PREPARATION OF METAL-ORGANIC FRAMEWORKS CONTAINING N-HETEROCYCLIC CARBENE CATALYSTS

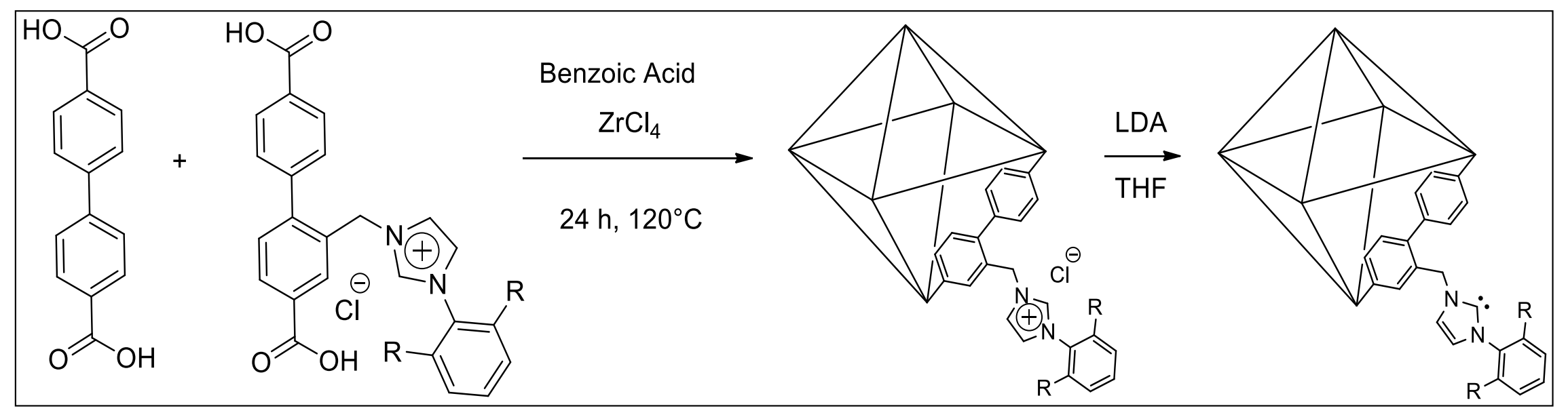
William Schumacher, Madeleine Mathews, Sean Larson, Carl Lemmon, Karin Campbell, Brendan Crabb, Laurance G. Beauvais*, and Marc C. Perry* Department of Chemistry, Point Loma Nazarene University, San Diego, CA, 92106

Introduction

Metal-organic frameworks (MOFs) have been studied for use in a wide range of applications, such as gas storage, chemical sensors, and catalysis. Due to their high surface area and ease of modification, they are ideal platforms to study as heterogeneous catalysts. We choose to use UiO-67 as our MOF platform because of its stability and large pore sizes. UiO-67 is constructed from Zr_6 nodes connected via biphenyl dicarboxylate linkers.[1] Our goal was to replace some of these inert linkers with linkers containing imidazolium salts which could be converted to catalytically active N-heterocyclic carbene (NHC) species upon treatment with an appropriate base. Thus, we synthesized a new linker containing an NHC precursor with bulky groups.

In order to incorporate the organic linkers into the zirconium MOF, the synthesis of UiO-67 was carried out with a 1:1 ratio of the typical linker (bpdc) and the synthesized linker (carbene ligand).[2-4] This resulted in a typical 5-10% incorporation of the synthesized linker. This doped MOF could then be utilized in organocatalysis. Since the MOF retains its integrity, it is ultimately able to be reused in subsequent catalysis reactions, as designed in this project.

