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Microwave Synthesis of Mixed Carboxylato Osmium-Containing Sawhorse Compounds

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Microwave Synthesis of Mixed Carboxylato

Osmium-Containing Sawhorse Compounds

An Honors College Project Thesis

Presented to

The Department of Chemistry and Biochemistry

Abilene Christian University

In Partial Fulfillment

of the Requirements for

Honors Scholar

by

James Edgar Johnstone

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This Project Thesis, directed and approved by the candidate's committee,
has been accepted by the Honors College of Abilene Christian University
in partial fulfillment of the requirements for the distinction

HONORS SCHOLAR

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Dr. Jason Morris, Dean of the Honors College

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ABSTRACT

Three new osmium-containing sawhorse complexes of the formula $Os_2(\mu\text{-}O_2CR1)(\mu\text{-}O_2CR2)(CO)_4(L)_2$ were synthesized using microwave radiation. These complexes are the first examples of mixed-carboxylate ligand sawhorse complexes and offer a proof-of-concept to the idea of "cluster customization." The structures of these compounds are analyzed for their properties including how they interact with solvent molecules and how different axial ligands affect the amount of disorder in their crystal structures. Several follow-up investigations, including experiments using dicarboxylate ligands and axially connected sawhorse complexes, are described.

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1. Introduction

Sawhorse complexes are inorganic complexes containing a metal dimer which is surrounded by four equatorial CO ligands, two bridging carboxylate ligands, and two axial CO ligands. These complexes were given the name "sawhorse complexes" because of their resemblance to the workshop tool with the same name. The axial CO ligands are commonly replaced with other ligands, such as phosphines, which have been observed to increase stability of the sawhorse complexes[1]. The generic structure of a sawhorse complex can be seen in Schematic 1.
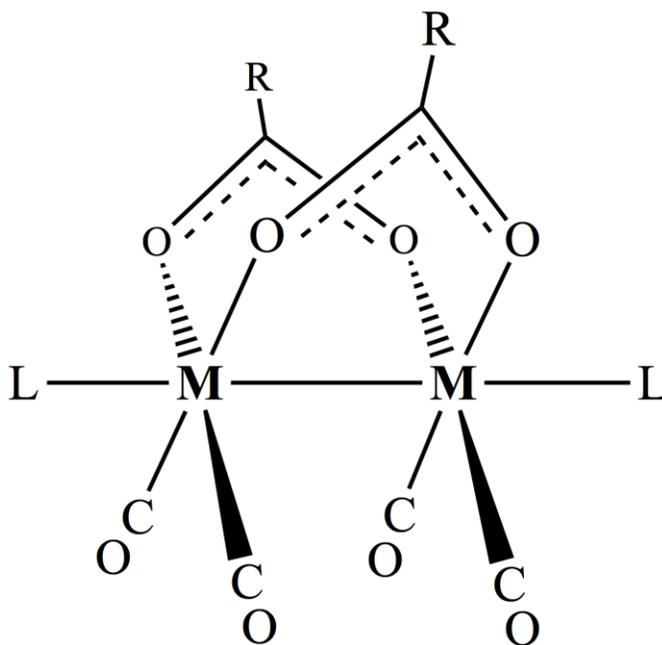
Schematic 1. Illustration of the generic structure of sawhorse complexes.

The synthesis of osmium-containing sawhorse complexes from dodecacarbonyltriosmium(0) was first conducted in the 1960s[2]. These first complexes had two bridging acetate or two bridging propionate ligands. Few other complexes were added until 2013 when Pyper, et al. made osmium sawhorse complexes with bridging

formate and benzoate ligands[3]. No sawhorse complexes have been prepared with two different carboxylate ligands on the same molecule.

Dicarboxylic acids can also be used in the synthesis of sawhorse complexes with varying results. One, two, three, or four metal dimers can be linked through dicarboxylate groups depending on the length and rigidness of the dicarboxylic acid precursor[1][4][5]. The larger of these compounds have shown the ability to capture and retain external molecules such as solvents within a molecular pore[1]. The ability of sawhorse complexes to bind external molecules is associated with the size and properties of this pore which varies based on which dicarboxylate groups are used in the synthesis of the sawhorse complex.

