectra feature resonances assignable to three aliphatic CH protons and, unexpectedly, the absence of an imine proton resonance. Single-crystal X-ray diffraction analyses of **3** and **4**, respectively, identified the products to be unusual mononuclear dioxidomolybdenum compounds coordinated in a tetradentate fashion by dianionic phenolate-imidazolidine moieties, resulting from C–C and C–N coupling ($[\text{MoO}_2(\text{L1}^{\text{Cyc}})]$ (**3**) and $[\text{MoO}_2(\text{L2}^{\text{Cyc}})]$ (**4**), where L1^{Cyc} and L2^{Cyc} denote dianionic imidazolidine moieties, respectively). Whereas such cyclizations are known for α -iminoesters,^{8,19–21} a similar reactivity has not been described for the corresponding amides. Only *N*-(2-pyridylmethyl)imines were found to undergo cycloaddition at Cu(II) or Cd(II) centers leading to imidazolidine coordinated compounds.^{17,22} However, such compounds are known to undergo intermolecular self-cyclization at room temperature in the absence of metal,^{19,20} a reaction not observed with the herein discussed molecules (vide infra). A reactivity related to the cyclization step disclosed herein has been previously reported to occur in the reaction of the dioxidomolybdenum salicylate precursor $[\text{MoO}_2(\text{sal})_2]$ and L-ornithine monohydrochloride.²³

Scheme 2. Synthesis of complexes **1–4** coordinated by C–C and C–N coupling products.

In proton NMR spectra of crude $[\text{MoO}_2(\text{L2}^{\text{C-C}})]$ (**2**), resonances assignable to small quantities of $[\text{MoO}_2(\text{L2}^{\text{C-N}})]$ (**4**) were noticed, pointing to a synthetic dependence between the two structural types. To confirm this hypothesis, complexes **1** and **2** were dissolved in dry methanol and stirred for 5 h at 50 °C under inert conditions. Proton NMR spectroscopy showed quantitative conversion of **1** into **3** and **2** into **4**, respectively. This contrasts previous observations where addition of an α -iminoamide to a dipolarophile catalyzed by LiBr/NEt_3 led to a mixture of the heterocycle and a Michael-type adduct in a competitive rather than sequential fashion.^{11,24}

Scheme 3. Synthesis of complex **5** and formation of minor product **6**.

All described yields for complexes **1–4** correspond to diastereopure compounds and were obtained with dry solvents in an N₂ atmosphere; however the products are also accessible under ambient conditions, albeit with significantly lower yields. Furthermore, by reacting another common molybdenum precursor, [MoO₂Cl₂], with 2 equiv of **HL1** and 2 equiv of 2,6-lutidine as HCl scavenger in dry acetonitrile, mixtures of **1** and **3** were obtained. It is interesting to note that the exchange of the amide *tert*-butyl substituent (**HL1**) by an electron withdrawing phenyl substituent (**HL2**) does not affect the ligand's reactivity, despite the significant impact on the acidity of the NH proton (6.27 ppm in **HL1** vs. 8.42 ppm in **HL2** in their ¹H NMR spectra).

Analogous reactions employing the sterically more demanding ligand **HL3** led to mixtures of several species and significant amount of decomposed ligand since **HL3** is very sensitive towards moisture. Nevertheless, careful work-up of the reaction of [MoO₂(acac)₂] and **HL3** allowed the isolation of product **5** in low yield (Scheme 3). Recrystallization from acetonitrile afforded the compound as yellow crystals. Additionally, in the crystalline batch we observed a small quantity of bright orange crystals. Both, the yellow (**5**) and the orange (**6**) crystals proved to be suitable for single-crystal X-ray diffraction analyses identifying complex **5** as a complex of the formula [MoO₂(L3^{ac})], with L3^{ac} being a dianionic C–C coupled adduct of **HL3** and one acac[−] ligand, and complex **6** as [MoO₂(L3^{C–C})], a structural analogue to **1**. Steric hindrance is the plausible explanation for the formation of **6** in only trace amounts (Scheme 3).

Depending on the nature of the carbonyl derivative, auto-cyclization of dipolar compounds related to **HL1–HL3** at elevated temperatures was reported.^{9,19,20} To ensure that the observed reaction is in fact metal-dependent, blank experiments where **HL1–HL3** were stirred in dry methanol with and without addition of catalytic amounts of trifluoroacetic acid for 24 h at 60 °C were carried out. Proton NMR spectra of the residues showed only **HL1–HL3** accompanied by

decomposition products (mainly aldehyde), but no coupled species. Complexes **1** and **3** are well soluble, complexes **4** and **5** are moderately soluble and complex **2** is only slightly soluble in polar solvents (e.g. CHCl₃, CH₂Cl₂, MeCN). All complexes are practically insoluble in non-polar solvents and prone to decomposition upon prolonged exposure to DMSO as well as water-containing solvents. Compounds **1–5** were characterized via ¹H, ¹³C NMR and FT-IR spectroscopy, elemental analyses and with the exception of **2** by single-crystal X-ray diffraction analyses (vide infra). Furthermore, HSQC spectra of complexes **1–5** were recorded.