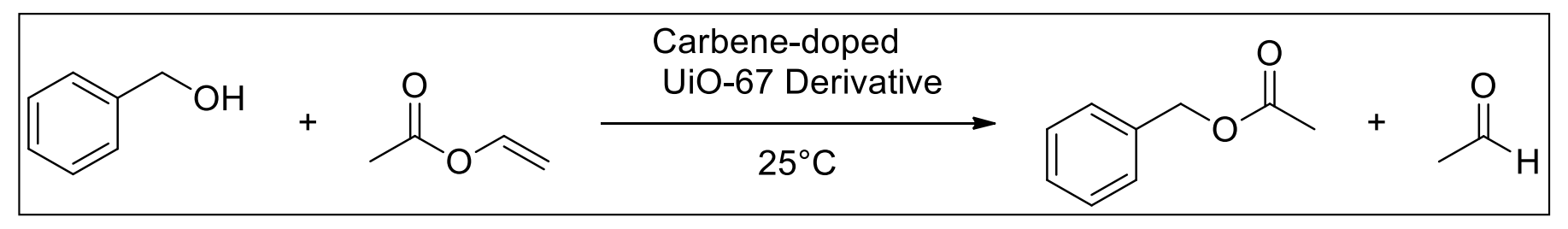
Synthesis

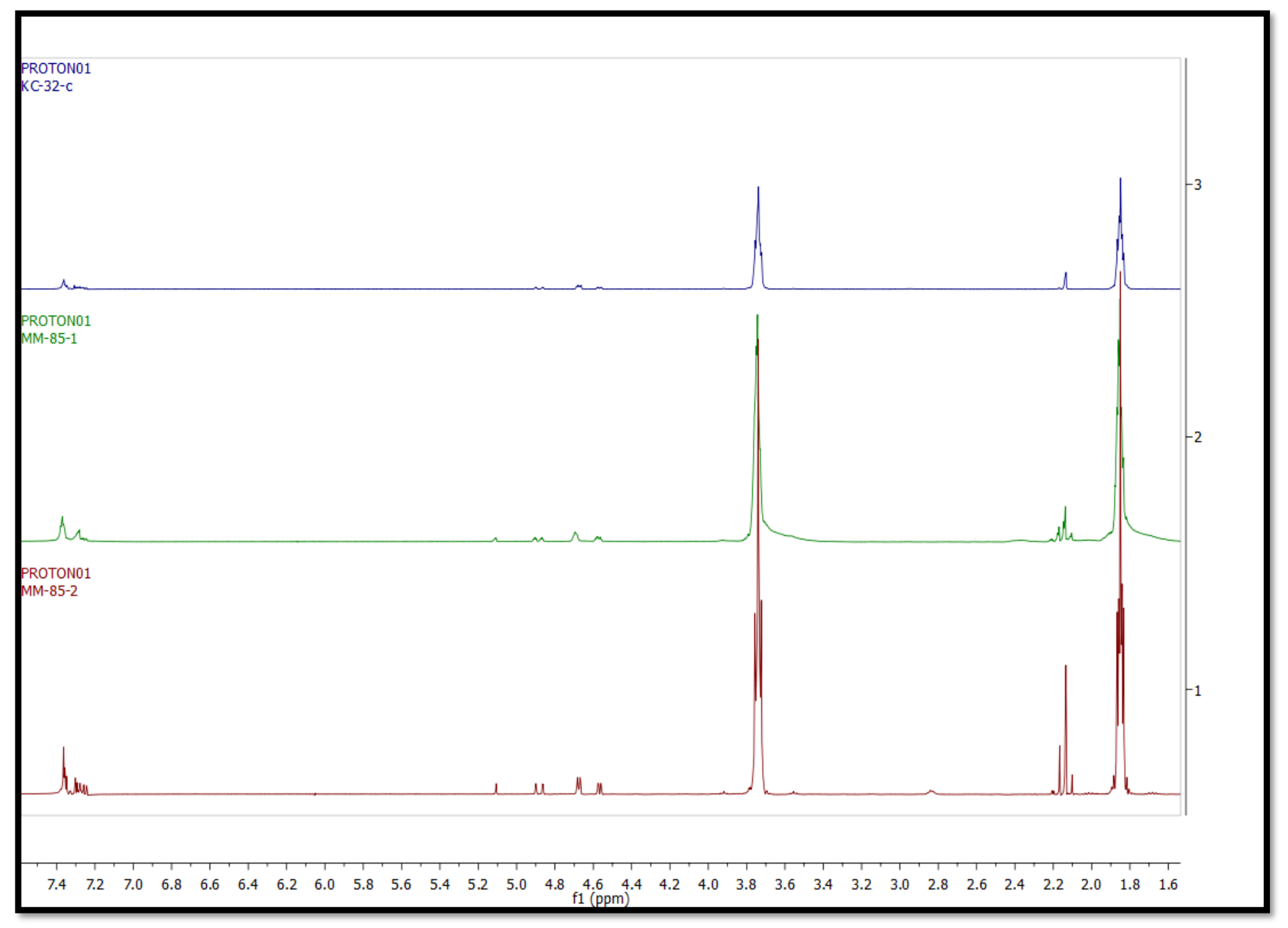


Synthesis of carbene-doped UiO-67 derivative

Catalysis