This study is an attempt to synthesize the first mixed carboxylate sawhorse complexes. Creation of such complexes would speak to the viability of the idea of "cluster customization." If sawhorse complexes can be efficiently customized for shape or property, then the synthesized compounds could be tailored to specific purposes such as drug delivery or gas storage.

2. Experimental

2.1 Materials and Methods

All syntheses were conducted using a Discover-SP microwave reactor (2455MHz, CEM Corp., Matthews, NC). Reactions were carried out in 35-mL glass reaction vessels with Teflon caps. The microwave reactor was set to high stir rate, maximum pressure of 300 PSI, and maximum power of 300 W. All reactions and manipulations of synthesized compounds were carried out in a highly efficient fume hood. All chemicals were used as received. Thin-layer chromatography (TLC) was performed using silica gel coated glass

plates purchased from Analtech. IR spectra were obtained using a Nicolet Avatar 320 FTIR with a CaF$_2$ solution cell. ^{1}H NMR spectra were obtained using an EM360 NMR spectrometer.

*2.2 Synthesis of Os$_2$(μ-acetate)(μ-propionate)(CO)$_4$(P(p-tolyl)$_3$)$_2$ (**1**)*

Os$_3$(CO)$_{12}$ (102.4 mg, 0.113 mmol), excess acetic acid (2.5 mL), and excess propionic acid (3.0 mL) were combined in a 35-mL glass reaction vessel. This mixture was irradiated during high stirring in the microwave reactor at 180°C for 10 minutes. The resulting solution was pale yellow. All solvent from the reaction was allowed to evaporate before the residue was reacted with 0.1089 g of tri(p-tolyl)phosphine in 25mL of 1,2-dichloroethane and 5mL of acetonitrile. This solution was refluxed in the microwave reactor at 88°C for 50 minutes. All solvent was again allowed to evaporate and the residue was dissolved in CH$_2$Cl$_2$ before TLC separation. A 4:1 hexanes/CH$_2$Cl$_2$ eluent gave three bands, which were visible under UV radiation. Band 3 (R_f = 0.156) and the baseline were recombined and subject to TLC in a 1:1 eluent of hexanes:CH$_2$Cl$_2$. Two bands were visible under UV radiation. Band 1 (R_f = 0.710) consisted of cluster **1**. IR (v_{CO}, CHCl$_3$): 2011(vs), 1967(m), 1933(vs), 1900(w) cm^{-1}. Band 2 (R_f = 0.129) consisted of an unknown compound. IR (v_{CO}, CHCl$_3$): 2045(s), 2021(vs), 1998(vs), 1980(m), 1966(sh), 1940(sh) cm^{-1}.

*2.3 Synthesis of Os$_2$(μ-benzoate)(μ-pivalate)(CO)$_4$(P(p-tolyl)$_3$)$_2$ (**2**)*

Os$_3$(CO)$_{12}$ (75.5 mg, 0.0832 mmol), benzoic acid (22.9 mg, 0.188 mmol), and pivalic acid (23.5 mg, 0.230 mmol) were combined in a 35-mL glass reaction vessel with 8mL of 1,2-dichlorobenzene. This mixture was irradiated during high stirring in the microwave reactor at 186°C for 10 minutes. The resulting solution was orange. The

solvent from the reaction was allowed to evaporate before the residue was reacted with

0.0843 g of tri(p-tolyl)phosphine in 23mL of ethyl acetate. This solution was stirred on a

hot plate at 85°C for 30 minutes. All solvent was again allowed to evaporate and the

residue was dissolved in CH_2Cl_2 before TLC separation. A 3:2 hexanes/CH_2Cl_2 eluent

resulted in four bands which visible under UV radiation. Band 3 (R_f = 0.639) and band 4

(R_f = 0.482) were recombined and subject to TLC in a 7:3 eluent of hexanes:CH_2Cl_2.