Proposed Reaction Mechanism. A Reaction mechanism is proposed for the formation of complexes of structural types **1** and **3**, respectively, starting from [MoO₂(acac)₂] (Scheme 4). The first step involves the substitution of one monoanionic acetylacetonate ligand (acac⁻) by the incoming iminophenolate. The electrophilic metal center activates one keto carbon in the remaining acac⁻ or the imine carbon in a second molecule of coordinated iminophenolate. It also renders the amide- α -CH₂ group acidic so that a deprotonation and subsequent nucleophilic attack on the activated keto or imine carbon is facilitated, leading to adducts of either two α -iminoamide moieties (**1**, **2** and **6**) or one α -iminoamide with one acac⁻ ligand (**5**). Cyclization to the five-membered imidazolidine ring occurs via a nucleophilic attack of the amine at the activated imine carbon. This second step only takes place in methanol, the protic solvent facilitating the associated proton transfer. With **HL3**, the cyclization is presumably prevented by steric hindrance leading only to mono C-C coupled adducts **5** or **6**.

Scheme 4. Proposed reaction pathway of the C–C coupling and subsequent cyclization at the $[\text{MoO}_2]^{2+}$ metal center.

Molecular Structures. Molecular structures of C–C coupled complexes **1**, **5** and **6**, as well as imidazolidine complexes **3** and **4** were determined by single-crystal X-ray diffraction analysis. For **3**, two different modifications were observed, dependent on the co-crystallizing solvent. Herein, the more exact measurement is discussed in detail, data corresponding to the other modification can be found in the electronic supplementary information (SI). Molecular views of **1**, **5** and **6** are given in Figure 2, and of **3** and **4** in Figure 3. Important bond lengths and angles for complexes **1** and **3–6** are given in Table 1, full crystallographic details such as intramolecular hydrogen bonding, structure refinement and experimental details are provided within the SI.

Figure 2. Molecular views (50% probability level) of **1** (top left), **5** (top right) and **6** (bottom); H atoms (except involved in hydrogen bonding or bound to atoms affected by coupling) as well as solvent molecules are omitted for clarity reasons. Intramolecular hydrogen bonds to oxido groups are indicated by dashed lines, the open bond in **5** depicts an unusual long Mo–L contact. The *tert*–butyl substituents on the phenyl rings in **6** are drawn with small spherical atoms and line bonds for clarity reasons.

Figure 3. Molecular views (50% probability level) of **3** (left) and **4** (right); H atoms (except imidazolidine ring protons) as well as solvent molecules are omitted for clarity reasons. Intramolecular hydrogen bonds to oxido groups are indicated by dashed lines, open bonds depict unusual long Mo–L contacts.

In all complexes, the molybdenum atoms are coordinated in a distorted octahedral fashion by the tetradentate ligand and two terminal oxido ligands. In complex **1**, an intramolecular H–bond between an amide hydrogen and an oxido group is present (N15 $\cdots$ O2 2.868(2)Å). The occurrence of such a hydrogen bond is interesting providing ample reasoning for the choice of the ligands. During complexation a C–C bond between C13 and C31 is formed, bridging two ligand moieties in an asymmetric fashion. The saturated rings in complexes **3** and **4** adopt envelope conformation in which the N32 atom is bent out of plane (C11–N12–C13–C31 - 0.50(11)°, **3**) and (C11–N12–C13–C31 -1.4(2)°, **4**), respectively. The saturated N32 atoms of the imidazolidine rings coordinate to the Mo centers via rather long Mo–N contacts of 2.4407(9)Å

(**3**) and 2.4239(19)Å (**4**), whereas the N12 atoms are involved in intramolecular hydrogen bonding to O2, (N12⋯O2 2.9903(13)Å, **3**) and (N12⋯O2 2.984(3)Å, **4**). In complex **5**, the oxygen atoms of the acac[−] derived ligand are inequivalent (C32–O32 1.429(3)Å, O32–Mo1 1.9270(19)Å vs. C34–O34 1.234(3)Å, O34–Mo1 2.314(2)Å) due to a C–C bond formation between C13 and C32. Similar to complex **1**, an intra-molecular hydrogen bond between N15 and O2 can be observed (N15⋯O2 2.952(3)Å) in **5**. Compounds **1**, **5** and **6** contain three chiral carbon centers. As expected, they crystallized in a racemic fashion. However, it is interesting to note that upon comparing the molecular structures of the two adducts **1** and **6** (Figure 2), two different racemates are formed. This is due to the different orientation of the amide side chain at C13, leading to an overall structure of SRR/RSS in **1** and RRR/SSS in **6** with respect to C13, C31, and N32. Thus, an intra-molecular hydrogen bond between N15 and O2 as observed in **1** is not possible in **6**. This difference is presumably caused by the larger steric demand in **6**. In contrast, the substituents at the imidazolidine rings in complexes **3** and **4** (Figure 3) show the same configuration with respect to each other. Another noteworthy observation is that in complexes **1** and **2** the phenolate oxygens O21 and O41 are oriented *cis* to each other, whereas in their related imidazolidine compounds **3** and **4** they are arranged *trans*. This flexibility of the ligand framework is unusual due to the tetradentate coordination motif. A comparison of the Mo=O bond lengths of the herein reported complexes, especially for the structurally related complexes **3/4** and **1/6**, points to only minor influence of hydrogen bonding in the present case. Generally, all observed molybdenum oxido bond lengths are within expected ranges (Table 1).²⁵

Table 1. Selected Bond Lengths [Å] and Angles [°] for Complexes **1** and **3–6**.