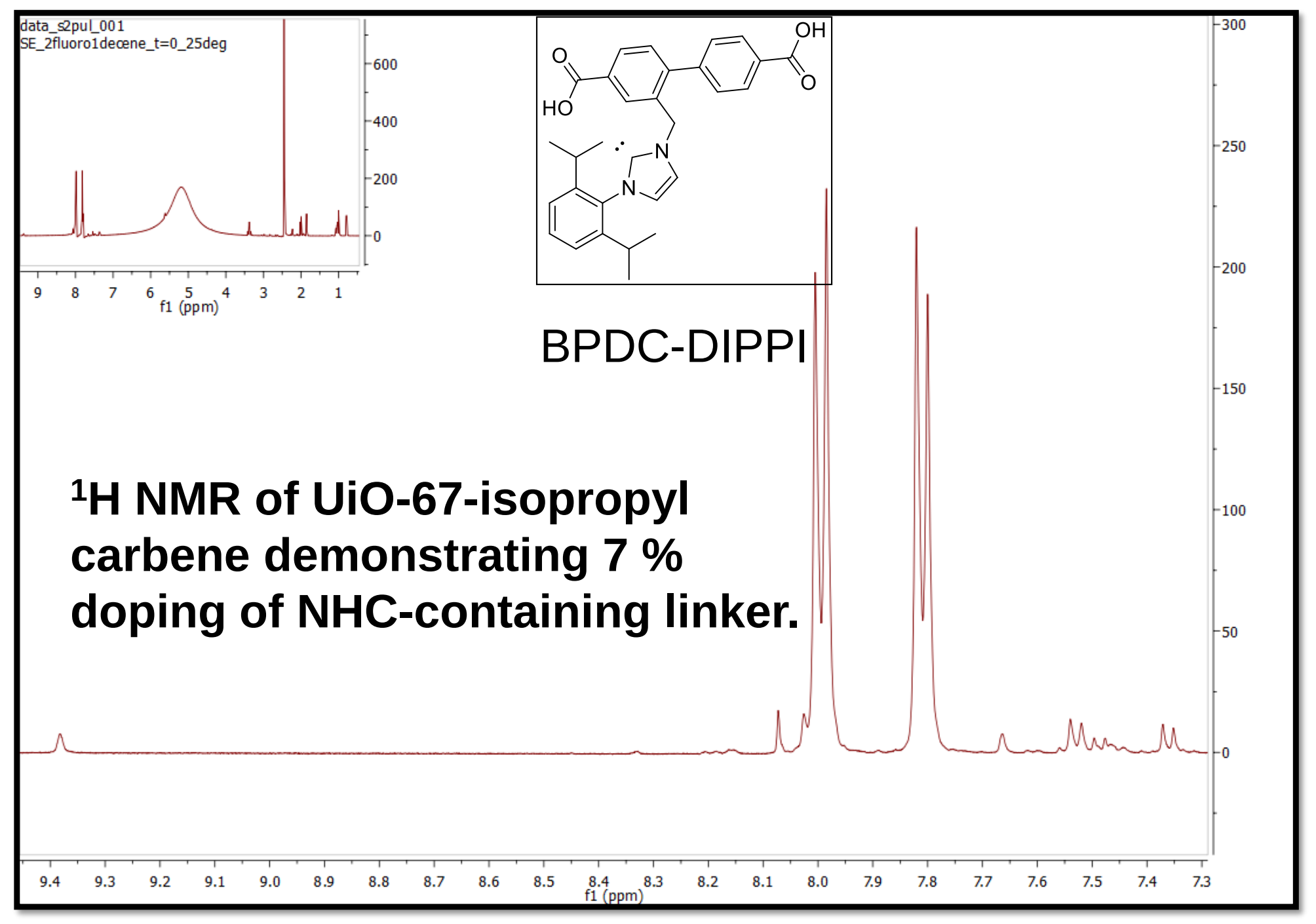
Transesterification





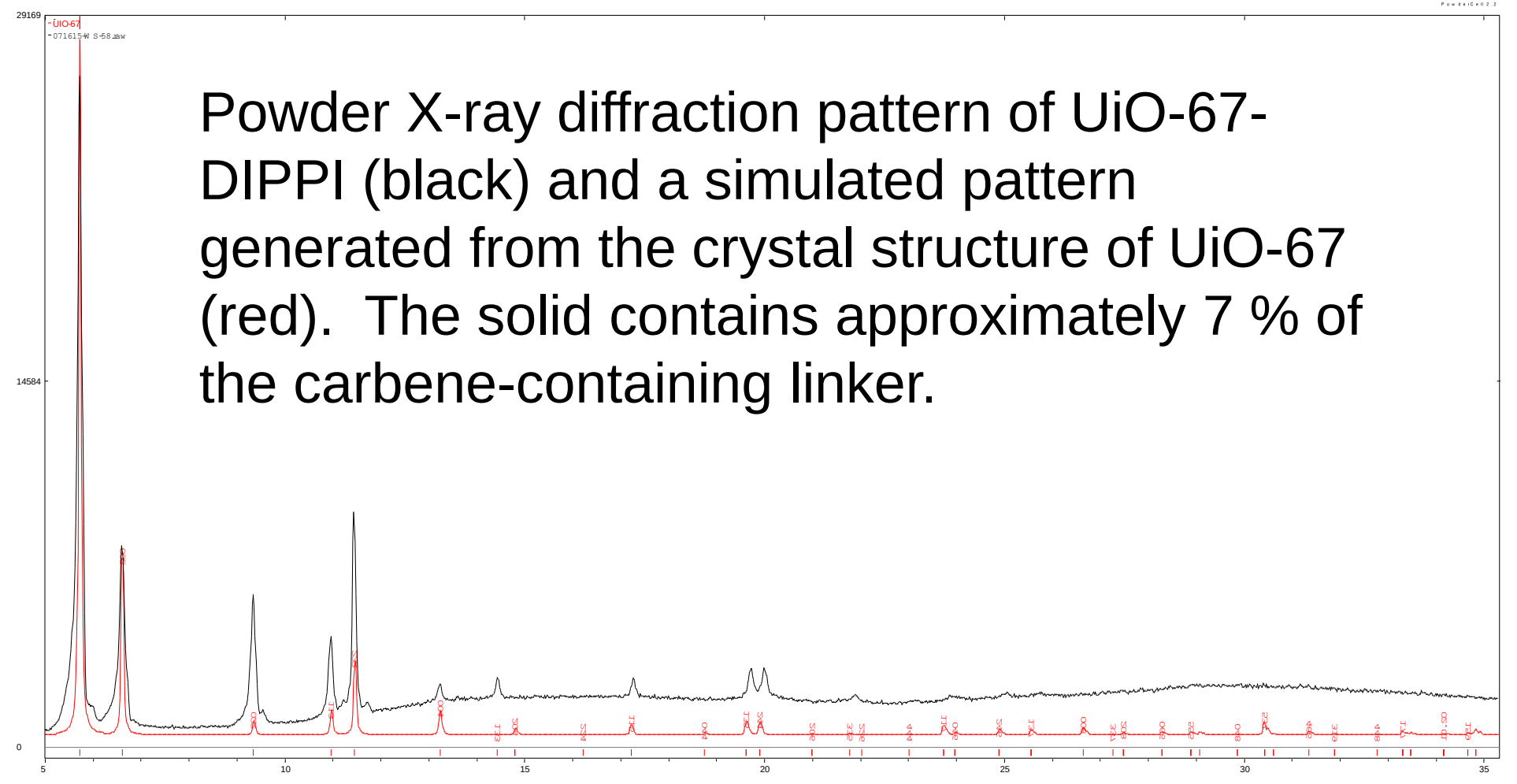
KC-32-c: UiO-67-isopropyl carbene catalysis without LDA. MM-85-1: UiO-67 catalysis without LDA deprotection. MM-85-2: UiO-67 catalysis with LDA deprotection. Ten minutes of catalysis for all.