Five bands were visible under UV radiation. Band 1 (R_f = 0.763) consisted of an

unknown compound. IR (v_{CO}, $CHCl_3$): 2085(m), 2067(s), 2035(sh), 2016(vs), 1940(s)

cm^{-1}. Band 2 (R_f = 0.525) consisted of an unknown compound. IR (v_{CO}, $CHCl_3$):

2034(m), 2015(m), 1950(m) cm^{-1}. Band 3 (R_f = 0.4375) consisted of an unknown

compound. IR (v_{CO}, $CHCl_3$): 2094(w), 2054(m), 2016(s), 1999(m), 1962(m) cm^{-1}. Band

4 (R_f = 0.375) consisted of an unknown compound. IR (v_{CO}, $CHCl_3$): 2034(m), 2014(s),

1959(sh), 1939(vs) cm^{-1}. Band 5 (R_f = 0.1563) consisted of cluster **2**. IR (v_{CO}, $CHCl_3$):

2011(vs), 1967(m), 1935(vs), 1902(w) cm^{-1}.

*2.4 Synthesis of Os$_2$(μ-benzoate)(μ-pivalate)(CO)$_4$(dmso)$_2$ (**3**)*

Os$_3$(CO)$_{12}$ (74.6 mg, 0.0823 mmol), benzoic acid (20.8 mg, 0.170 mmol), and

pivalic acid (25.0 mg, 0.245 mmol) were combined in a 35-mL glass reaction vessel with

8mL of 1,2-dichlorobenzene. This mixture was irradiated during high stirring in the

microwave reactor at 186°C for 10 minutes. The resulting solution was an amber color.

All solvent from the reaction was allowed to evaporate before the residue was redissolved

in CH_2Cl_2 for TLC separation in a 4:1 eluent of hexanes:CH_2Cl_2. The separation

produced three bands which were visible under UV radiation. Band 1 (R_f = 0.724)

consisted of an unknown compound. IR (v_{CO}, $CHCl_3$): 2089(m), 2084(w), 2065(vs),

2013(s), 1995(vs) cm^{-1}. Band 2 (R_f = 0.625) was assumed to be the desired product and reacted in the microwave reactor at 70°C for 40 minutes with 5mL of CHCl$_3$ and 0.5mL of dimethylsulfoxide (DMSO). This resulted in cluster **3**. IR (v_{CO}, CHCl$_3$): 2039(vs), 1996(m), 1963(vs) cm^{-1}. Band 3 (R_f = 0.507) consisted of an unknown compound. IR (v_{CO}, CHCl$_3$): 2099(m), 2066(vs), 2014(s), 1998(vs) cm^{-1}.

2.5 X-ray crystallography

Crystal structure data for clusters **1**, **2**, and **3** were obtained from single crystals mounted on nylon loops in a Rigaku Supernova Single-Crystal Diffractometer. Single crystals of all clusters reported in this paper were obtained through slow diffusion of n-hexane into CH$_2$Cl$_2$ solutions of each of the clusters. The molecular structure was solved in Olex2 as carried out by Dr. Greg Powell at Abilene Christian University with the assistance of Dr. Lee Daniels of Rigaku Oxford Diffraction.

3. Results and Discussion

3.1 Analysis of X-ray diffraction structures

All clusters synthesized in this paper were structurally similar to previously-synthesized sawhorse complexes. Table 1 provides structural information for clusters **1**, **2**, and **3** as well as structural information of the symmetrically-substituted sawhorse complex analogs (previously-synthesized sawhorse complexes with equivalent carboxylate groups) of each cluster. Select bond lengths, bond angles, and torsion angles are given. The only significant structural difference between a symmetrically-substituted complex and its asymmetrically-substituted analog appears in the torsional strains. The symmetrically-substituted Os$_2$(μ-pivalate)$_2$(CO)$_4$(PPh$_3$)$_2$ has an average torsional angle around the osmium-osmium center of 21.37(5)° and the asymmetrically-substituted

clusters **2** and **3** have average torsional angles of 8.69(3)° and 6.70(3), respectively.

Thus, the previously-synthesized pivalate sawhorse complex exhibits high torsion angles

around the osmium-osmium center. Clusters **1** and **2**, which both contain a singular

equatorial pivalate ligand, do not have such high torsion angles. The high torsional strain

present in $Os_2(\mu\text{-pivalate})_2(CO)_4(PPh_3)_2$ likely comes from steric interactions of the large

tert-butyl moiety of the pivalate ligands. These interactions are not as influential in either

cluster **1** or **2** which explains the lower torsional strain.

Table 1. Structural data for all clusters and their symmetrically-substituted sawhorse
complex analogs.

