ORGANOMETALLICS

Syntheses and Structures of $[CH_2(NC_nH_{2n})_2]Mo(CO)_4$ (n = 4,5) Complexes with Bis(cycloamine) Ligands Easily Prepared from CH_2CI_2

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S Supporting Information

ABSTRACT: Dipyrrolidylmethane, $CH_2(pyr)_2$, and dipiperidylmethane, $CH_2(pip)_2$, are synthesized via the condensation of their respective secondary amine precursors and dichloromethane at room temperature in the absence of light. Their use as chelating ligands is shown by the isolation and complete characterization of $[CH_2(pyr)_2]Mo(CO)_4$ and $[CH_2(pip)_2]$ - $Mo(CO)_4$ complexes. X-ray analysis reveals the methylene bis(cycloamines) to possess a sharp bite angle between 61° and 63° and a strong steric impact on the surrounding carbonyl ligands as a result of their ring conformations.

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INTRODUCTION

Methylene bridged cyclic amines (Figure 1) are used as heterocyclic building blocks through amino methylations in





organic synthesis.¹⁻⁶ They can also be employed as organocatalysts in aldol condensations and transesterifications.⁷⁻⁹ Their use in coordination chemistry as chelating ligands, however, has been largely unexplored. The earliest reported metal complexes, characterized only by infrared spectroscopy, were $[CH_2(pyr)_2]Mo(CO)_4$, **1**, and $[CH_2(pip)_2]Mo(CO)_4$, **2**, published in a brief communication by Lüttringhaus and Kullick in 1959.¹⁰ Jung et al. have used $CH_2(pip)_2$ as a coligand in the preparation of a benzoquinonatocobalt complex back in 2001.¹¹ And finally, in a recent 2014 article, Szymańska-Buzar et al. published a crystal structure of the $[CH_2(pip)_2]W(CO)_4$ complex, synthesized photochemically using $W(CO)_6$ thereby establishing the coordinating nature of $CH_2(pip)_2$.¹²

Preparing these methylene bis(cycloamines) is typically done by refluxing the mono secondary amines with paraformaldehyde in a high-boiling solvent.^{1,5,9} Another method involves the transamination with $N_i N_i N'_i N'_i$ tetramethyldiaminomethane using Sm(NO₃)₂ or CuCl catalysts.² The use of fulvenes as a methylene source has also been noted.¹³ In their 2014 work, the authors noticed the formation of dipiperidylmethane from piperidine at room temperature in the presence of the bispiperidine complex, *cis*-(pip)₂W(CO)₄ with dichloromethane as solvent.¹² As the authors were involved in studying the catalytic properties of molybdenum and tungsten carbonyls for various chemical transformations, they had prematurely concluded that the *cis*-(pip)₂W(CO)₄ complex acts as the catalyst for this conversion. In reality, the transformation of piperidine to dipiperidylmethane with dichloromethane proceeds on its own (Scheme 1).

In this article, we wish to (1) summarize our efforts in elucidating the reaction conditions involved in preparing dipyrrolidyl- and dipiperidylmethanes directly from dichloromethane and (2) present the syntheses, structures, and complete characterizations of Lüttringhaus and Kullick's molybdenum complexes with said amines as ligands and the varying steric effects they exhibit around the metal center.

RESULTS AND DISCUSSION

Our initial interest was driven to understand the role of *cis*- $(pip)_2W(CO)_4$ complex as a catalyst in producing $CH_2(pip)_2$ from piperidine.¹² Upon running a series of experiments (Table 1), it soon became apparent that the metal does not play a role in this chemistry. In fact, both $CH_2(pyr)_2$ and $CH_2(pip)_2$ can be easily prepared by stirring pyrrolidine or piperidine, respectively, in dichloromethane at room temperature in the absence of light in good yields, as shown in Scheme 1. The

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Scheme 1. Synthesis of Dipyrrolidyl- And Dipiperidylmethanes from Dichloromethane



