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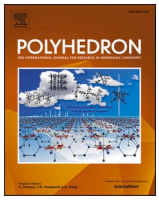

The synthesis and characterization of a bidentate complex of 1,1′-(1,3-phenylene)bis(3-butylimidazolium) pincer proligand with molybdenum – A non-pincer binding mode

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ABSTRACT

The synthesis of the bidentate Mo complex tetrachlorido[6-(3′-butylimidazolium-1′-yl)-2-(3″-butylimidazol-1″-yl-2″-idene-κC^2)phenyl-κC^1]molybdenum(IV) **3** was carried out using the metalation followed by transmetalation methodology. The transmetalation process led to a bidentate complex after the reaction of DCM with $HNMe_2$ formed an acidic ammonium ion that protonated the bidentate complex. Optimization of the synthetic methodology provided the tetrachlorido[6-(3′-butylimidazolium-1′-yl)-2-(3″-butylimidazol-1″-yl-2″-idene-κC^2)phenyl-κC^1]molybdenum(IV) complex in high yield. The crystal structure of the bidentate complex, **3**, is reported herein. Attempts to avoid the acidic reaction conditions with different solvents or starting materials produced the bisligated Mo complex bis[2,6-bis(3′-butylimidazol-1′-yl-2′-idene-κC^2)phenyl-κC^1]molybdenum(IV) dichloride based on MS analysis. Electronic and coordinative unsaturation in the resulting bidentate complex, **3**, open new possibilities for coordination of incoming substrates while also allowing access to the pincer-like motif via oxidative addition. Access to the interconversion of a NHC to/from imidazolium opens new avenues of non-innocent ligand pathways for proton shuttling in reactions such as nitrogen reduction to ammonia.

1. Introduction

Most of the nitrogen used for fertilizers and commodity chemicals comes from nitrogen fixation processes, most notably from the Haber-Bosch process (HBP) [1,2]. On the other hand, energy consumption for nitrogen fixation through the HBP presents a major challenge in the economy and climate of the world [1,2]. This energy is spent in the steam reforming processes for the production of H_2 used in the formation of ammonia, as well as in the high pressures and temperatures of the HBP [2].

An alternative for the HBP is the use of a well-defined catalyst for the reaction between N_2 and a synthetic equivalent of H_2 (H^+/e^-) [2,3]. Such a synthetic equivalent would be presented in the form of an acid (H^+) and a reductant (e^-) to replace the use of H_2 gas [4]. High pressures and temperatures would be potentially avoided this way. Ideally, water would take the role of the acid, and a cheap reagent that is easy to handle would take the role of the reductant. Alternatively, the reduction could be effected by an electrode [5]. Although most dinitrogen activation reports have used strong acids and reductants [6,7], significant progress has been made already by the Nishibayashi group. Recently, in 2019, they reported a set of conditions with a (PNP)Mo pincer complex, water or alcohol, and SmI_2 that showed up to 92% yield of NH_3 [8,9]. However, the SmI_2 is a stoichiometric reagent in this reaction. In addition to this example, Mo pincer ligands have shown great potential for nitrogen fixation in the last decade [7,10]. A relatively unexplored area of interest is the use of CCC-NHC ligands for the formation of Mo pincer complexes, of which there has been no report to date [3,4,6,7,11]. Strongly donating Mo CCC-NHC complexes [12] may accelerate catalysis and lower the energetic requirements enumerated above.

For this reason, the synthesis of the first Mo CCC-NHC pincer and its characterization are of special interest for its use as a potential nitrogen fixation catalyst. Herein, we report the application of the metalation-transmetalation procedure with a CCC-NHC proligand as applied to molybdenum. The usual methodology that has been used for the synthesis of previous pincer complexes has not been found to produce the desired Mo CCC-NHC monopincer complexes. Instead, a bidentate Mo complex has been isolated and characterized by NMR spectroscopy and X-ray crystallography. The chemical behavior of molybdenum is

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markedly distinct from metals that have been reported before (Rh [13,14], Ir [13], Ni [15] and Pt [16,17]). Additionally, attempted improvement in the methodology to yield the desired Mo CCC-NHC monopincer complex led to the observation of a bis-ligated pincer Mo complex.

2. Results and discussion

2.1. Initial attempted pincer synthesis – formation of a bidentate Mo complex (3)

Following the reported procedures for the metalation-transmetalation methodology [18], a homogeneous solution of the chloride salt **1** in dry DCM was allowed to react with a slight excess (1.1 eq) of freshly sublimed $Zr(NMe_2)_4$ in an NMR tube (Scheme 1). The disappearance of the imidazolium protons (11.9 ppm) of the chloride salt **1** and the appearance of a doublet of multiplets (4.6–4.0 ppm) was consistent with the successful metalation (Fig. S1) [19–21]. The doublet of multiplets has been reported to be the N-CH_2- diastereotopic signals of the butyl chain of the Zr pincer [22–25]. Subsequently, addition of $MoCl_3(thf)_3$ to the reaction mixture yielded a homogeneous purple solution which did not present a ^{1}H NMR spectrum with signals consistent with a paramagnetic species. Instead, the signals were in the region between 8 and 0 ppm, which is the zone expected for a diamagnetic complex. Furthermore, the Zr pincer diastereotopic signals disappeared and a new triplet signal (4.6 ppm) appeared, indicating a complete transmetalation reaction. The diamagnetic Mo pincer complex **2** with an indeterminate coordination sphere was the presumptive product of this reaction. Following the reaction by ^{1}H NMR spectroscopy showed the slow appearance of a second diamagnetic species during the course of 20 h. A signal at 9.06 ppm was assigned to a protonated imidazolium moiety, evidencing the decomplexation of one of the NHCs of the ligand (Scheme 1, Fig. S1). Removal of the solvent after observing the formation of complex **2** yielded an intractable solid composed of a mixture of the Mo complex and Zr by-products.

