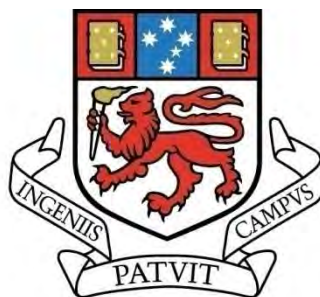


**Scission of Small Multiply Bonded Molecules using  
Transition Metal Complexes. A DFT Study.**

by

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Submitted in fulfilment of the requirement for the Degree of  
Doctor of Philosophy



**UNIVERSITY  
OF TASMANIA**

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Hobart, Australia  
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## Abstract

The analysis described herein applies density functional theory to the activation and scission of the small multiply bonded molecules dinitrogen, carbon monoxide and carbon dioxide using transition metal catalysts.

Starting from the Laplaza-Cummins 3-coordinate molybdenum amide complex  $\text{MoL}_3$  ( $\text{L} = \text{N}(\text{tBu})\text{Ar}$ ) we have applied electronic structure methods in combination with the ONIOM approach to complete a comprehensive study of the effect of ligand bulk on the activation of dinitrogen. Our results show that not only is there expected destabilisation of the intermediate on the pathway, due to direct steric interactions of the bulky groups, but also there is significant electronic destabilisation as the size of the ligand increases. This latter destabilisation is due to the inability of the molecule to accommodate a rotated amide group bound to the molybdenum once the amide reaches a certain size.

Interestingly the Laplaza-Cummins catalyst is experimentally inactive towards carbon dioxide despite binding and cleaving one C-S bond in the similar  $\text{CS}_2$  molecule. We have used density functional theory (DFT) to show that, at first glance, the reaction of  $3 \text{L}_3\text{Mo} + \text{CO}_2$  should proceed smoothly to give  $\text{L}_3\text{Mo-O} + \text{L}_3\text{Mo-CO-MoL}_3$ . However, initial coordination of the  $\text{CO}_2$  molecule to  $\text{L}_3\text{Mo}$  does not take place because of the bending of  $\text{CO}_2$ , the energy required to cross from the doublet to the quartet state, and the lower metal- $\text{CO}_2$  binding energy compared to metal- $\text{CS}_2$ .

From this analysis we predicted that replacement of the central metal with a  $d^2$  transition metal would provide improved binding. Our calculations in this regard suggest that the tantalum analogue,  $\text{TaL}_3$ , will successfully bind to  $\text{CO}_2$  in a mononuclear  $\eta^2$  arrangement and, importantly, will strongly activate one C-O bond to a point where spontaneously C-O cleave occurs. This strongly exothermic reaction takes into

consideration formation transition barriers, spin crossings, ligand bulk and even the DFT functional choice.

The product from this reaction, CO, is known to react with a similar 3-coordinate Ta(silox)<sub>3</sub> (silox = OSi(<sup>t</sup>Bu)<sub>3</sub>) complex, initially forming a ketenylidene (silox)<sub>3</sub>Ta-CCO, followed by a dicarbide (silox)<sub>3</sub>Ta-CC-(silox)<sub>3</sub> structure. We again applied DFT methods to this reaction revealing an intricate mechanism whereby the previously unknown intermediate [(silox)<sub>3</sub>Ta-CO]<sub>2</sub> was identified. The mechanism has been extended to consider the effect of altering both the metal species and the ligand environment. Specifically we predict that introducing electron-rich metals to the left of Ta on the periodic table to create mixed metal dinuclear intermediates shows great promise, as does the ligand environment of the Cummins-style 3-coordinate amide structure.

Finally our interest in CO<sub>2</sub> reactions lead to the exciting oxygen-atom transfer from carbon dioxide to a Fischer Carbene at (PNP)Ir reaction by the Grubbs group. We have confirmed the mechanism for the important CO<sub>2</sub> reaction and have successfully rationalised the selective cleavage of the CS and CN bonds in OCS and PhNCO. The formation of the iridium-supported carbene itself has also been investigated and a fascinating autocatalytic mechanism has been discovered which nicely fits the observed experimental behaviour. This formation analysis has also been extended to consider the reactions with other linear and cyclic ethers that are known to form either carbenes or vinyl ether adducts. We have successfully rationalised the factors dictating reaction direction where both ether structural arrangement and (PNP) ligand environment contribute to the formation reaction outcomes.

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## Abbreviations

B3LYP:	DFT Functional
BMK:	DFT Functional
BP86:	DFT Functional
DEE	Diethyl ether
DFT:	Density Functional Theory
DIO	1,4 dioxane
ECP:	Effective Core Potential
G03:	Gaussian 03 program
GBS:	General Basis Set
GGA:	Generalised Gradient Approximation
HF:	Hartree Fock
HIPT:	3,5-(2,4,6- <i>i</i> -Pr <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>
HOMO:	Highest occupied Molecular Orbital
LDA:	Local Density Approximation
LSDA:	Local Spin Density Approximation
LUMO:	Lowest Unoccupied Molecular Orbital
MECP:	Minimum Energy Crossing Point
MGGA:	Meta Generalised Gradient Approximation
MIT:	The Massachusetts Institute of Technology
MM:	Molecular Mechanics
MP2:	Second order Moller-Plesset perturbation theory
NBE	<i>n</i> -butyl methyl ether
NBO:	Natural Bond Orbital
ONIOM:	Our N-Layered Integrated Molecular Orbital Model
PNP:	Bis(2-diisopropylphosphino-4-methylphenyl)amide ligand
QMMM:	Combined Quantum Mechanics and Molecular Mechanics
QMQM:	Two level quantum mechanics calculation
THF	Tetrahydrofuran
TPSS:	DFT Functional

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## List of Publications

Parts of this work have been published (or in submission for publication).

1. The Influence of Peripheral Ligand Bulk on Nitrogen Activation by 3-Coordinate Molybdenum Complexes – A Theoretical Study using the ONIOM Method.  
N. J. Brookes, D. C. Graham, G. J. Christian, R. Stranger and B. F. Yates, *J. Comput. Chem.*, **2009**, 30, 2146
2. Cleavage of Carbon Dioxide by an Iridium-Supported Fischer Carbene. A DFT Investigation.  
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3. Reactivity of CO<sub>2</sub> towards Mo[N(R)Ph]<sub>3</sub>.  
N. J. Brookes, A. Ariaifard, R. Stranger and B. F. Yates, *Dalton Trans.*, **2009**, Advance Article
4. Scission of Carbon Monoxide using TaR<sub>3</sub>, R = (N(tBu)Ph) or OSi(tBu)<sub>3</sub>. A DFT Investigation.  
N. J. Brookes, A. Ariaifard, R. Stranger and B. F. Yates, *In press*.
5. Tuning the Laplaza-Cummins Catalyst to Activate and Cleave CO<sub>2</sub>.  
N. J. Brookes, A. Ariaifard, R. Stranger and B. F. Yates, *In press*.
6. Factors dictating carbene formation at (PNP)Ir.  
N. J. Brookes, A. Ariaifard, R. Stranger, M. Whited, R. H. Grubbs and B. F. Yates, *In press*.