Complex	Os-Os bond length (Å)	Os-L_{ax} bond length (Å)	Os1-Os2-L_{ax} angle (°)	Eq1-Os1-Os2-Eq2 angle (°)
$Os_2(\mu\text{-acetate})_2(CO)_4(PPh_3)_2$ [2]	2.7716(5)	2.4344(8)	163.34(2)	6.00(1)
$Os_2(\mu\text{-propionate})_2(CO)_4(P(p\text{-tolyl})_3)_2$ [2]	2.7677(3)	2.4030(2)	165.16(5)	6.89(1)
$Os_2(\mu\text{-benzoate})_2(CO)_6$ [3]	2.748(1)	1.989(8)	169.80(4)	5.66(4)
$Os_2(\mu\text{-pivalate})_2(CO)_4(PPh_3)_2$ [9]	2.7198(3)	2.404(2)	167.61(5)	21.37(5)
Cluster **1** *	2.762(2)	2.397(5)	165.77(4)	6.38(5)
Cluster **2** *	2.7578(4)	2.411(5)	166.31(9)	8.69(3)
Cluster **3** *	2.763(4)	2.382(2)	163.33(8)	6.70(3)

*Described in this paper

     Figure 1 provides an illustration of cluster **1**, the acetate/propionate mixed

carboxylate diosmium sawhorse complex. The two $P[(p\text{-tolyl})_3]$ phosphine ligands,

which replaced the axial CO ligands, can be seen on the left and right sides of the figure.

Figure 2 illustrates the location of the dichloromethane solvent molecule found in the

lattice with cluster **1**. It is common to have solvent molecules become trapped in the

crystal lattice as the crystal forms. A similar phenomenon happens with cluster **2** with
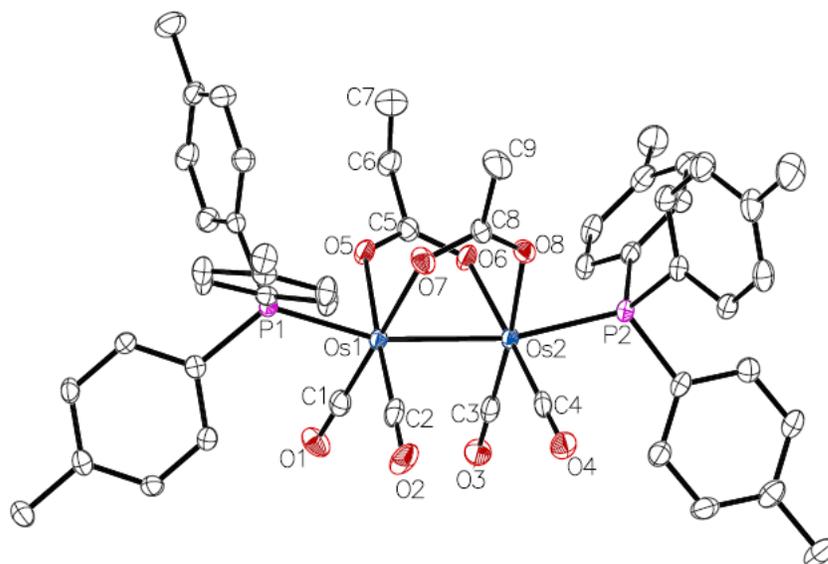
greater implications.

Figure 1. Thermal ellipsoid plot of the molecular structure of **1** with all hydrogens removed.
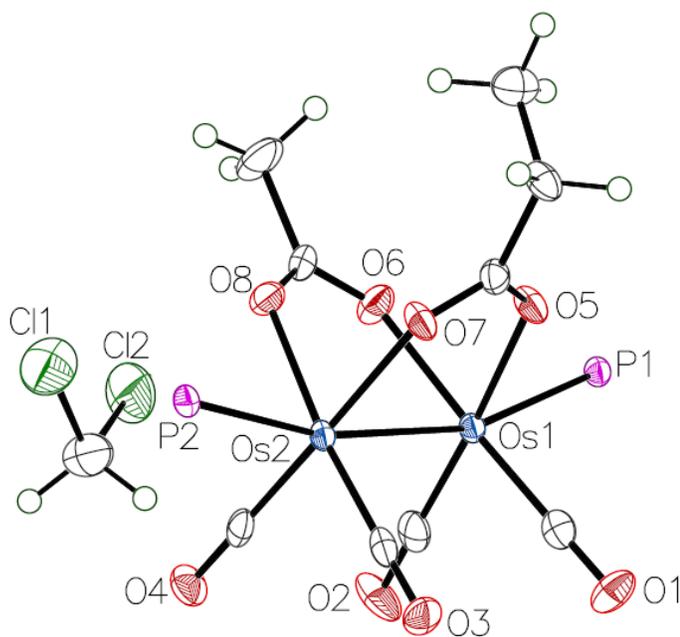