	1	3	4	5	6
Mo1–O1	1.7107(12)	1.7054(8)	1.7170(17)	1.714(2)	1.7062(15)
Mo1–O2	1.7225(13)	1.7116(8)	1.7082(17)	1.722(2)	1.7346(15)
Mo1–O21	1.9344(12)	1.9573(8)	1.9440(17)	1.920(2)	1.9155(14)
Mo1–O41 ^[a]	2.0507(12)	1.9513(9)	1.9395(18)	1.927(2)	2.0067(14)
Mo1–O34	–	2.2108(8)	2.2329(16)	2.314(2)	–
Mo1–N12	2.3182(14)	–	–	2.280(2)	2.3173(17)
Mo1–N32	2.2364(14)	2.4407(9)	2.4239(19)	–	2.2261(18)
O1–Mo1–N12	166.73(6)	–	–	158.23(9)	170.54(7)
O2–Mo1–O41	159.65(6)	95.59(4)	95.95(8)	–	156.94(7)
O21–Mo1–N32	155.13(5)	75.15(3)	74.66(7)	–	155.43(6)

[a] O32 in complex **5**

Conclusions

The synthesis of three new iminophenolate ligands bearing *tert*-butyl and phenyl amide functionalities is reported. They react with [MoO₂(acac)₂] to form five dioxidomolybdenum(VI) complexes **1–5**, coordinated by tetradentate ligands including imidazolidine heterocycles, arising from unprecedented metal-mediated C–C coupling and subsequent cyclization reactions. Complexes **1** and **2** are coordinated by dianionic adducts of two **HL1/HL2** moieties, **3** and **4** by the corresponding cyclized imidazolidine moieties and **5** by a dianionic C–C coupled adduct of **HL3** with acetyl acetate. Whereas Huisgen-type [2+3] cycloaddition reactions between azomethine ylides and dipolarophiles are widespread in literature, intermolecular self-cyclizations of dipoles bearing amide functionalities have not been described. Here, we therefore

report the first observation of a diastereoselective self-cyclization reaction at an electron poor metal center (Mo^{VI} , d^0) yielding complexes employing a coordinated asymmetric imidazolidine moiety. Mono C–C coupled complexes were found to be intermediate products to the final imidazolidine complexes. All moderately air- and moisture-sensitive complexes **1–5** were fully characterized by spectroscopic means and, except **2**, via single-crystal X-ray diffraction analysis. Intramolecular H-bonds could be observed in the molecular structures of **1**, **3**, **4** and **5**, albeit their influence on the molybdenum oxo bond lengths is negligible. Additionally, a reaction mechanism for the cyclization reaction at the metal center with the single C–C coupled adduct complexes acting as intermediates is proposed. The novel reactivity at the Mo(VI) metal center could allow for the development of new catalytic systems promoting the stereoselective synthesis of imidazolidine-heterocycles from a broad scope of 1,3-dipole precursors including α -iminoamides. Further studies thereof are on the way.

Experimental Section

General. Unless specified otherwise, experiments were performed under inert conditions using standard Schlenk equipment. Commercially available chemicals were purchased from Sigma-Aldrich and used as received. No further purification or drying operations have been performed. The metal precursor $[\text{MoO}_2(\text{acac})_2]$ was synthesized according to known procedures.²⁶ Solvents were purified via a Pure-Solv MD-4-EN solvent purification system from Innovative Technology, Inc. Methanol was refluxed over activated magnesium for at least 24 h and then distilled prior to use. Amine syntheses have been carried out in a Parr Instrument 4560 mini reactor coupled to a Parr Instrument 4840 temperature controller. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Optics instrument at 300/75 MHz. Peaks are denoted as singlet (s), broad singlet (bs), doublet (d), doublet of doublets (dd), triplet (t), pseudo-doublet (“d”), pseudo-triplet (“t”) and multiplet (m). Used solvents and peak assignment are mentioned at the specific data sets. ^{13}C NMR spectra recorded in CD_3CN have been referenced to the deuteromethyl-carbon. Due to insolubility, meaningful ^{13}C NMR data for complex **2** could not be obtained, HSQC data is given instead.

Electron impact mass spectroscopy (EI–MS) measurements have been performed with an Agilent 5973 MSD mass spectrometer with push rod. Peaks are denoted as cationic mass peaks, and the unit is the according ions mass/charge ratio. Mass spectroscopy reveals no useful data for complexes **3–5**, likely due to decomposition during measurement. Gas chromatography mass spectroscopy (GC–MS) measurements have been performed with an Agilent 7890 A gas chromatograph (column type, Agilent 19091J–433), coupled to an Agilent 5975 C mass spectrometer. Samples for infrared spectroscopy were measured on a Bruker Optics ALPHA FT–IR Spectrometer. IR bands are reported with wavenumber (cm^{-1}) and intensities (s, strong; m, medium; w, weak). All elemental analyses were measured at the University of Vienna, microanalytical laboratory.