Table 1. Conditions Investigated for the Reaction of Piperidine with Dichloromethane a

test	addition of metal complex (mol %)	stirring under ambient light vs darkness	observed products
1	5% cis-(pip) ₂ W(CO) ₄	light	only salt
2	5% cis-(pip) ₂ W(CO) ₄	dark	ligand + salt
3	1% cis-(pip) ₂ W(CO) ₄	light	ligand + salt
4	1% cis-(pip) ₂ W(CO) ₄	dark	ligand + salt
5	1% W(CO) ₆	dark	ligand + salt
6	1% cis-(pip) ₂ Mo(CO) ₄	light	ligand + salt
7	1% cis-(pip) ₂ Mo(CO) ₄	dark	ligand + salt
8	-	light	only salt
9	-	dark	ligand + salt
10	-	dark	ligand + salt

^{*a*}Test reactions: 0.25 mL piperidine in 20 mL CH_2Cl_2 with or without metal addition in an open or Al foil covered vial. Stirred 24 h, excess CH_2Cl_2 removed and product composition determined via ¹H NMR on crude mixture.

starting amines themselves can double up as a base driving the reaction forward to give methylene bis(cycloamines) along with 2 equiv of the respective ammonium chloride salt. In an earlier work, Matsumoto et al. have shown this to occur for various secondary cyclic amines, albeit under high pressures, which is clearly not required.¹⁴ Their use of pressure may stem from alkylated amine byproducts observed in other high pressure organic reactions carried out in dichloromethane. The pressure could accelerate the reaction rate for tertiary amines to produce a chloromethylammonium salt, but it is not required for the reaction to take place.^{15,16} Mills et al. followed up with a detailed NMR study in 1987 showing the reaction of pyrrolidine with dichloromethane to proceed under ambient conditions.¹⁷ They present evidence for the formation of 1methylenepyrrolidinium chloride after the condensation of the first amine with dichloromethane followed by its rapid reaction with a second amine to yield dipyrrolidylmethane. The reaction of piperidine with various halomethanes have also been described as early as 1964.¹⁸ Rapid formation of dipiperidylmethane is seen to occur with a benzene solution of dibromomethane. More recent examples of alkyl and aromatic amine reactivities without the need of a catalyst or pressing conditions with dichloromethane can also be found in the literature.^{19,20}

An interesting observation from our test runs was the effect of ambient light on this reaction. While we do not have a complete understanding of its role, what can be said of a reaction under light is its unpredictability, yielding the piperidinium chloride salt as the sole product half the time (Table 1). Thus, all large-scale syntheses were carried out in aluminum foil covered flasks. The methylene bis(cycloamines) were spectroscopically pure after removal of salt and excess dichloromethane and can be used for further reactions without the need for distillation.

The chelation of $CH_2(pyr)_2$ and $CH_2(pip)_2$ to molybdenum carbonyls can be achieved either in a refluxing hexane solution for a couple days or in heptane over a few hours yielding the products as yellow solids in moderate yields (Scheme 2). Complex 2, $[CH_2(pip)_2]Mo(CO)_4$, containing dipiperidylmethane, is air-stable and can be stored in contact with air for long periods of time unlike its well-known bispiperidine analogue, $cis-(pip)_2Mo(CO)_4$, 3, which decomposes in the absence of inert atmosphere within a few days. It also exhibits somewhat better solubility than 3 being fully soluble in DMSO, partially soluble in CH₂Cl₂ and THF and minimally soluble in acetone, MeOH and Et₂O. Complex 1, $[CH_2(pyr)_2]Mo(CO)_4$ has similar if not slightly poorer solubility in the same solvents and is not air-stable, unlike 2. While some exposure to air is tolerable, storage for longer than a day needs to be under an inert atmosphere.