Figure 2. Thermal ellipsoid plot of the molecular structure of **1** and a CH_2Cl_2 solvent molecule. The p-tolyl groups have been removed from both of the phosphine ligands.

Figure 3 provides an illustration of cluster **2**, the benzoate/pivalate mixed carboxylate diosmium sawhorse complex. This crystal had some disorder in it. At the

same location in the lattice, the diosmium molecule contains two benzoate ligands 24%

of the time, but one benzoate ligand and one pivalate ligand 76% of the time. This points

to the product not being purified completely. This becomes more interesting because of

Figure 4 which shows cluster **2** with an n-hexane solvent molecule and a water molecule.

The polarity of these two molecules should exclude them from being in the same crystal.

Further examination reveals that the water molecule is not present all the time. The water

molecule's presence correlates with the presence of the pivalate group. This seems to

show progress toward the goal of this experiment: customizing complexes to be

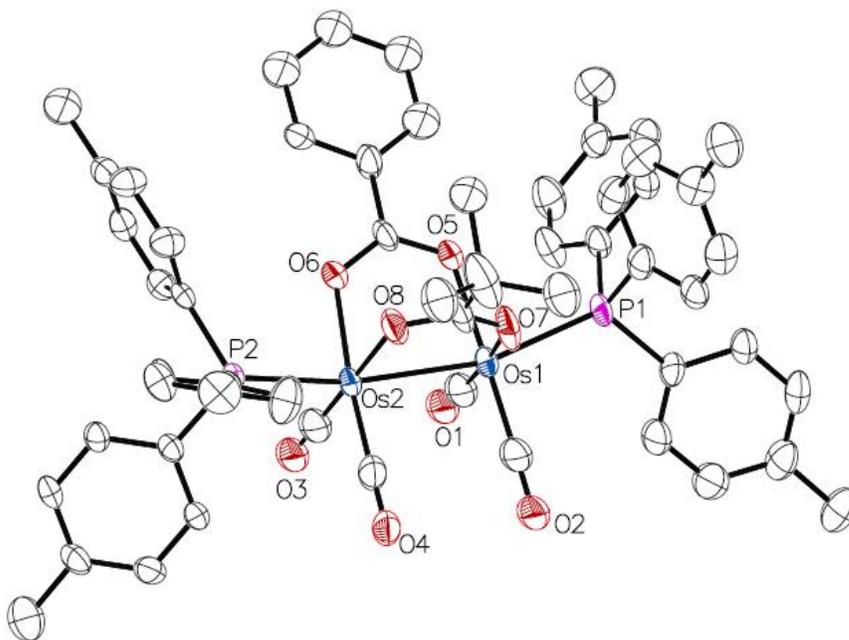optimized to hold different external molecules.