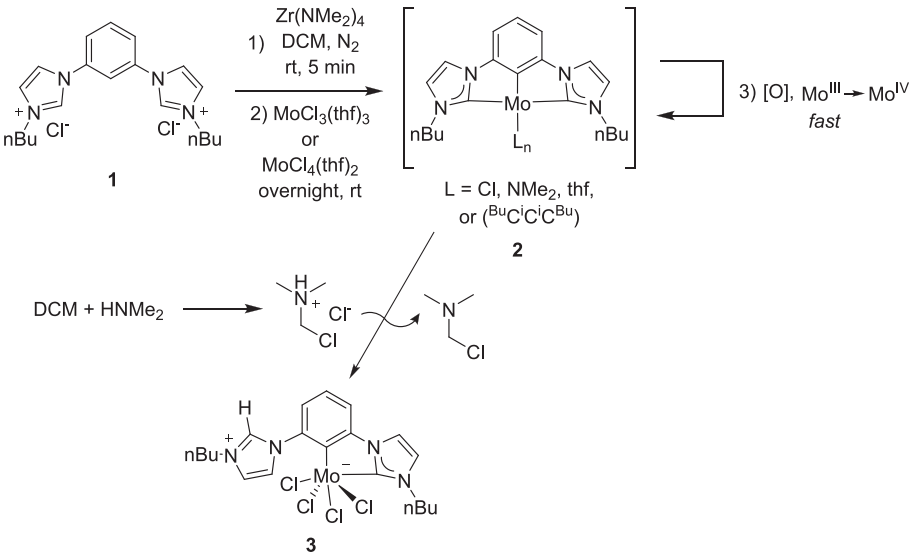
Originally, the goal of this metalation-transmetalation reaction with $MoCl_3(thf)_3$ was the synthesis of a monoligated Mo(III) pincer complex. Attempts at crystallization of the crude reaction mixture yielded X-ray quality crystals of Mo(IV) complex **3**. This result was consistent and reproducible. The same reaction procedure was repeated with $MoCl_4(thf)_2$ and the ^{1}H NMR spectra of the reaction mixture was collected immediately after addition. The signals observed were characteristic of a diamagnetic complex as in the transmetalation with $MoCl_3(thf)_3$. This observation was consistent with the formation of the same diamagnetic CCC-NHC Mo(IV) complex **2**, supporting the conclusion that the oxidation step from Mo(III) to Mo(IV) happened before the protonation of the ligand. After letting the reaction mixture sit overnight, the signals of the bidentate Mo complex **3** were also observed.

The protonation of the Mo complex **2** was explained by the presence of ammonium ions ($R_3NH^+Cl^-$) in the reaction medium. The ammonium ions were formed from the reaction between DCM and dimethylamine that was previously released by the metalation of the chloride salt **1** with $Zr(NMe_2)_4$ [26,27]. The reaction rate of dimethylamine and DCM has been measured to have a half-life of 14.5 h [26], which is consistent with the rate of formation of the bidentate Mo complex **3**.

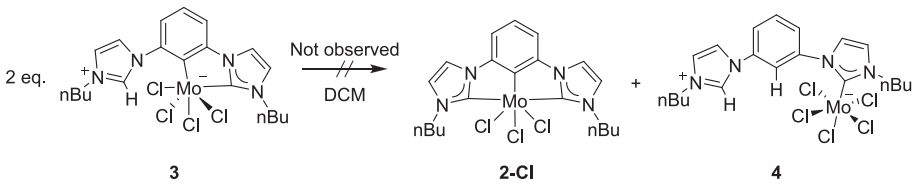
Additionally, if the reaction was left to sit for more than 1 day, the signals corresponding to Mo complex **3** slowly disappeared and an intractable, purple solid formed. Further attempts at characterizing this solid by ^{1}H NMR spectroscopy or by mass spectrometry produced no peaks in the observed spectra. The solid was also insoluble in DMF and DCM. Thus, it is presumed that Mo complex **3** either decomposed into a polymeric material of unknown structure or reacted further to form an insoluble oligomeric complex or a bimetallic complex with a second Mo bidentate moiety.