¹H NMR spectroscopy shows distinct changes in the chemical shifts of the free ligands versus the coordinated complexes. The bridging methylene protons experience a downfield shift of 1.2 ppm when bound to molybdenum (δ $3.21 \rightarrow 4.42$ ppm, CH₂(pyr)₂; δ 2.86 \rightarrow 4.09 ppm, CH₂(pip)₂). The methylene protons on the rings become diastereotopic with their signals splitting into pairs upon coordination. Hence, two pairs of multiplets for $CH_2(pyr)_2$ and three pairs of multiplets for $CH_2(pip)_2$ are observed for their complexes. This effect was also noted for the $[CH_2(pip)_2]W(CO)_4$ complex.¹² In the ${}^{13}C{}^{1}H$ NMR spectra, the bridging methylene carbons have a discrete signal between 80 and 90 ppm for all species. Furthermore, two downfield signals at 206 and 222 ppm representing the axial (cis to N) and equatorial (trans to N) carbonyl carbons on the molybdenum can be observed for the complexes. Infrared data reveal similar carbonyl stretching frequencies for complexes 1 and 2 indicating the electron donating capability to be nearly identical for both ligands (Figure 2).

Single crystals for X-ray diffraction studies were obtained via slow evaporation of Et_2O and CH_2Cl_2 solutions for complexes 1 and 2, respectively. Thermal ellipsoid plots and relevant bond distances are shown in Figure 3. Comparison of 2, $[CH_2(pip)_2]Mo(CO)_4$, with the previously determined structure of 3, ²¹ cis-(pip)_2Mo(CO)_4, shows the $CH_2(pip)_2$ ligand to

Scheme 2. Synthesis of $[CH_2(pyr)_2]Mo(CO)_4$, 1, (n = 1) and $[CH_2(pip)_2]Mo(CO)_4$, 2, (n = 2) Complexes





Figure 2. Infrared spectra of $[CH_2(pyr)_2]Mo(CO)_4$, 1 (red), and $[CH_2(pip)_2]Mo(CO)_4$, 2 (blue), complexes in dichloromethane.

have a larger steric impact on the surrounding carbonyls leading to a distorted octahedral geometry (Figure 4). With the amines tied back by the methylene group, a small bite angle of $62.55(14)^{\circ}$ is observed and the six-membered rings adopt a conformation that points toward the metal center, compressing the equatorial carbonyls and giving a C(2)-Mo(1)-C(2)'angle of $86.0(2)^{\circ}$. The average distance calculated between the equatorial carbonyl carbons and the closest ligand hydrogens is only 2.82 Å. This distance is a bit longer, 2.90 Å, and hence a lesser compression of the equatorial carbonyls, $88.76(13)^{\circ}$, is noted for the tungsten analogue.¹² The angle between the axial carbonyls of **2** is also compressed, with C(1)-Mo(1)-C(4)measuring $166.9(2)^{\circ}$, about 5° less than what is seen for complex **3**.

The crystal structure of 1 reveals the $CH_2(pyr)_2$ ligand to have a slightly smaller bite angle than $CH_2(pip)_2$ measuring at $61.25(8)^\circ$. The five-membered ring size of the pyrrolidyl groups exerts less influence sterically on the equatorial carbonyl carbons with the average distance separating them from the closest ligand hydrogens now at 3.16 Å. Thus, the angle between the equatorial carbonyls is closer to 90° with C(2)– Mo(1)-C(3) measuring 89.28(12)°. The influence on the axial carbonyls, however, remains similar to $CH_2(pip)_2$ with C(1)– Mo(1)-C(4) measuring 166.53(10)°. Co^{II}, Ni^{II}, and Zn^{II} complexes bearing the tetradentate N_2O_2 ligand $CH_2(pyr-2 COO)_2$, where each pyrrolidyl ring is substituted with a