X-ray Diffraction Analyses. Single-crystal X-ray diffraction analyses were measured on a BRUKER–AXS SMART APEX II diffractometer equipped with a CCD detector. All measurements were performed using monochromatized Mo K_{α} radiation from an Incoatec microfocus sealed tube at 100K (cf. Table S1). Absorption corrections were performed semi-empirical from equivalents. Structures were solved by direct methods (SHELXS–97)²⁷ and refined by full-matrix least-squares techniques against F^2 (SHELXL–2014/6).²⁷ CCDC 1420762–1420766 and 1422193 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Full experimental details for single-crystal X-ray diffraction analyses of all compounds are provided in the SI.

Synthesis of Primary Amines. N-(*tert*-butyl)-2-chloroacetamide and 2-chloro-N-phenylacetamide were synthesized in 84 and 88 % yield, respectively, following a published procedure.¹³ In contrast to literature procedure, N-(*tert*-butyl)-2-chloroacetamide was isolated as white crystalline needles instead of an oily product. Analytical data are consistent with literature,^{13,28} here, ^1H and ^{13}C NMR shifts in CD_3CN are given for comparison reasons.

N-(*tert*-butyl)-2-chloroacetamide: ^1H NMR (300 MHz, CD_3CN , 25 °C) δ : 6.51 (bs, 1H, NH), 3.89 (s, 2H, CH_2), 1.31 (s, 9H, *t*Bu) ppm; ^{13}C NMR (75 MHz, CD_3CN , 25 °C) δ : 166.18 (C=O), 52.07 (q-*t*Bu), 44.25 (CH_2), 28.60 (*t*Bu) ppm.

2-chloro-N-phenylacetamide: ^1H NMR (300 MHz, CD_3CN , 25 $^\circ\text{C}$) δ : 8.59 (bs, 1H, NH), 7.56 ("d", 2H, ArH), 7.35 ("t", 2H, ArH), 7.14 ("t", 1H, ArH), 4.16 (s, 2H, CH_2) ppm; ^{13}C NMR (75 MHz, CD_3CN , 25 $^\circ\text{C}$) δ : 165.66 (C=O), 138.99, 129.86, 125.44, 120.98 (Ar), 44.33 (CH_2) ppm.

Synthesis of 2-Amino-N-(*tert*-butyl)acetamide (A1). For the synthesis of **A1**, N-(*tert*-butyl)-2-chloroacetamide (5.00 g, 33 mmol) was suspended in aqueous ammonia (200 mL, 35 % sol. in H_2O). The suspension was subsequently stirred in an autoclave (5 atm, 60 $^\circ\text{C}$) for 3 h. The resulting clear aqueous solution was extracted four times with dichloromethane (100 mL each). The combined organic fractions were washed with brine, dried over MgSO_4 and evaporated *in vacuo*. The crude product, which contained a mixture of primary (2-amino-N-(*tert*-butyl)acetamide) and secondary (2,2'-azanediylbis(N-(*tert*-butyl)acetamide)) amine in a ratio of approximately 90:10 (GC-MS), could be used for subsequent syntheses without further purification (yield, calculated for **A1**: 59%). Nonetheless, pure **A1** was obtained after isocratic column chromatography of a crude mixture (1.00 g) with $\text{CHCl}_3/\text{MeOH}/\text{NH}_3\cdot\text{H}_2\text{O}$ (35%) (50/20/1) as eluent. Product loaded fractions have been identified via TLC using KMnO_4 stain. Evaporation of the solvent *in vacuo* gave **A1** as yellow oil (88 %, 0.88 g). NMR data in CDCl_3 is inconsistent with literature and denoted subsequently.¹⁴ ^1H and ^{13}C NMR shifts in CD_3CN are given for comparison reasons. ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ : 7.06 (bs, 1H, NH), 3.23 (s, 2H, CH_2), 1.71 (s, 2H, NH_2), 1.35 (s, 9H, *t*Bu) ppm; ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ : 171.95 (C=O), 50.56 (q-*t*Bu), 45.45 (CH_2), 28.88 (*t*Bu) ppm; ^1H NMR (300 MHz, CD_3CN , 25 $^\circ\text{C}$) δ : 7.12 (bs, 1H, NH), 3.06 (s, 2H, CH_2), 1.96 (s, 2H, NH_2), 1.30 (s, 9H, *t*Bu) ppm; ^{13}C NMR (75 MHz, CD_3CN , 25 $^\circ\text{C}$) δ : 172.95, 50.76 (q-*t*Bu), 45.84 (CH_2), 28.96 (*t*Bu) ppm.