The reaction between DCM and dimethylamine has not posed an inconvenience in the synthesis of late transition metal CCC-NHC complexes of Rh [13,14], Ir [13], Ni [15] and Pt [16,17]. These complexes were air- and moisture-stable [18,28], and they were stable towards the mildly acidic protons of the ammonium chloride salt that is present in the metalation-transmetalation reaction in DCM. Another explanation for the oxidation of the elusive Mo pincer complex is the reaction of Mo (III) directly with DCM. This type of oxidation has been discussed before, where $Mo(N(Ar)(t\text{Bu}))_3$ complexes have reacted with DCM, yielding $Mo(N(Ar)(t\text{Bu}))_3Cl$ and $Mo(N(Ar)(t\text{Bu}))_3CH$ complexes [29,30]. Oxidation of the starting metal sources was previously reported during the synthesis of a CCC-NHC Rh(III) pincer complex [14,20], and a CCC-NHC Co (III) pincer complex [25,31]. On the other hand, the synthesis of Re complexes has not shown this behavior [32].

Surprisingly, in an interesting observation, the NHC was protonated instead of the aryl anion, even though the imidazolium proton is more acidic (pKa: 18.6) than the aryl proton (pKa: ~44) (Scheme 2) [33]. It is likely that the chelation effect of the bidentate complex stabilizes the aryl anion, avoiding the subsequent protonation from the acidic protons produced by the solvent. Such chelation effect was strong enough to even avoid the deprotonation of the bidentate Mo complex **3** in a



Scheme 1. Synthesis of bidentate Mo(IV) complex **3**.



Scheme 2. The acid-base disproportionation reaction of **3** was not observed.

disproportionation reaction (Scheme 2). Neither the Mo pincer complex **2-Cl**, nor the protonated NHC-complex **4** were observed by ^{1}H NMR spectroscopy of a solution of the bidentate Mo complex **3** in DCM. This type of chemical reactivity of the ligand and the stability of the bidentate complex **3** opens the possibility of using one of the NHCs bound to the metal center as a proton shuttle for reactions such as N_2 reduction to NH_3 [34–36].

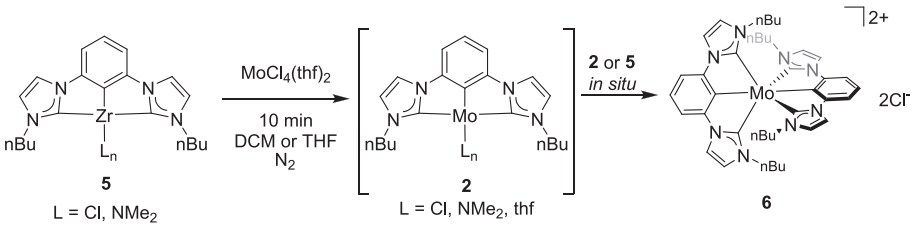
2.2. Attempted optimization of the reaction conditions

The previous observations on the behavior of DCM and dimethylamine led to the design of an experiment that limited the amount of dimethylamine in the reaction environment. The hypothesis was that no free dimethylamine would be released by using an isolated Zr pincer complex for the synthetic procedure. The (CCC-NHC)Zr pincer complex **5**, described in previous reports [14,24,32], was dissolved in DCM in an NMR tube at room temperature under inert atmosphere (Scheme 3). After the addition of $MoCl_4(thf)_2$, the solution slowly turned deep purple and a solid precipitated after 10 min. The ^{1}H NMR spectrum showed the disappearance of the two signals of $MoCl_4(thf)_2$ (12.6 ppm, −35.0 ppm) and the appearance of signals at 3.7 and 1.8 ppm [37], which are consistent with the dissociation of THF from $MoCl_4(thf)_2$ to free THF (Fig. S6). At the same time, broad signals appeared in the region between 4 ppm and 1 ppm. The presence of a lone triplet at 4.42 ppm was indicative of a successful transmetalation and the formation of a single Mo complex. Most notably, the signals for the bidentate Mo complex **3** did not appear after letting the NMR tube sit overnight. No further changes were observed after two days of standing (Fig. S7). The mixture was passed through a Celite plug and the filtrate was analyzed by exact mass determination. The mass spectrum showed a mixture of complexes with masses consistent with the Mo complex of one pincer ligand (**2**) and the Mo complex with two pincer ligands (**6**) (Fig. S8). The signals with the highest intensity are consistent with fragments **7**, **8** and **9** (Fig. 1). The proposed formulas for these fragments were compared against chemical formulas with the same nominal mass and different elemental composition (Table S9, S10). The formulas containing oxygen had the smallest difference in mass (ppm) to the observed signals. Trace amounts of fragments **10** and **11** were observed in the spectrum. Additionally, a signal consistent with the proligand with an oxygen atom **12** was detected. Although the position of the oxygen atoms cannot be determined from the mass spectrometry data, the observation of the oxidated proligand **12** suggested that the oxygen had been inserted between the Mo-C^{NHC} bond instead of being bound to the metal in fragments **7**, **8** and **9**. Furthermore, since the ^{1}H NMR spectrum showed the formation of a single product, fragments **10** and **11** may be forming during the collection of the mass spectrometry data after ligand decomplexation of Mo complex **6**. The parent ions for the Mo pincer complex **6** were not detected (Table S11A, B). Likewise, no signals consistent with the Mo pincer complex **2-Cl** were detected. Since the synthesis of complex **6** was made under inert atmosphere with degassed and dry solvent, the oxygen addition may be happening during the handling of the sample when the exact mass determination is taking place. The data above implied the formation of the Mo bis-ligated complex **6** instead of the monoligated complex **2**.