Characterization

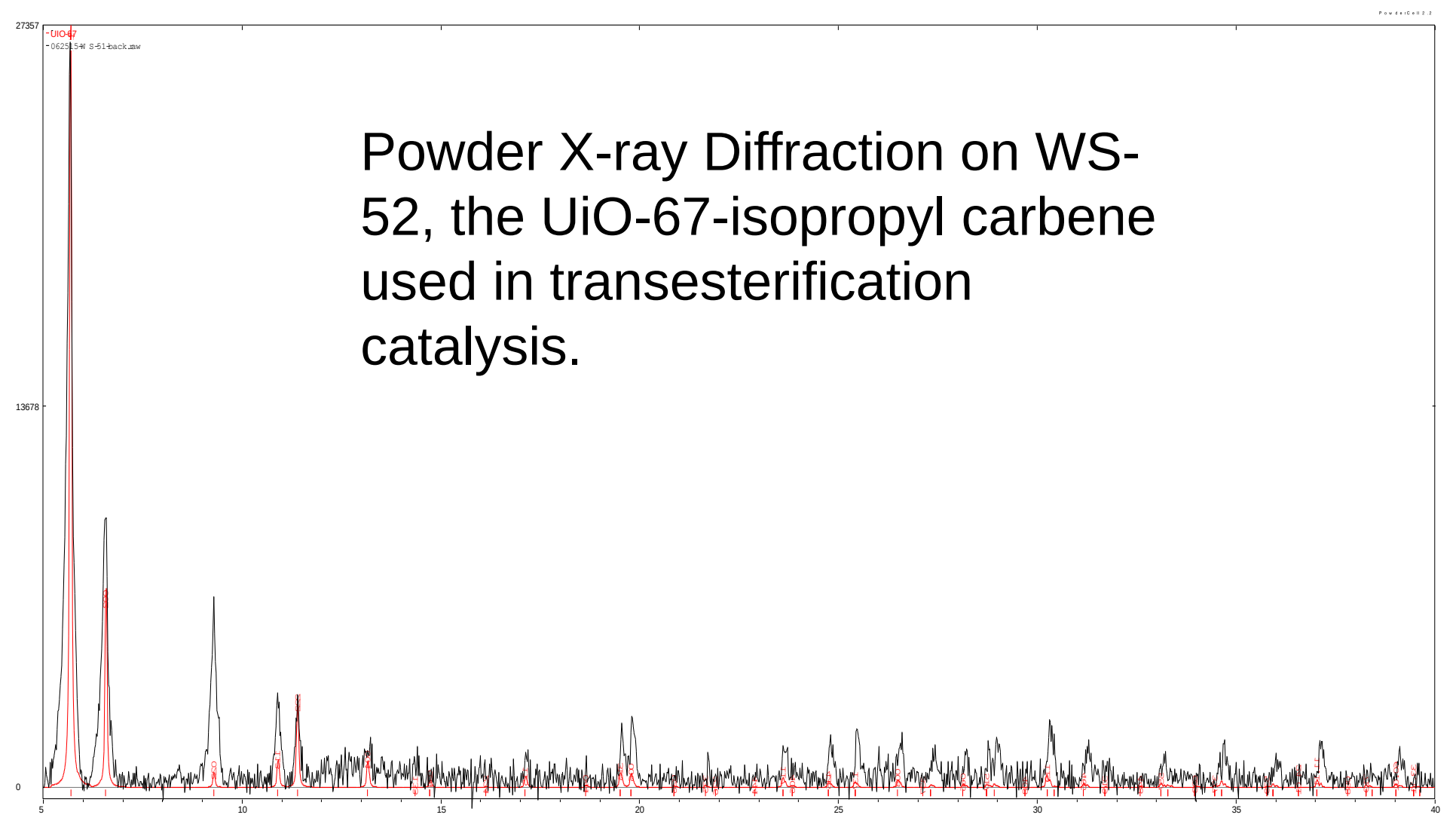


BPDC-DIPPI

^{1}H NMR of UiO-67-isopropyl carbene demonstrating 7 % doping of NHC-containing linker.



Powder X-ray diffraction pattern of UiO-67-DIPPI (black) and a simulated pattern generated from the crystal structure of UiO-67 (red). The solid contains approximately 7 % of the carbene-containing linker.



Powder X-ray Diffraction on WS-52, the UiO-67-isopropyl carbene used in transesterification catalysis.

Discussion

Proton NMR of the digested UiO-67-isopropyl carbene reveals that approximately 7 % of the imidazolium linker has been incorporated into the solid. The solids were reacted with LDA and DBU to form the N-heterocyclic carbene. The activated solids were then compared to pure UiO-67 in transesterification and cyanosilylation reactions. The NHC-doped UiO-67 derivative was a successful catalyst for the transesterification reaction listed above. We are currently exploring different activation methods and other frameworks in order to better study the behavior of NHC-containing MOFs. Furthermore, our research group will look to perform oxidative catalysis with possible other linkers, which may require post-synthetic modification

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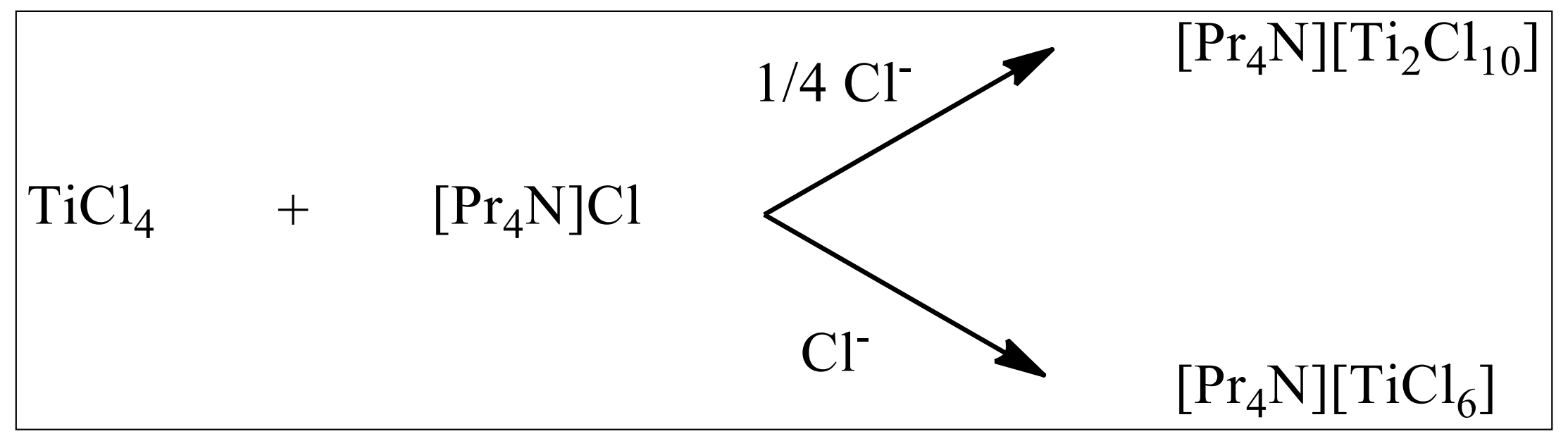
NEW SYNTHETIC ROUTES TO THE TITANIUM CHLORIDE PRECURSORS, $[Ti_2Cl_{10}]^{2-}$ AND $[TiCl_6]^{2-}$

Brendan Crabb, Merna Shoukry, Laurance G. Beauvais*, Dr. Miriam Bennett* Department of Chemistry, Point Loma Nazarene University, San Diego, CA, 92106

Introduction

Polynuclear molecules are recognized and utilized as precursors to a variety of materials. Homoleptic chlorometallates are a wide class of fundamentally important coordination compounds that are attainable by the addition of halide ions to the neutral metal halide. Our research group explored new synthetic pathways and collected crystallographic data for the decachloroditinate $[Ti_2Cl_{10}]^{2-}$ and hexachlorotitanate $[TiCl_6]^{2-}$.