Synthesis of 2-Amino-N-phenylacetamide (A2). For the synthesis of **A2**, 2-chloro-N-phenylacetamide (5.00 g, 29.5 mmol) was suspended in aqueous ammonia (200 mL, 35 % sol. in H_2O). The suspension was subsequently stirred in an autoclave (5 atm, 60 $^\circ\text{C}$) for 3 h. The resulting clear aqueous solution was extracted four times with dichloromethane (100 mL each). The combined organic fractions were washed with brine, dried over MgSO_4 and evaporated *in vacuo*. The crude product contained the desired product **A2** accompanied by minor impurities of aniline. Pure **A2** was obtained via heating *in vacuo* (10^{-4} atm, 60 $^\circ\text{C}$) for 4 h as a light brown solid (70 %, 3.10 g). Analytical data are consistent with literature.¹⁵ ^1H and ^{13}C NMR shifts in CD_3CN are given for comparison reasons. ^1H NMR (300 MHz, CD_3CN , 25 $^\circ\text{C}$) δ : 9.33 (bs, 1H, NH), 7.61 ("d", 2H, ArH), 7.32 ("t", 2H, ArH), 7.08 ("t", 1H,

ArH), 3.34 (s, 2H, CH₂), 1.87 (bs, 2H, NH₂) ppm; ¹³C NMR (75 MHz, CD₃CN, 25 °C) δ: 172.62 (C=O), 139.53, 129.79, 124.52, 120.17 (Ar), 45.99 (CH₂) ppm.

Ligand Synthesis. All ligands are stable towards air but sensitive towards moisture. They can be stored in a desiccator over P₂O₅ for several weeks without decomposition.

Synthesis of (E)-N-(*tert*-Butyl)-2-((2-hydroxybenzylidene)amino)acetamide (HL1)

For the synthesis of **HL1**, 1 equiv of **A1** (500 mg, 3.84 mmol) was mixed with 1 equiv of salicylic aldehyde (469 mg, 3.84 mmol) in a round flask. The yellow, initially liquid mixture was subsequently stirred at room temperature for 2 h, whereupon it solidified. Reaction completion was monitored via GC-MS. **HL1** was isolated after washing with cold pentane and drying *in vacuo* as a microcrystalline citron yellow solid (93 %, 763 mg). m.p. 111 °C; ¹H NMR (300 MHz, CD₃CN, 25 °C) δ: 13.00 (bs, 1H, OH), 8.42 (s, CH=N) 7.40–7.33 (m, 2H, ArH), 6.92 (“t”, 2H, ArH), 6.27 (bs, 1H, NH), 4.14 (s, 2H, CH₂), 1.32 (s, 9H, *t*Bu) ppm; ¹³C NMR (75 MHz, CD₃CN, 25 °C) δ: 169.51 (C=O), 168.55 (C=N), 161.80 (Ar-OH), 133.62, 132.97, 119.89, 119.79, 117.56 (Ar), 63.40 (CH₂), 51.78 (q-*t*Bu), 28.81(*t*Bu) ppm; IR (ATR, cm⁻¹): $\tilde{\nu}$ 3329 (m), 1639 (s), 1637 (s), 1542 (s), 1282 (m), 1280 (m), 884 (m), 758 (s), 580 (m); EI-MS: m/z 234.2 [M⁺].

Synthesis of (E)-2-((2-Hydroxybenzylidene)amino)-N-phenylacetamide (HL2). For the synthesis of **HL2**, 1 equiv of **A2** (1202 mg, 8.00 mmol) was dissolved in acetonitrile (25 mL) in a round flask. Subsequently 1 equiv of salicylic aldehyde (978 mg, 8.00 mmol) was added and the reaction mixture stirred at room temperature for 3 h, whereupon the initially colorless solution turned pale yellow. Reaction completion was determined via TLC. The reaction solution was dried over MgSO₄ and the solvent was evaporated *in vacuo* to give **HL2** as a yellow solid (96%, 1953 mg). m.p. 134 °C; ¹H NMR (300 MHz, CD₃CN, 25 °C) δ: 12.94 (s, 1H, OH), 8.51 (s, 1H, CH=N), 8.42 (bs, 1H, NH), 7.58 (“d”, 2H, ArH), 7.44–7.30 (m, 4H, ArH), 7.11 (t, 1H, ArH), 6.96–6.92 (m, 2H, ArH), 4.41 (s, 2H, CH₂) ppm; ¹³C NMR (75 MHz, CD₃CN, 25 °C) δ: 170.27 (C=O), 168.14 (C=N), 161.80 (Ar-OH), 139.39, 133.77, 133.11, 129.79, 125.03, 120.91, 119.95, 119.83, 117.61 (Ar), 63.38 (CH₂) ppm; IR (ATR, cm⁻¹): $\tilde{\nu}$ 2981 (w), 1673 (w), 1626 (m), 1595 (m), 1538 (s), 1445 (m), 751 (s), 695 (m); EI-MS: m/z 254.1 [M⁺].