In an attempt to keep the Mo complex **2** from forming the bis-ligated Mo complex **6**, slow addition of the Zr complex **5** to a solution of $MoCl_4(thf)_2$ in DCM was conducted. During the addition, the amount of $MoCl_4(thf)_2$ was always in excess with respect to the Zr complex **5**. Even with an excess of $MoCl_4(thf)_2$, the major product detected by mass spectrometry was the bis-ligated complex **6**. Changing the reaction solvent to THF also yielded bis-ligated complex **6**. Attempts at crystallization of complex **6** have been met with failure to this date.

2.3. Crystal structure of bis-ligated Mo complex *3*

Complex **3** contained a formally Mo(IV) anion arranged in a distorted octahedral geometry in the solid state (Fig. 2). In the crystal, two molecules (A and B, Fig. S12) of complex **3** crystallized together in the asymmetric unit. To the best of our knowledge, no crystal structures of aryl-NHC bidentate complexes similar to complex **3** have been reported [11]. Lacking chelating examples, we compared the Mo-C^{aryl} and the Mo-C^{NHC} bond lengths from different complexes. The length of the Mo-C^{aryl} bond was 2.34(3) Å in molecule A and 2.32(2) Å in molecule B. These bond lengths were significantly longer than previously reported Mo-C^{aryl} distances in pincer complexes. Shorter bond distances can be found in [(OCO)Mo(CMes)(thf)$_2$] (2.1479(13) Å) [38], [(POCOP)Mo(N)(I)][Na(15-crown-5)] (2.167(3) Å) [39], [K(thf)$_2$][(PCP)Mo(CO)$_3$] (2.242(3) Å) [40], and [(PCP)Mo(Br)(CO)$_3$] (2.286(4) Å) [41]. Likewise, the Mo-C^{NHC} bond distance is longer than those reported in the literature (2.39(4) Å) (Fig. 3). A Mo(VI) complex reported by the Land group presents a Mo complex **13** with a slightly longer Mo-C^{NHC} bond length of 2.414 Å [42]. When compared to Mo(IV) complexes, the Mo-C^{NHC} distance in **3** was longer than the longest Mo-C^{NHC} distance of complexes **14**, **15**, and **16** (2.318(2) Å) [43]. They are also longer than reported Mo (0) complexes **17** [44], **18** [45], and **19** [46], which have been found to possess some of the longest Mo-C^{NHC} bond lengths among the monodentate NHC-Mo complexes. The long bond lengths of the bidentate Mo complex **3** may be caused by a high electron density in the Mo center. This electron density results from the presence of the strongly electron-donating bidentate ligand and the formally anionic molybdate metal



Scheme 3. Synthesis of bis-ligated Mo pincer complex **6**, [(CCC)$_2$Mo]Cl$_2$.