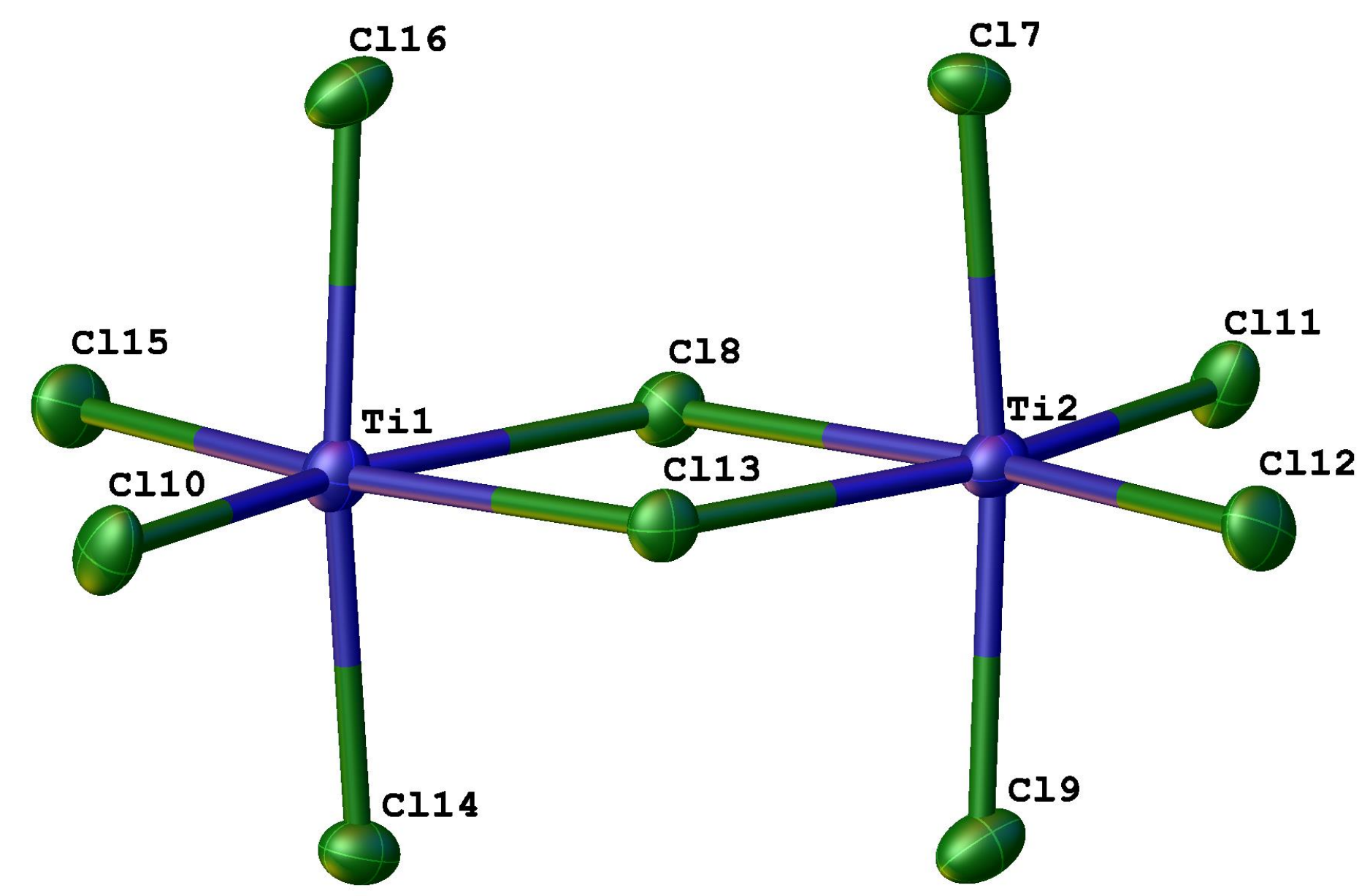
Synthesis



Synthesis of decachloroditinate $[Ti_2Cl_{10}]^{2-}$ and hexachlorotitanate $[TiCl_6]^{2-}$ precursors. All reactions were performed using anhydrous DCM.