Figure 3. Thermal ellipsoid plot of the molecular structure of **2** with all hydrogens removed.
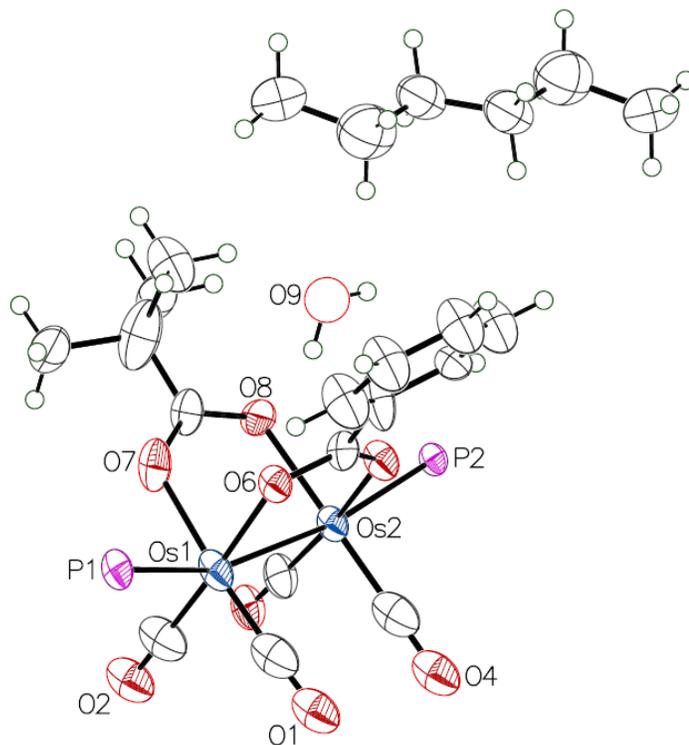
Figure 4. Thermal ellipsoid plot of the molecular structure of **2**, a water molecule, and an n-hexane solvent molecule. The p-tolyl groups have been removed from both of the phosphine ligands.

Figure 5 provides an illustration of cluster **3**, the benzoate/pivalate mixed carboxylate diosmium sawhorse complex with dmso ligands. An attempt was made to synthesize the benzoate/pivalate mixed product with dmso ligands in order to get a more ordered crystal structure. This attempt was successful as little to no disorder was observed in cluster **3**. Some CH_2Cl_2 solvent, from which the crystals of cluster **3** were made, may have still been present in cluster **3** similar to the solvent present in cluster **2** but this could not be confidently confirmed.
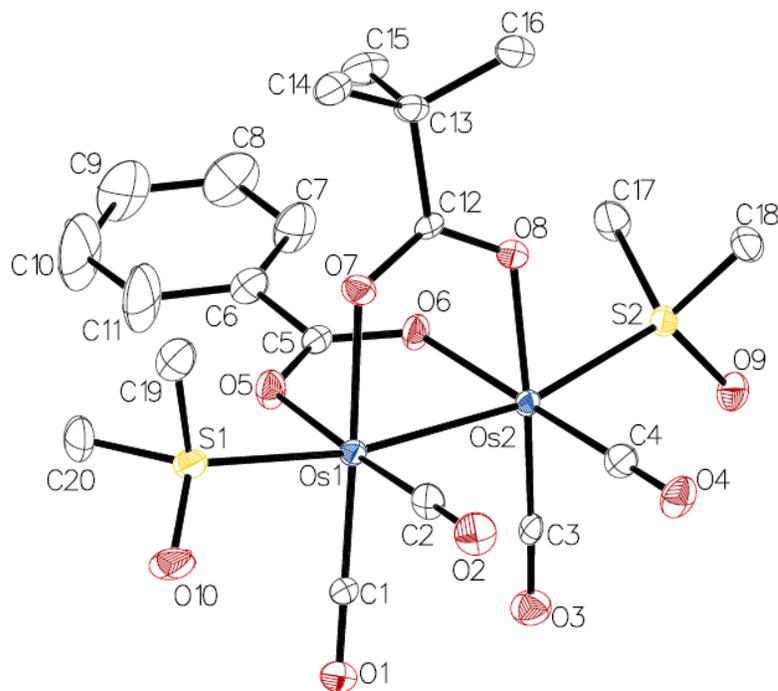
Figure 5. Thermal ellipsoid plot of the molecular structure of **3** with all hydrogens removed.

4. Conclusion

4.1 Summary and Review

The first ever mixed carboxylate sawhorse complexes were synthesized. A microwave reactor was used to simultaneously react $Os_3(CO)_{12}$ with excess amounts of acetic acid and propionic acid. Addition of the tri(p-tolyl)phosphine ligand resulted in cluster **1**. Similarly, a microwave reactor was used to simultaneously react $Os_3(CO)_{12}$ with stoichiometric amounts of benzoic acid and pivalic acid. The addition of tri(p-tolyl)phosphine and dimethylsulfoxide ligands resulted in clusters **2** and **3**, respectively. The synthesis of all three clusters serves as a proof-of-concept for the idea of "cluster customization". If the idea of custom-building a molecule can be expanded to larger, more complex structures, then complexes could be optimized for specific purposes such

as drug delivery or gas storage. Below are described future investigations which could be carried out in order to make this concept more applicable to gas storage or drug delivery.