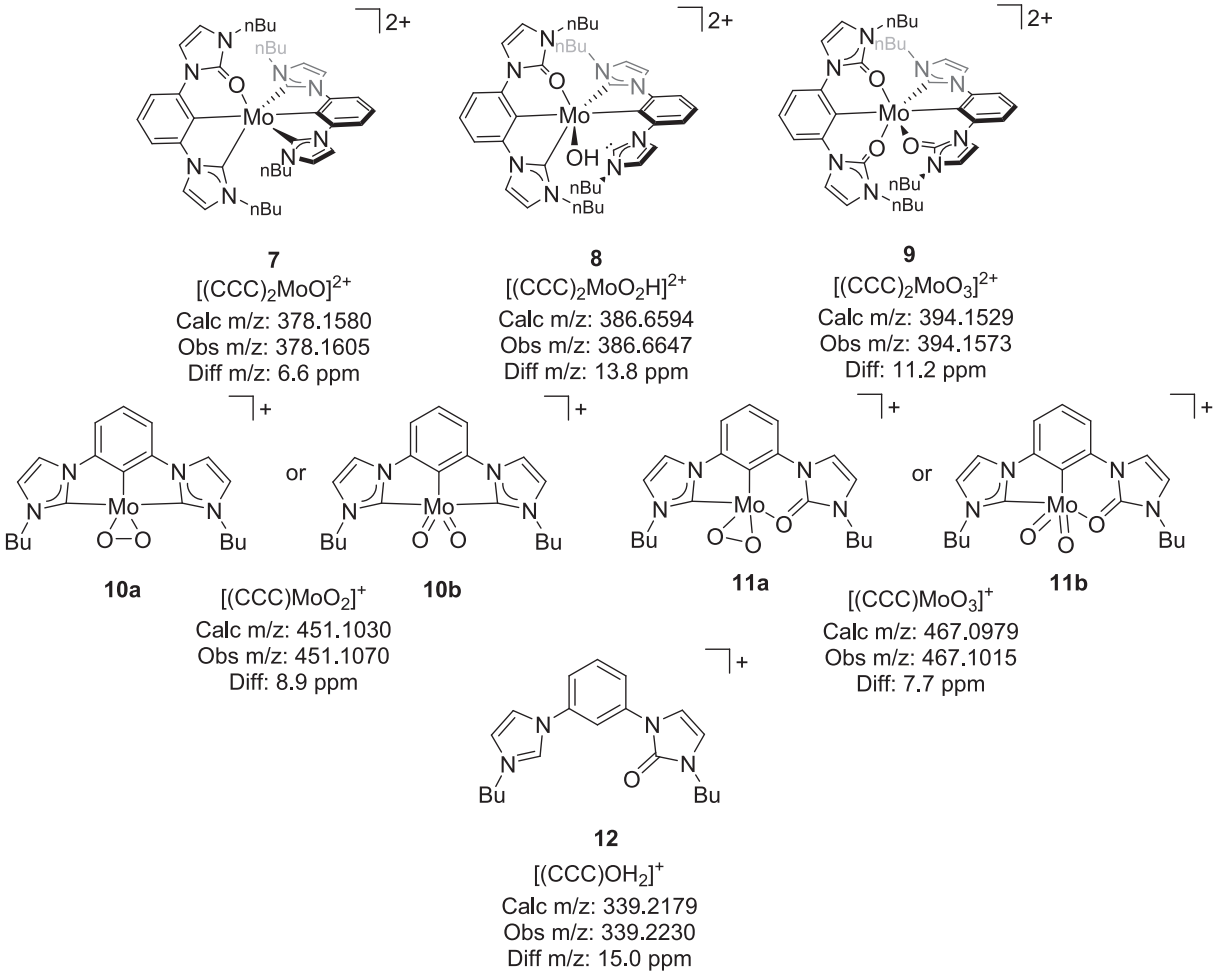


Fig. 1. Proposed structures for the fragments observed in the mass spectrometry spectrum.

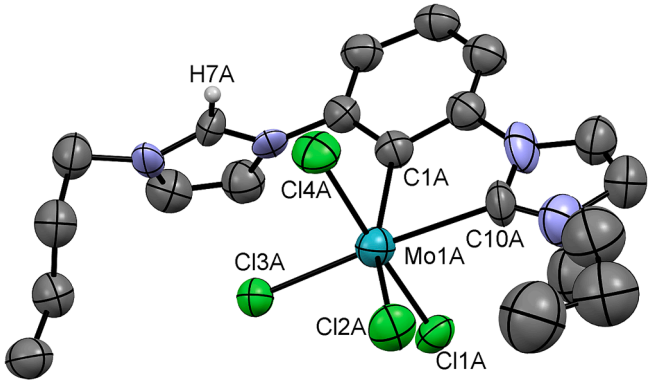


Fig. 2. ORTEP drawing of one of the molecules in the unit cell of **3**. H atoms except H7A are omitted for clarity. Ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (°): Mo1A-C1A, 2.34(3); Mo1A-C10A, 2.39(4); Mo1A-Cl1A, 2.451(8); Mo1A-Cl2A, 2.455(8); Mo1A-Cl3A, 2.433(7); Mo1A-Cl4A, 2.436(9); C1A-Mo1A-C10A 71.2(11), C1A-Mo1A-Cl2A 160.0(8). The second molecule is shown in the SI.

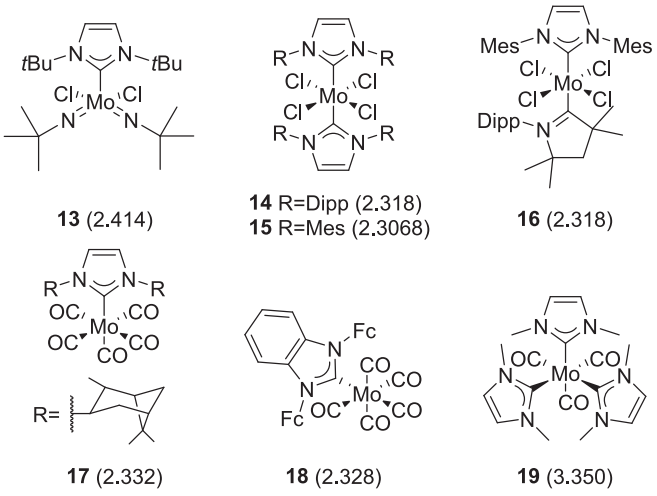


Fig. 3. Comparison of Mo-C^{NHC} bond lengths of select Mo complexes (Å). Fc = ferrocenyl.

center.

3. Conclusions

The synthesis and crystal structure of the first example of a stable Mo bidentate complex from a CCC-NHC pincer proligand has been reported herein. The synthesis was carried out using a metalation-transmetalation methodology yielding the bidentate complex, **3**, as a major product. An alternative synthetic procedure utilizing an isolated CCC-NHC pincer Zr complex yielded the bis-ligated complex **6**. The acidic environment reported in this work, although relatively inert to late transition metals, may pose a problem in the synthesis of pincer

complexes of mid-transition metals. The formally negative Mo center presents longer bond lengths to the ligand in comparison to known Mo complexes with NHC or aryl ligands. Further studies to convert the bidentate complex to the tridentate complex and establish the reversibility of the protonation are ongoing.