carboxylate group in the 2-position, are the only other structural examples thus far with a N,N'-methylene bridged bis(cycloamine)-type ligand.^{22,23} The N–M–N angles measure 65.5(1)° (Co^{II}), 67.5(2)° (Ni^{II}), and 63.5(3)° (Zn^{II}), displaying again the severe bite angles imposed by these constrained chelates. Diamines with two carbons separating the nitrogen atoms show a much larger bite angle. The N-Mo-N angle for the less electron-releasing 1,10-phenanthroline ligand in the airstable complex, (phen)Mo(CO)₄, is seen to be $73.62(7)^{\circ}$, while the more electron-donating N,N,N',N'-tetramethylethylenediamine ligand reveals a bite angle of $77.98(9)^{\circ}$ for its air-stable complex, (TMEDA) $Mo(CO)_4^{24-27}$ Moving down the periodic group, methylene bridged phosphines display bite angles toward the higher end of the observed range for methylene bridged amines and larger. For example, dicyclohexylphosphinomethane shows 67.397(17)° and 75.70(2)° for (dcpm)Mo-(CO)₄ and (dcpm)NiCl₂ complexes, respectively.^{28,29}

CONCLUSIONS

The search for new ligands, especially those that offer a modular approach to their synthesis, is of constant interest to the inorganic community. We have demonstrated here that a sterically demanding diamine ligand can be prepared by the simple condensation of piperidine with dichloromethane. The coordination environment of the $[CH_2(pip)_2]Mo(CO)_4$ complex is starkly different to its untied $cis-(pip)_2Mo(CO)_4$ analogue as a result of the dipiperidylmethane rings now directed around the metal center as seen via single-crystal X-ray diffraction studies. The steric effect has less influence on neighboring ligands when the ring size is reduced by one carbon as with the dipyrrolidylmethane complex, $[CH_2(pyr)_2]$ -Mo(CO)₄. This ligand synthesis can be extended to less basic cyclic amines such as morpholine,³⁰ while on the other hand, employing substituted piperidines (ex: 3,5-dimethylpiperidine) could introduce even more bulk around the metal center. Sterically encumbering ligands are used in various transition metal chemistries and the surprisingly bulky nature of these methylene bis(cycloamines) with its extreme bite angles could prove useful as a new ligand toolset.



Figure 3. Structures of $[CH_2(pyr)_2]Mo(CO)_4$, 1 (left), and $[CH_2(pip)_2]Mo(CO)_4$, 2 (right). Thermal ellipsoids, probability level 50%, with select atom labeling. Hydrogen atoms omitted for clarity. Select bond distances (Å): Complex 1: N-Mo_{ave} = 2.326(2); axial C-O_{ave} = 1.147(3); equatorial C-O_{ave} = 1.166(3). Complex 2: N-Mo_{ave} = 2.338(3); axial C-O_{ave} = 1.123(7); equatorial C-O_{ave} = 1.157(4).



Figure 4. View down the axial carbonyls of *cis*-(pip)₂Mo(CO)₄, ²¹ **3** (left), [CH₂(pip)₂]Mo(CO)₄, **2** (center), and [CH₂(pyr)₂]Mo(CO)₄, **1** (right). Capped stick representations with angles around the molybdenum center. Average distance to the closest ligand hydrogens from the equatorial carbonyl carbon is shown by arrow. Inset figures display the angle facing away from ligand and between the axial carbonyls.

EXPERIMENTAL SECTION

Methods and Materials. Piperidine and pyrrolidine were purchased from Alfa Aesar and used as received. $Mo(CO)_6$ was obtained from Strem and GC grade heptane was purchased from EMD chemicals. Dichloromethane and hexane were purified by an MBraun Manual Solvent Purification System packed with Alcoa F200 activated alumina desiccant. NMR spectra were recorded on either a Varian INOVA 300 or 500 MHz spectrometer. ¹H and ¹³C NMR spectra were referenced to residual solvent resonances. Infrared spectra were obtained on a Bruker Tensor 27 FTIR spectrometer. Elemental analyses were determined by Atlantic Microlab (Norcross, GA).