Synthesis of (E)-N-(*tert*-Butyl)-2-((2-hydroxybenzylidene)amino)acetamide (HL3). For the synthesis of **HL3**, 1 equiv of **A1** (500 mg, 3.84 mmol) was added to a solution of 1.04 equiv of 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (937 mg, 4.00 mmol) in MeOH (5mL) in a round flask. The solution, which turned dark yellow immediately, was stirred at room temperature for 1 h. After a few minutes a precipitate started to form. Reaction completion was monitored via GC-MS. After filtration and wash with a small portion of cold MeOH, **HL3** was isolated as a fluffy, light yellow solid (92 %, 1227 mg). m.p. 155 °C; ¹H NMR (300 MHz, CD₃CN, 25 °C) δ: 13.64 (s, 1H, OH), 8.41 (s, 1H, CH=N), 7.43 (d, 1H, ArH), 7.25 (d, 1H, ArH), 6.26 (bs, 1H, NH), 4.13 (s, 2H, CH₂), 1.42 (s, 9H, *t*Bu), 1.32 (s, 9H, *t*Bu), 1.30 (s, 9H, *t*Bu) ppm; ¹³C NMR (75 MHz, CD₃CN, 25 °C) δ: 170.52 (C=O), 168.62 (C=N), 158.76 (Ar-OH), 141.41, 137.28, 128.23, 127.64, 119.08 (Ar), 63.13 (CH₂), 51.77, 35.66, 34.82 (q-*t*Bu), 31.67, 29.65, 28.82 (*t*Bu) ppm; IR (ATR, cm⁻¹): $\tilde{\nu}$ 3271 (m), 2960 (s), 1651 (s), 1634 (s), 1556 (s), 1439 (s), 1391 (m), 1360 (s), 1273 (s), 1224 (s), 1172 (m), 713 (w), 586 (w); EI-MS: m/z 346.3 [M⁺].

Complex Syntheses. All complexes are moderately sensitive towards air and sensitive towards moisture. They can be stored in an N₂-filled glovebox for several weeks without decomposition. L1^{C-C} and L2^{C-C} denote dianionic adducts of two **HL1/HL2** ligands, L1^{Cyc} and L2^{Cyc} denote dianionic cyclized imidazolidine moieties and L3^{ac} denotes the dianionic C-C coupled adduct of **HL3** with acetyl acetate.

Synthesis of [MoO₂(L1^{C-C})] (1). For the synthesis of **1**, 1 equiv of [MoO₂(acac)₂] (489 mg, 1.50 mmol) was suspended in dry CH₃CN (10 mL) in a Schlenk tube under N₂ atmosphere. Subsequently, 2 equiv of **HL1** (703 mg, 3.00 mmol) were added and the yellow to orange reaction mixture stirred at 60 °C for 3 h. Complete ligand consumption was monitored via TLC, whereupon the orange reaction mixture was concentrated *in vacuo* and stored at -25 °C for 24 h. The precipitate was filtered off and washed with cold pentane. Subsequently, the orange solid was dissolved in a minimal amount of dry CH₂Cl₂ and white residue was removed via filtration through a glass frit packed with Celite. Evaporation of the solvent *in vacuo* gave **1** as an orange powder (77 %, 683 mg). Crystals suitable for single-crystal X-ray diffraction analysis were obtained via recrystallization from CH₂Cl₂. m.p. 243 °C (decomp.); ¹H NMR (300 MHz, CD₃CN, 25 °C) δ: 8.17 (s, CH=N), 7.55 ("t", 1H, ArH), 7.36 ("d", 1H, ArH), 7.14-6.93 (m, 4H, ArH), 6.92 (bs, 1H, NH), 6.70 (bs, 1H, NH), 6.67 ("t", 1H, ArH), 6.46 ("d", 1H, ArH), 6.16 (bs, 1H, NH), 4.67 (d, 1H, CH), 4.32 (s, 1H, CH), 3.53-3.27 (m, 2H, CH₂), 1.32 (s, 9H, *t*Bu), 1.29 (s, 9H, *t*Bu) ppm; ¹³C

NMR (75 MHz, CD₃CN, 25 °C) δ : 167.88 (CH=N), 167.32, 166.66 (RC=ONH), 161.93, 160.66 (Ar-O), 137.09, 136.22, 131.15, 130.29, 122.40, 121.97, 121.90, 120.70, 119.21 (Ar), 118.29 (Ar, concealed by solvent peak, clarified via HSQC), 80.60 (CH), 67.46 (CH), 56.68 (CH₂), 52.88, 52.28 (q-*t*Bu), 28.80, 28.70 (*t*Bu) ppm; IR (ATR, cm⁻¹): $\tilde{\nu}$ 1668 (s), 1541 (m), 1449 (m), 1285 (s), 1271 (m), 1215 (m), 914 (Mo=O, s), 880 (Mo=O, s), 758 (s), 639 (m), 614 (m); EI-MS: *m/z* 580.4 [M⁺-O]; Anal. calcd. for C₂₆H₃₄MoN₄O₆·0.4 CH₂Cl₂: C, 50.45; H, 5.58; N, 8.91. Found: C, 50.36; H, 5.48; N, 9.16.