4.2 Potential new clusters

Several clusters have been synthesized using both osmium and ruthenium which use dicarboxylate groups to bridge multiple metal-metal dimers[1][6]. These show high promise for intentional capture of an external molecule by a sawhorse complex[1]. The binding of an external molecule to a sawhorse complex may be associated with the size of the cavity within the sawhorse complex. Changing the size of this cavity may thus help to optimize the capture of desired molecules.

4.2.1 Synthesis of a molecular pocket

Several "molecular triangles" (sawhorse complexes containing three metal dimers) have been synthesized[1][7][8]. One such cluster is $Os_6(CO)_{12}(\mu_4\text{-}isophthalate)_3(P(p\text{-}tolyl)_3)_6$ [1]. This cluster shows great promise for molecular binding and storage because it has a shape much like a basket or pocket. The structure, however, is highly strained. In addition, the pocket of the structure has been shown to become filled by phosphine ligands added to the molecule. If one of the isophthalate groups were to be replaced with a terephthalate group, this could have the results of lowering strain and also freeing the pocket of any phosphine ligands. An inorganic complex such as this could be invaluable for its ability to mimic biological features such as actives sites.

4.2.2 Synthesis of a molecular rectangle

Recently the Dr. Greg Powell research group out of Abilene Christian University synthesized the first osmium-containing "molecular square" (sawhorse complex containing four metal dimers)[8]. The cluster, $Os_8(CO)_{16}(\mu_4\text{-}2,6\text{-}$

napthalenedicarboxylate)$_4$(P(p-tolyl)$_3$)$_8$, has some deviations from a perfect square but does have four sides all of the same length. Exchanging two of the 2,6-napthalenedicarboxylate groups for a different bridging ligand such as two terephthalate groups could lead to the characterization of the first "molecular rectangle". This would lead to a change in the size of the cluster's cavity and should therefore lead to a change in the cluster's ability to bind external molecules.

4.2.3 Customization of molecular wires

Osmium-containing sawhorse complexes can be connected axially as opposed to being connected through the dicarboxylato ligands[9]. This connection could be thought of as a molecular wire, capable of conducting signal across its length. Selectively choosing the carboxylate ligands of this sawhorse complex chain will change the electrical properties of the chain thereby allowing the conductivity of the wire to be optimized to its specific situation. Additionally, this experiment has shown the possibility of customizing sawhorse complexes through mixing carboxylate ligands. This opens the door to customizing sawhorse complexes through mixing metals within the metal dimer backbone. Having multiple metals within the sawhorse backbone would have profound effects on the electrical properties of this molecular wire.

Acknowledgements

References

[1] N. Gwini, D.M. Marolf, S. H. Yoon, A. G. Fikes, A. C. Dugan, G. L. Powell, V. M. Lynch, V. N. Nesterov, G. T. McCandless., J. Organomet. Chem., accepted 2017, http://doi.org/10.1016/j.jorganchem.2017.01.026

[2] G. R. Crooks, B. F. G. Johnson, J. Lewis, and I. G. Williams., G. Gamlen, J. Chem. Soc. (A), 1969, 2761

[3] K. J. Pyper, J. Y. Jung, B. S. Newton, V. N. Nesterov, and G. L. Powell, J. Organomet. Chem. 2013, 723, 103

[4] A. G. Fikes, N. Gwini, S. H. Yoon, V. N. Nesterov, and G. L. Powell, J. Organomet. Chem. 2014, 773, 188-191

[5] D.F. Zometa, G. L. Powell. Unpublished results

[6] B. Therrien, G. Süss-Fink, Coord. Chem. Rev., 2009, 253, 2639

[7] M. Auzias, B. Therrien, G. Süss-Fink, Inorg. Chem. Commun., 2007, 10, 1420

[8] K.-B. Shiu, H.-C. Lee, G.-H. Lee, B.-T. Ko, Y. Wang, C.-C. Lin, Angew. Chem. Int. Ed., 2003, 42, 2999

[9] B. Y. Chor, R. Ganguly, W. K. Leong, J. Organomet. Chem. 2016, 804, 114-117