Synthesis of Dipiperidylmethane, CH₂(pip)₂. Piperidine (10 mL, 8.62 g, 0.101 mol) and CH₂Cl₂ (20 mL) were stirred together in an aluminum foil covered vial. After 24 h, the solution was filtered to remove the white piperidinium chloride salt and the filtrate rotovaped to remove excess CH₂Cl₂. The resulting cloudy oil was treated with THF followed by filtration to precipitate and remove any additional salt. Removal of THF yields a pale yellow liquid product (4.21 g, 91%). Distillation was not required for further experiments. The NMR spectrum is clean and matches that previously reported:¹² ¹¹ H (CDCl₃) δ 1.43 (m, 4H), 1.55 (m, 8H), 2.42 (m, 8H), 2.86 (s, 2H, NCH₂N).

Synthesis of Dipyrrolidylmethane, $CH_2(pyr)_2$. A similar procedure to $CH_2(pip)_2$ was followed to give $CH_2(pyr)_2$ in greater than 70% yield. When crashing out pyrrolidinium chloride salt, Et_2O is used instead of THF. This salt is very hygroscopic and tends to dissolve in THF. Pure by NMR:¹⁷ ¹H (CDCl₃) δ 1.76 (m, 8H), 2.57 (m, 8H), 3.20 (s, 2H, NCH₂N).

Synthesis of [CH₂(pip)₂]Mo(CO)₄. Mo(CO)₆ (0.200 g, 0.757 mmol) and CH₂(pip)₂ (0.150 g, 0.823 mmol) were brought to reflux under an argon atmosphere in heptane (20 mL). After 2 h, a bright yellow product was filtered and washed with hexanes (0.122 g, 41%). IR data in CH₂Cl₂ (ν_{CO}): 1830 (m), 1870 (sh), 1890 (s), 2015 (w). ¹H NMR (CDCl₃): δ 1.17 (m, 2H), 1.71 (m, 4H), 1.77 (m, 2H), 2.00 (m, 4H), 2.55 (m, 4H), 3.20 (m, 4H), 4.09 (s, 2H, NCH₂N). ¹³C{¹H} NMR (*d*₆-DMSO): δ 22.1, 24.9, 63.7, 89.1 (NCH₂N), 206 (CO), 222 (CO). Anal. Calcd for C₁₅H₂₂MoN₂O₄: C, 46.16; H, 5.68; N, 7.18. Found: C, 45.86; H, 5.60; N, 7.06%.

Synthesis of $[CH_2(pyr)_2]Mo(CO)_4$. $Mo(CO)_6$ (0.157 g, 0.594 mmol) and $CH_2(pyr)_2$ (0.106 g, 0.687 mmol) were brought to reflux

under an argon atmosphere in hexane (30 mL). After 3 days, a bright yellow product was filtered and washed with hexanes (0.166 g, 77%). IR data in CH₂Cl₂ (ν_{CO}): 1832 (m), 1870 (sh), 1887 (s), 2014 (w). ¹H NMR (CDCl₃): δ 1.87 (m, 4H), 2.13 (m, 4H), 2.77 (m, 4H), 3.45 (m, 4H), 4.42 (s, 2H, NCH₂N). ¹³C{¹H} NMR (d_6 -DMSO): δ 22.5, 63.5, 82.7 (NCH₂N), 206 (CO), 223 (CO). Anal. Calcd for C₁₃H₁₈MoN₂O₄: C, 43.10; H, 5.01; N, 7.73. Found: C, 42.47; H, 5.19; N, 7.61%.

ASSOCIATED CONTENT

G Supporting Information

CIF file giving X-ray structural data for 1 and 2. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b00396.

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Notes

The authors declare no competing financial interest.

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(30) (a) Preparing dimorpholinylmethane requires reflux in dichloromethane over many days. Adding a base could accelerate the reaction as well as convert all the cyclic amine to the desired ligand (see ref 17). (b) Dimorpholinylmethane (CAS# 5625-90-1) and dipiperidylmethane (CAS# 880-09-1) can be purchased commercially from Alfa Aesar. Last checked on May 01, 2015.