4. Experimental section

4.1. General

An N_2 glove box was used for the experiments. The imidazolium salts for the starting materials were prepared using previously reported literature procedures [19,20]. All solvents used in these experiments were degassed with N_2 and passed through two columns of activated alumina. $MoCl_3(thf)_3$ was used as received from Strem, under inert, dry conditions. $MoCl_4(thf)_2$ was synthesized following a modified literature procedure [47]. Freshly made $MoCl_4(thf)_2$ was used for the reactions. Zr$(NMe_2)_4$ was purchased from Strem, further purification was performed via sublimation on a cold finger under high vacuum before use. CD_2Cl_2 was purchased from Cambridge Isotope Laboratories and passed through two columns of activated basic alumina prior to use. ^1H and ^{13}C NMR spectra were collected on a Bruker Avance 300 MHz and a Bruker Avance DRX 500 MHz. X-ray crystallography data was collected on a Bruker single crystal diffraction facility at Mississippi State University. The X-ray intensity data was measured at low temperature (T = 273 K), using a three circles goniometer Kappa geometry with a fixed Kappa angle at = 54.74 deg Bruker AXSD8 Venture, equipped with a Photon 100 CMOS active pixel sensor detector. A monochromatized copper X-ray radiation (λ = 1.54178 Å) was selected for the measurement. All frames were integrated with the aid of the Bruker SAINT software 1 using a narrow-frame algorithm. Using the Bruker SHELXT Software Package 3, refinement of the structure was carried out by least squares procedures on weighted F2 values using the SHELXTL-2018/3 4 included in the APEX3 v2019 1.0, AXS Bruker program 5. Graphics were performed using softwares: Mercury V.4.2.0: (https://www.ccdc.cam.ac.uk/) and POV-Ray v3.7: (The Persistence of Vision Raytracer, high quality, free software tool).

4.2. Syntheses

4.2.1. Synthesis of $MoCl_4(thf)_2$ following a modified literature procedure [47]

$MoCl_5$ (200 mg) was dissolved in MeCN (2 mL). The reaction was stirred overnight, followed by removal of the solvent by decanting, yielding a purple powder. The powder was triturated with MeCN (2 mL) and the solvent was decanted again. THF (2 mL) was added and the solution was stirred for 2 h. A microcrystalline yellow-orange powder slowly formed during the stirring. The powder was allowed to settle, the supernatant was decanted, and the powder was dried under reduced pressure. (141.9 mg, 46 %). ^1H NMR (300 MHz, CH_2Cl_2): δ 12.58 (br s, 8H, *FWHM* = 8.1 Hz), −35.04 (br s, 8H, *FWHM* = 15.2 Hz).

4.2.2. Synthesis of tetrachlorido[6-(3′-butylimidazolium-1′-yl)-2-(3″-butylimidazol-1″-yl-2″-idene-κC^2)phenyl-κC^1]molybdenum(IV) (3)

General procedure with $MoCl_3(thf)_3$: The 1,1′-(1,3-phenylene)bis(3-butylimidazolium) dichloride salt (**1**) (24 mg, 0.061 mmol) was carefully dissolved in DCM (2 mL) at room temperature yielding a clear and colorless solution. Zr$(NMe_2)_4$ (18 mg, 0.067 mmol) was added to this solution and the resulting mixture was left to stand for 5 min yielding a clear yellow solution. To this mixture, $MoCl_3(thf)_3$ (25 mg, 0.061 mmol) was added and was left to stand overnight under an inert atmosphere. The reaction mixture was then filtered through Celite and the filtrate was collected. Et_2O (2 mL) was added dropwise to the filtrate, resulting in a precipitate which was filtered and dried under reduced pressure to yield a brown powder of **3**. (12 mg, 35 %). X-ray quality crystals were grown on the walls of a vial via vapor diffusion of hexane into a saturated solution of **3** in DCM at −35 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ 9.06 (s, 1H), 7.56 (s br, 2H), 7.45 (d, J = 7.98 Hz, 1H), 7.38 (t, J = 7.52 Hz, 1H), 7.27 (s br, 1H), 7.07 (s br, 1H), 7.05 (d, J = 7.06 Hz, 1H), 4.57 (t, J = 7.57 Hz, 2H), 4.18 (t, J = 7.66 Hz, 2H), 2.01 (m, 2H), 1.93 (m, 2H), 1.46 (m, 4H), 1.02 (m, 3H), 0.97 (m, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 178.8, 147.6, 141.0, 136.9, 128.7, 124.0, 122.5, 122.4, 121.9, 115.2, 115.1, 51.1, 50.6, 34.2, 31.7, 20.1, 20.0, 13.9, 13.5.

NMR tube procedure with $MoCl_4(thf)_2$: The 1,1′-(1,3-phenylene)bis(3-butylimidazolium) dichloride salt (**1**) (7.9 mg, 0.020 mmol) was carefully dissolved in DCM (0.5 mL) at room temperature yielding a clear and colorless solution. Zr$(NMe_2)_4$ (5.9 mg, 0.022 mmol) was added to this solution and the resulting mixture was left to stand for 5 min yielding a clear yellow solution. To this mixture, $MoCl_4(thf)_2$ (8.1 mg, 0.021 mmol) was added and the reaction was monitored by ^1H NMR for 15 h. Complex **3** slowly formed in the reaction mixture.