Characterization

Single crystals of $[Pr_4N][Ti_2Cl_{10}]$ **(1)** (small red crystals) were grown in a DCM solution by performing a vapor diffusion with pentane. Single crystals of $[Pr_4N][TiCl_6]$ **(2)** (small red cubic crystals) and $[Ph_4P]_2[Ti_2Cl_8O]$ **(3)** (large yellow rods) were grown in a DCM solution by performing a vapor diffusion with pentane using three scintillation vials in a larger jar, followed by recrystallized using vapor diffusion from acetonitrile with ethyl ether.

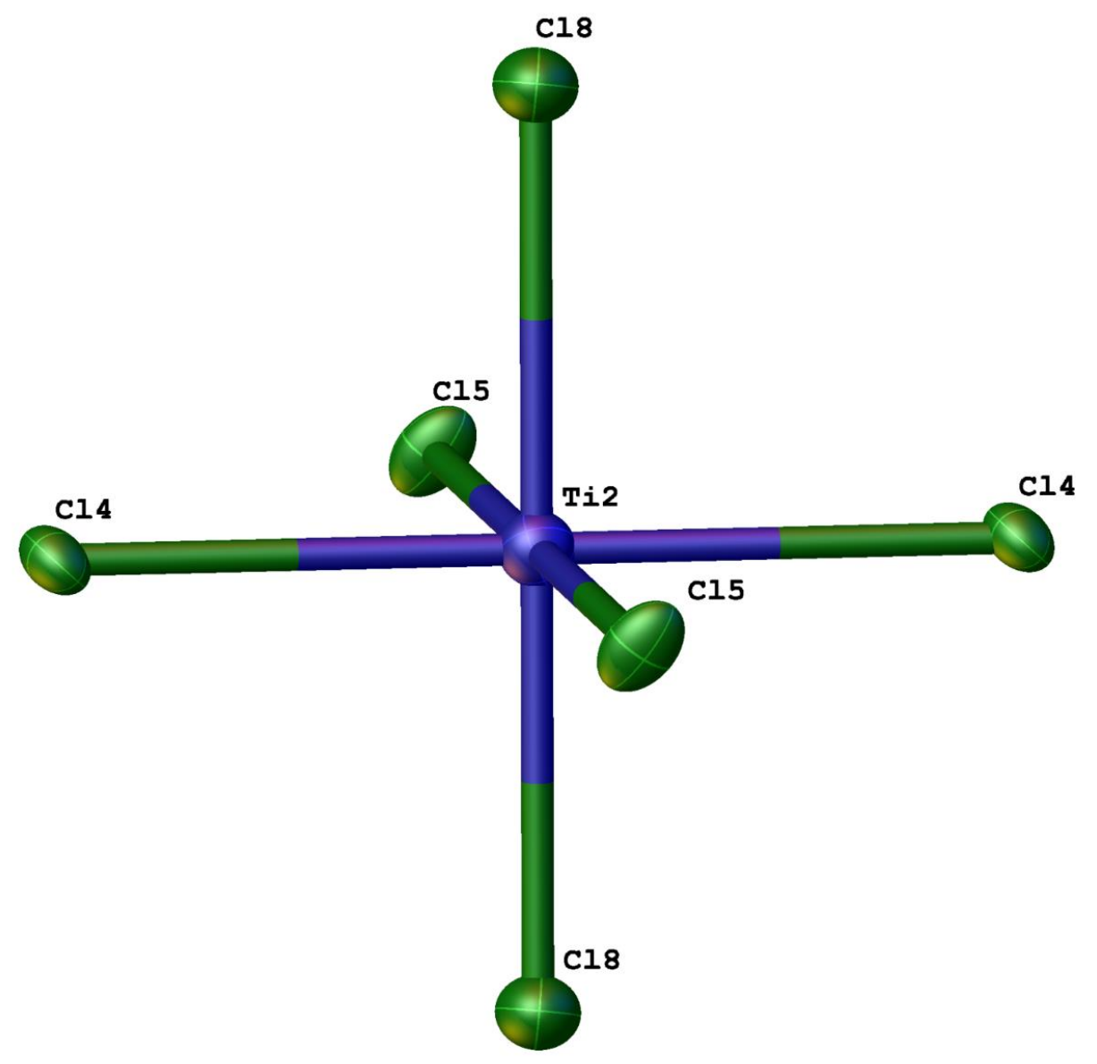


Crystal structure for compound **1**, $[Pr_4N][Ti_2Cl_{10}]$.