Synthesis of [MoO₂(L^{2C-C})] (2). For the synthesis of **2**, 1 equiv of [MoO₂(acac)₂] (489 mg, 1.50 mmol) as well as 2 equiv of **HL2** (763 mg, 3.00 mmol) were suspended in dry toluene (10 mL) in a Schlenk tube under N₂ atmosphere. Subsequently the reaction mixture was stirred at 60 °C for 1.5 h, whereupon an orange solid started to precipitate from the initially yellow solution. Complete ligand consumption was monitored via TLC. The precipitate was filtered off and washed twice with a small portion of cold dry CH₂Cl₂ to give **2** as an orange powder (75 %, 718 mg). m.p. 209 °C (decomp.); ¹H NMR (300 MHz, CD₃CN, 25 °C) δ : 8.73 (bs, 1H, NH), 8.31 (s, CH=N), 8.29 (bs, 1H, NH), 7.60–7.52 (m, 5H, ArH), 7.42–7.31 (m, 5H, ArH), 7.23–6.92 (m, 7H, 6 ArH, 1 NH), 6.73 (“t”, 1H, ArH), 6.52 (“d”, 1H, ArH), 4.93 (d, 1H, CH), 4.64 (s, 1H, CH), 3.82–3.59 (m, 2H, CH₂) ppm; ¹³C NMR (75 MHz, CD₃CN, 25 °C, HSQC, q-C obscured) δ : 167.75 (CH=N), 136.20, 136.08, 135.29, 129.82, 128.95, 128.90, 128.88, 128.83, 124.88, 124.21, 120.98, 120.96, 119.78, 119.75, 119.60, 119.46, 118.30, 117.88 (Ar), 79.41 (CH), 65.81 (CH), 55.19 (CH₂) ppm; IR (ATR, cm⁻¹): $\tilde{\nu}$ 1598 (m), 1442 (m), 1268 (s), 1247 (m), 907 (Mo=O, s), 876 (Mo=O, s), 751 (s), 689 (m), 640 (m), 495 (m); Anal. calcd for C₃₀H₂₆MoN₄O₆·0.3 CH₂Cl₂: C, 55.14; H, 4.06; N, 8.49. Found: C, 54.97; H, 3.90; N, 8.65.

Synthesis of [MoO₂(L^{1Cyc})] (3). For the synthesis of **3**, 1 equiv of [MoO₂(acac)₂] (49 mg, 0.15 mmol) was suspended in dry MeOH (5 mL) in a Schlenk tube under N₂ atmosphere. Subsequently, 2 equiv of **HL1** (70 mg, 0.30 mmol) were added and the yellow reaction mixture stirred at 50 °C for 2 h. Complete ligand consumption was monitored via TLC, whereupon the yellow solution was filtered through a glass frit packed with Celite, concentrated *in vacuo*, layered with heptane and stored at –25 °C for 24 h. The residual precipitate was filtered off, washed with cold heptane and dried *in vacuo* to give **3** as a yellow crystalline solid (51 %, 45 mg). Crystals suitable for single-crystal X-ray diffraction analysis were obtained via recrystallization from MeOH layered with heptane or CH₃CN. Alternatively, **3** was obtained in excellent yield starting with **1**. Therefor **1** (100 mg, 0.17 mmol) was suspended in

dry MeOH (10 mL) and stirred for 5 h at 50 °C under N₂ atmosphere. The resulting yellow solution was filtered through a glass frit packed with Celite and subsequently evaporated *in vacuo* to obtain pure **3** as a yellow powder (97 %, 97 mg). m.p. 230 °C (decomp.); ¹H NMR (300 MHz, CD₃CN, 25 °C) δ: 7.38–7.18 (m, 6H, 4 ArH, 2 NH), 6.98–6.92 (m, 1H, ArH), 6.88–6.74 (m, 3H, ArH), 4.82 (d, 1H, CH), 4.28–4.20 (m, 1H, NH), 4.11–4.08 (m, 1H, CH), 4.01–3.95 (m, 1H, CH), 3.58–3.36 (m, 2H, CH₂), 1.35 (s, 9H, *t*Bu), 0.97 (s, 9H, *t*Bu) ppm; ¹³C NMR (75 MHz, CD₃CN, 25 °C) δ: 173.12, 171.38 (RC=ONH), 164.28, 162.73 (Ar–O), 132.76, 132.10, 130.96, 130.81, 123.89, 122.38, 121.68, 121.42, 119.99, 119.82 (Ar), 82.97, 74.98, 64.94 (CH), 56.50 (CH₂), 54.20, 51.25 (q-*t*Bu), 28.81, 28.05 (*t*Bu) ppm; IR (ATR, cm⁻¹): ν 1626 (m), 1263 (m), 1236 (m), 1017 (m), 924 (s), 889 (Mo=O, s), 875 (Mo=O, s), 752 (s), 635 (s), 441 (s); EI-MS: m/z 578.4 [M⁺–H₂O]; Anal. calcd for C₂₆H₃₄MoN₄O₆: C, 52.53; H, 5.76; N, 9.42. Found: C, 52.37; H, 5.51; N, 9.26.