4.2.3. Synthesis of bis[2,6-bis(3′-butylimidazol-1′-yl-2′-idene-κC^2)phenyl-κC^1]molybdenum(IV) dichloride (6)

General reaction: The (CCC-NHC)ZrL_n complex (**5**) (10.6 mg, 0.020 mmol) was dissolved in DCM or THF (3 mL). $MoCl_4(thf)_2$ (7.8 mg, 0.020 mmol) was added in one portion to the solution. The vial was left to sit 30 min, during which a brown-purple solid slowly precipitated. The reaction mixture was filtered through Celite and the solvent was removed.

Inverse addition: The (CCC-NHC)ZrL_n complex (**5**) (7.1 mg, 0.013 mmol) was dissolved in DCM (1 mL). The mixture was slowly added dropwise to a solution of $MoCl_4(thf)_2$ (5.0 mg, 0.013 mmol) in DCM (1 mL) in the course of 30 min. After every two drops, the vial was shaken manually. The vial was left to sit 30 min, during which a brown-purple solid slowly precipitated. The reaction mixture was filtered through Celite, and the solvent was removed.

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Author Contributions

Study design, data analysis, investigation, supervision, writing, reviewing, and revising of the manuscript by T.K.H. Initial observations and the rough outline of the manuscript were carried out by S.D. Extensive rewriting, final data collection, analysis, revising of the text, and revising of the manuscript were carried out by S.D.J. X-Ray crystallographic data collection and solution of the structures were performed by B.D.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data are included in the manuscript and supporting information.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2023.116714.

References

[1] FAO, Annual Report, 296 (2017) 1-180.
[2] G. Hochman, A.S. Goldman, F.A. Felder, J.M. Mayer, A.J.M. Miller, P.L. Holland, L. A. Goldman, P. Manocha, Z. Song, S. Aleti, ACS Sustain. Chem. Eng. 8 (2020) 8938–8948.