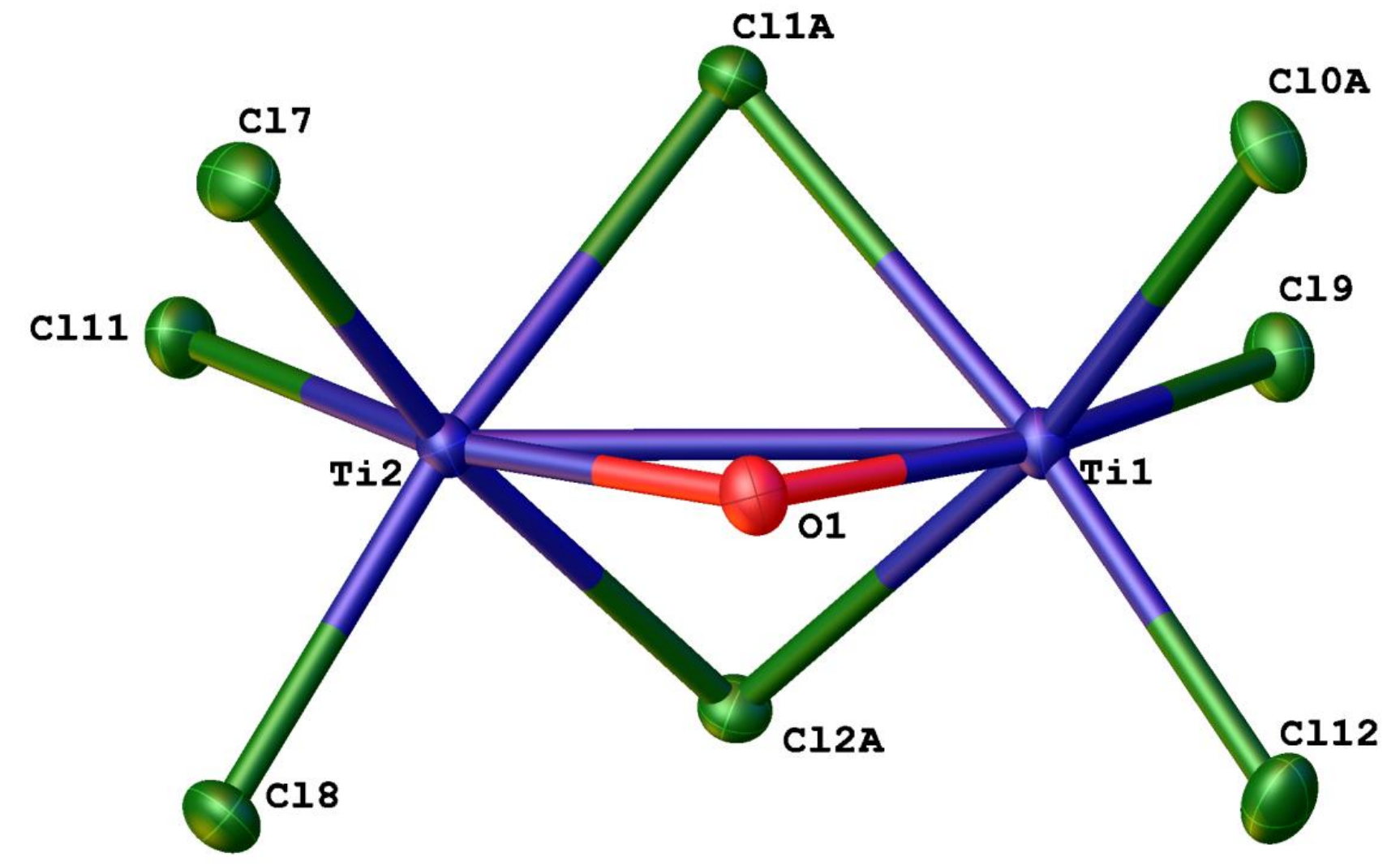
Crystallographic Data

	1	**2**	**3**
form.	$C_3H_{28}NCl_{10}Ti_2$	$C_{12}H_{28}NCl_6Ti$	$[Ph_4P]_2Ti_2Cl_8O$
f. wt.	528.56	446.95	1074.
temp. K	296.15	100	296.15
s. group	P1	P-1	P-1
Z	2	4	2
a/Å	10.0946(5)	9.6217(5)	10.2979(17)
b/Å	10.4837(5)	11.4815(6)	13.483(2)
c/Å	11.1595(5)	15.1818(8)	21.650(4)
β/°	68.124(2)	88.010(3)	78.462(8)
Vol./Å^3	971.93(8)	1673.34(15)	2766.2(8)
ρ g/cm^3	1.806	1.774	1.290
R_1, wR_2%	0.0387, 0.1516	0.0381, 0.1126	0.0221, 0.0558

Crystallographic data and structure refinement parameters for $[Pr_4N][Ti_2Cl_{10}]$ **(1),** $[Pr_4N][TiCl_6]$ **(2)**, and $[Ph_4P]_2[Ti_2Cl_8O]$ **(3)**



Crystal structure for compound **2**, $[Pr_4N][TiCl_6]$. This compound has mononuclear octahedral geometry and is triclinic with Ti-Cl bond lengths of 2.4027(4), 2.3833(4), and 2.3276(5) Å.



Unprecedented crystal structure for compound **3**, $[Ph_4P]_2[Ti_2Cl_8O]$.

Acknowledgements

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