Synthesis of [MoO₂(L2^{Cyc})] (4**).** For the synthesis of **4**, 1 equiv of [MoO₂(acac)₂] (98 mg, 0.30 mmol) as well as 2 equiv of **HL2** (153 mg, 0.60 mmol) were suspended in dry MeOH (3 mL) in a Schlenk tube under N₂ atmosphere. Subsequently, the yellow reaction mixture was stirred at 50 °C for 3 h whereupon a yellow solid started to precipitate from the solution. Complete ligand consumption was monitored via TLC, whereupon the precipitate was filtered off and washed twice with a small portion of cold dry methanol to obtain **4** as a yellow powder (66 %, 126 mg). Crystals suitable for single-crystal X-ray diffraction analysis have been obtained via recrystallization from a CH₃CN solution containing OPMe₃ as additive. Analogous to the procedure described for the synthesis of **3**, **4** can be obtained in high yield via transformation of **2** in methanol. Therefor **2** (100 mg, 0.17 mmol) was suspended in dry MeOH (10 mL) and stirred for 5 h at 50 °C under N₂ atmosphere. The resulting yellow reaction mixture was filtered and the precipitate dried *in vacuo* to obtain pure **4** as a yellow powder (95 %, 95 mg). m.p. 248 °C (decomp.); ¹H NMR (300 MHz, CD₃CN, 25 °C) δ: 9.64 (bs, 1H, NH), 9.05 (bs, 1H, NH), 7.68 (“d”, 2H, ArH), 7.56 (dd, 1H, ArH), 7.47 (dd, 1H, ArH), 7.40–7.12 (m, 8H, ArH), 7.06–6.95 (m, 3H, ArH), 6.93–6.83 (m, 3H, ArH), 5.07 (d, 1H, CH), 4.50–4.30 (m, 3H, 2 CH, NH), 3.88–3.59 (m, 2H, CH₂) ppm; ¹³C NMR (75 MHz, CD₃CN, 25 °C) δ: 173.22, 170.65 (RC=ONH), 164.30, 162.71 (Ar–O), 139.16, 135.74, 133.11, 132.33, 131.21, 131.09, 130.04, 129.87, 127.90, 125.08, 123.49, 123.17, 122.21, 121.95, 121.76, 120.80, 120.09, 119.81 (Ar), 82.50, 74.79, 64.90 (CH), 56.47 (CH₂) ppm; IR (ATR, cm⁻¹): ν 1633 (m), 1598 (m), 1529 (m), 1446 (m), 1264 (m), 1232 (m), 915 (Mo=O, s), 894 (Mo=O,

s), 868 (s), 833 (m), 740 (s), 688 (m), 636 (m), 493 (m), 443 (m); Anal. calcd for C₃₀H₂₆MoN₄O₆: C, 56.79; H, 4.13; N, 8.83. Found: C, 56.07; H, 4.10; N, 8.30.

Synthesis of [MoO₂(L3^{ac})] (5). For the synthesis of **5**, 1 equiv of [MoO₂(acac)₂] (100 mg, 0.30 mmol) as well as 1 equiv of **HL3** (104 mg, 0.30 mmol) were dissolved in dry CH₃CN (5 mL) in a Schlenk tube under N₂ atmosphere. Subsequently, the initially yellow to orange reaction solution was stirred at room temperature for 24 h accompanied by a darkening to deep brown. The reaction solution was then filtered through a glass frit packed with Celite and the solvent evaporated *in vacuo*. The brown solids were dissolved in dry Et₂O (5 mL) and the solution allowed to stand at ambient temperature. The initially brown solution turned orange gradually and white solids started to precipitate. After concentration of the orange liquid layer to a minimum, the precipitate was filtered off and washed twice with a small portion of cold dry Et₂O to give **5** as a pale yellow, crystalline solid (26 %, 43 mg). Crystals suitable for single-crystal X-ray diffraction analysis have been obtained via recrystallization from CH₃CN. m.p. 222 °C (decomp.); ¹H NMR (300 MHz, CD₃CN, 25 °C) δ: 8.52 (s, 1H, CH=N), 7.68 (d, 1H, ArH), 7.42 (d, 1H, ArH), 7.16 (bs, 1H, NH), 4.39 (s, 1H, CH), 3.15–2.98 (m, 2H, CH₂), 2.15 (s, 3H, CH₃), 1.44 (s, 9H, *t*Bu), 1.39 (s, 3H, CH₃), 1.32 (s, 9H, *t*Bu), 1.27 (s, 9H, *t*Bu) ppm; ¹³C NMR (75 MHz, CD₃CN, 25 °C) δ: 215.49 (RC=OR), 169.47 (RC=ONH), 168.81 (CH=N), 159.09 (Ar–O), 143.86, 140.07, 132.47, 129.76, 121.38 (Ar), 85.51 (CH), 83.78 (C–O), 53.29 (CH₂), 52.61, 36.10, 35.04 (q-*t*Bu), 31.60 (CH₃), 31.44, 29.88, 28.66 (*t*Bu), 26.02 (CH₃) ppm; IR (ATR, cm⁻¹): ν 1661 (m), 1626 (m), 916 (Mo=O, s), 895 (Mo=O, s), 874 (s), 857 (s), 572 (m); Anal. calcd for C₂₆H₄₀MoN₂O₆: C, 54.54; H, 7.04; N, 4.89. Found: C, 54.41; H, 6.95; N, 4.90.

Supporting Information.

NMR spectra and full crystallographic details are provided within the electronic supporting information (SI).

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Reaction of bidentate iminophenolate ligands employing amide functionalities with a $[\text{MoO}_2]^{2+}$ source results in the formation of mononuclear dioxidomolybdenum(VI) complexes, coordinated by tetradentate C–C coupled adduct or imidazolidine ligand frameworks arising from unprecedented metal mediated C–C bond formation and subsequent cyclization via C–N bond formation.