[3] Y. Tanabe, Y. Nishibayashi, Coord. Chem. Rev. 472 (2022), 214783.
[4] Y. Tanabe, Y. Nishibayashi, Chem. Soc. Rev. 50 (2021) 5201–5242.
[5] Y. Sun, Y. Wang, H. Li, W. Zhang, X.-M. Song, D.-M. Feng, X. Sun, B. Jia, H. Mao, T. Ma, J. Energy Chem. 62 (2021) 51–70.
[6] S. Kuriyama, Y. Nishibayashi, Tetrahedron 83 (2021) 131986.
[7] D.N. Stephens, M. O'Hagan, E. Hulley, M.T. Mock, Transition metal complexes for dinitrogen coordination and activation, in: E.C. Constable, G. Parkin, L. Que (Eds.), Comprehensive Coordination Chemistry III, Elsevier, 2021, pp. 363–409.
[8] Y. Ashida, K. Arashiba, K. Nakajima, Y. Nishibayashi, Nature 568 (2019) 536–540.
[9] Y. Ashida, S. Kondo, K. Arashiba, T. Kikuchi, K. Nakajima, S. Kakimoto, Y. Nishibayashi, Synthesis (Germany) 51 (2019) 3792–3795.
[10] S.J.K. Forrest, B. Schluschaß, E.Y. Yuzik-Klimova, S. Schneider, Chem. Rev. 121 (2021) 6522–6587.
[11] The search was carried out in the CCDC database on the 26th of July, 2023.
[12] T.R. Helgert, X. Zhang, H.K. Box, J.A. Denny, H.U. Valle, A.G. Oliver, G. Akurathi, C.E. Webster, T.K. Hollis, Organometallics 35 (2016) 3452–3460.
[13] E.B. Bauer, G.T. Andavan, T.K. Hollis, R.J. Rubio, J. Cho, G.R. Kuchenbeiser, T. R. Helgert, C.S. Letko, F.S. Tham, Org. Lett. 10 (2008) 1175–1178.
[14] E.D. Amoateng, J. Zamora-Moreno, G. Kuchenbeiser, B. Donnadieu, F. Tham, V. Montiel-Palma, T. Keith Hollis, J. Organomet. Chem. 979 (2022).
[15] J.D. Cope, N.P. Liyanage, P.J. Kelley, J.A. Denny, E.J. Valente, C.E. Webster, J. H. Delcamp, T.K. Hollis, Chem. Commun. 53 (2017) 9442–9445.
[16] X. Zhang, A.M. Wright, N.J. DeYonker, T.K. Hollis, N.I. Hammer, C.E. Webster, E. J. Valente, Organometallics 31 (2012) 1664–1672.
[17] X. Zhang, B. Cao, E.J. Valente, T.K. Hollis, Organometallics 32 (2013) 752–761.
[18] J.A. Denny, G.M. Lang, T.K. Hollis, CCC-NHC Pincer Complexes: Synthesis, Applications, and Catalysis, in: D. Morales-Morales (Ed.), Pincer Compounds: Chemistry and Applications, Elsevier, 2018, pp. 251–272.
[19] R.J. Rubio, G.T.S. Andavan, E.B. Bauer, T.K. Hollis, J. Cho, F.S. Tham, B. Donnadieu, J. Organomet. Chem. 690 (2005) 5353–5364.
[20] G.T.S. Andavan, E.B. Bauer, C.S. Letko, T.K. Hollis, F.S. Tham, J. Organomet. Chem. 690 (2005) 5938–5947.
[21] H.U. Valle, G. Akurathi, J. Cho, W.D. Clark, A. Chakraborty, T.K. Hollis, Aust. J. Chem. 69 (2016) 565–572.
[22] T.R. Helgert, T.K. Hollis, E.J. Valente, Organometallics 31 (2012) 3002–3009.
[23] T.R. Helgert, T.K. Hollis, A.G. Oliver, H.U. Valle, Y. Wu, C.E. Webster, Organometallics 33 (2014) 952–958.
[24] W.D. Clark, J. Cho, H.U. Valle, T.K. Hollis, E.J. Valente, J. Organomet. Chem. 751 (2014) 534–540.
[25] S.W. Reilly, C.E. Webster, T.K. Hollis, H.U. Valle, Dalton Trans 45 (2016) 2823–2828.
[26] G.O. Nevstad, J. Songstad, Acta Chem. Scand. 38b (1984) 469–477.
[27] L.-M. Jiang, K. Xiang, H.-J. Jiao, J.-L. Yang, H.-T. Qu, X.-T. Xu, B. Wen, D.-Y. Zhu, S.-H. Wang, Tetrahedron Lett 123 (2023) 154564.
[28] S. Dey, M. Rawat, T.K. Hollis, Carbene-Based Pincer Ligands, in: E.C. Constable, G. Parkin, L. Que (Eds.), Comprehensive Coordination Chemistry III, Elsevier, 2021, pp. 607–649.
[29] A. Furstner, J. Am. Chem. Soc. 143 (2021) 15538–15555.
[30] A. Furstner, C. Mathes, C.W. Lehmann, Chem. Eur. J. 7 (2001) 5299–5317.
[31] J.A. Denny, R.W. Lamb, S.W. Reilly, B. Donnadieu, C.E. Webster, T.K. Hollis, Polyhedron 151 (2018) 568–574.
[32] H.H. Pham, B. Donnadieu, T.K. Hollis, Appl. Organomet. Chem. n/a (2022), e6789.
[33] F.G. Bordwell, Acc. Chem. Res. 21 (1988) 456–463.
[34] S. Qu, Y. Dang, C. Song, M. Wen, K.W. Huang, Z.X. Wang, J. Am. Chem. Soc. 136 (2014) 4974–4991.
[35] S.S. Nadif, M.E. O'Reilly, I. Ghiviriga, K.A. Abboud, A.S. Veige, Angew. Chem. Int. Ed. Engl. 54 (2015) 15138–15142.
[36] C. Hou, J. Jiang, Y. Li, C. Zhao, Z. Ke, ACS Catalysis 7 (2016) 786–795.
[37] G.R. Fulmer, A.J.M. Miller, N.H. Sherden, H.E. Gottlieb, A. Nudelman, B.M. Stoltz, J.E. Bercaw, K.I. Goldberg, Organometallics 29 (2010) 2176–2179.
[38] C.D. Roland, S. VenkatRamani, V.K. Jakhar, I. Ghiviriga, K.A. Abboud, A.S. Veige, Organometallics 37 (2018) 4500–4505.
[39] T.J. Hebden, R.R. Schrock, M.K. Takase, P. Müller, Chem. Commun. 48 (2012) 1851–1853.
[40] D. Himmelbauer, M. Mastalir, B. Stöger, L.F. Veiros, K. Kirchner, Organometallics 37 (2018) 3631–3638.
[41] W. Eder, B. Stöger, K. Kirchner, Monatsh. Chem. 150 (2019) 1235–1240.
[42] M.A. Land, K.N. Robertson, S.T. Barry, Organometallics 39 (2020) 916–927.
[43] C. Luz, E. Glok, G. Horrer, U. Radius, Dalton Trans 51 (2022) 18337–18352.
[44] M.W. Day, T.M. Trnka, R.H. Grubbs, CCDC 178188: Experimental Crystal Structure Determination, 2004.
[45] E.L. Rosen, C.D. Varnado, A.G. Tennyson, D.M. Khramov, J.W. Kamplain, D. H. Sung, P.T. Cresswell, V.M. Lynch, C.W. Bielawski, Organometallics 28 (2009) 6695–6706.
[46] K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, T. Priermeier, P. Kiprof, J. Organomet. Chem. 498 (1995) 1–14.
[47] J.R. Dilworth, R.L. Richards, G.J.J. Chen, J.W. McDonald, The Synthesis of Molybdenum and Tungsten Dinitrogen Complexes, in: R.J. Angelici (Ed.) Inorganic Syntheses: Reagents for Transition Metal Complex and Organometallic Syntheses, 1990, pp. 33-43. https://10.1002/9780470132593.ch7.