

Exploring the Chemistry of Re^I : Physical and Theoretical Investigations

by

Philip D. Bulsink

*Thesis submitted to the
Faculty of Graduate and Postdoctoral Studies
In partial fulfilment of the requirements
For the degree of*

***Master of Science
In
Chemistry***

*Ottawa-Carleton Chemistry Institute
University of Ottawa*

Supervisors: *Professors Darrin Richeson & Tom Woo*

© Philip D. Bulsink, Ottawa, Canada, 2014

Abstract

The development of Rhenium I photocatalysts has been pursued since Lehn first showed the excellent performance of the Re^{I} bipyridine tricarbonyl catalyst. Since then, development has modified the organic ligand to demonstrate continued or improved activity with other α -diimine bidentate geometries. Geometry has been limited to κ_2 motifs, with *fac*-(CO)₃ and axial halide. This work will demonstrate the synthesis, characterization, and testing of a new $\kappa_3(\text{L}_3)\text{-Re}^{\text{I}}\text{-mer}(\text{CO})_2\text{X}$ (X = Cl, Br, CN, OTf) family of compounds for CO₂ reduction, as well as computational investigations into the mechanism of the reduction,

Acknowledgements

Thanks to the members of the Richeson and Woo research groups, both past and present, for the assistance provided and for making the time spent researching and writing this thesis enjoyable. Thanks as well to Frank and Sean in the Brusso lab, for their willingness to allow use of their characterization equipment. Thanks to Jake and the Gambarotta laboratory for use of their GC, and to the Sciano Lab, especially Janice, Charles, and Deni, for the use of their photolysis equipment.

I'd like to thank Dr. Ilia Korobkov for his work measuring and solving the x-ray crystal structures of the compounds discussed. He assisted with some paper writing as well.

Finally, I'd like to thank my fiancé Leanne, and my parents for their unending support, and understanding when I came home frustrated or exhausted from work.

Contents

1	Introduction	1
1.1	Inorganic Chemistry	1
1.2	Photochemistry & Catalysis	2
1.3	Rhenium	3
2	New Geometries for Re^{I}	7
2.1	Section Title	7
2.2	Section Title	7
2.3	Section Title	7
2.4	Section Title	7
2.4.1	Subsection	7
2.4.2	Subsection	7
3	Photocatalysis of CO_2	8
3.1	Section	9
3.1.1	Subsection	9
3.1.2	Subsection	9
3.1.3	Subsection	9
3.2	Section	9
3.3	Section	9
3.3.1	Subsection	9
4	Mechanism of CO_2 Reduction	10
4.1	Section	11
4.1.1	Subsection	11
4.1.2	Subsection	11
4.1.3	Subsection	11

4.2	Section	11
4.3	Section	11
4.3.1	Subsection	11
5	Conclusions	12
5.1	Section	13
5.1.1	Subsection	13
5.1.2	Subsection	13
5.1.3	Subsection	13
5.2	Section	13
5.3	Section	13
5.3.1	Subsection	13

List of Tables

List of Figures

1.1	Two common bidentate complexes using terdentate ligands	4
-----	---	---

Chapter 1

Introduction

1.1 Inorganic Chemistry

Common distinctions split most chemical compounds into one of two categories: organic and inorganic. Organic molecules contain carbon and hydrogen, with or without additional nitrogen, oxygen, phosphorus, sulfur, and the halides. Inorganic chemistry is, therefore, considered to be the remainder of the molecules possible. While they may include some aspect of organic chemistry (especially in organometallic molecules), the main structural motif or reactive center is a non-organic feature. These inorganic compounds can range from compounds such as lithium or grignard reagents with significant organic influence, to metallic alloys or mineral compounds. With such a wide range of possibilities, inorganic chemistry has many facets. A widely active research area is the development and testing of transition metal complexes for catalytic, photo-physical, biochemical or manufacturing uses.

1.2 Photochemistry & Catalysis

A report of the first synthesized organometallic complex was published by Zeise in 1831.¹ To form what is now known as Zeise's salt, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]\cdot\text{H}_2\text{O}$, he mixed platinum chloride with ethanol, followed by a reaction with potassium chloride.² After some controversy to the composition of this, it was confirmed by Griess and Martius,³ and later expanded upon by Birnbaum.⁴

The field of organometallics was expanded greatly by Frankland, and many of his complexes were catalytically active. Further development of this new chemistry quickly led to useful catalysts for the conversion of petroleum products or the production or destruction of other chemicals to be developed using nearly all of the transition metals. These catalysts take all forms, from simple olefin and halide compounds to multi-metallic complexes with large organic ligands.

Some of the most interesting organometallic catalysts since the late 1990s have been the development of earth metal pincer complexes to replace noble metal or early transition metal catalysts, which are often more toxic or expensive to produce. Brookhart and Gibson published a series of papers⁵⁻⁸ on the use of iron and cobalt with bis-imino pyridine ligands to perform ethylene polymerization at rates exceeding those of similar noble metal complexes and metallocenes.⁹ The role of the ligand in the mechanism is still up for debate, but many modified systems have been synthesized and tested since the first work was published.¹⁰

Many of these types of pincer complexes are photochemically active. In transition metal complexes, the interaction between the metal atom(s) and the ligands can cause significant electron mobility upon the absorption of incident photons. The metal atom's d orbitals typically lie at or near the highest occupied molecular orbital (HOMO) energy, while the ligands often have low energy anti-bonding orbitals (π^*) at the lowest unoc-

cupied molecular orbital (LUMO) levels. When a photon is absorbed and is promoted from the ground state to the excited state, that state is geographically removed from the metal centre, this motion of the electron is labelled a metal-ligand charge transfer (MLCT). Formally, the metal atom is oxidized by the photons, this oxidation allows for redox reactivity at the metal centre for as long as the electron remains removed to the ligand. Relaxation (through photon emission via fluorescence or phosphorescence, or via vibrational or other motion processes) can return the electron to the metal to reform the ground electronic state.

1.3 Rhenium

Rhenium compounds display a broad scope of applications ranging from catalysis^{11–13} to radiopharmaceutical applications,^{14,15} as well as possessing interesting fundamental photophysical properties.¹⁶ Since the mid-1970's, complexes containing the α -diimine Re^{I} tricarbonyl core have attracted a great deal of attention due to their attractive photochemical properties with pseudo-octahedral *fac*- $[\text{L}_2\text{Re}(\text{CO})_3\text{X}]$ and *fac*- $[\text{L}_2(\text{L}')\text{Re}(\text{CO})_3]^+$ complexes being the dominant species.^{17–26} A large family of compounds with these formulations have been accessed by the addition of chelating diimine σ -donor ligands to $[\text{Re}(\text{CO})_5\text{X}]$ with the quantitative replacement of two *cis* carbonyls in the Re^{I} starting material.^{17,27–34} Significantly, these reactions form only bidentate coordinated ligands with *facial* tricarbonyl isomers as products even when a potentially tridentate σ -donor, such as bis(imino)pyridine or 2,2':6',2''-terpyridine are employed in the reaction (Figure 1.1).^{35–37} These robust species have been examined for potential applications in organic light-emitting diodes (OLEDs),³⁸ chemosensors and biotechnology probes,^{39–43} fluorescence microscopy imaging of cells,^{39,44,45} and the photochemical reduction of CO_2 to CO .^{46–50} Among the key photophysical features of these α -diimine Re^{I} compounds is the

electron transfer capability of this system and the interplay between the Re center and the well-known non-innocent redox-activity of the ligands.⁵¹

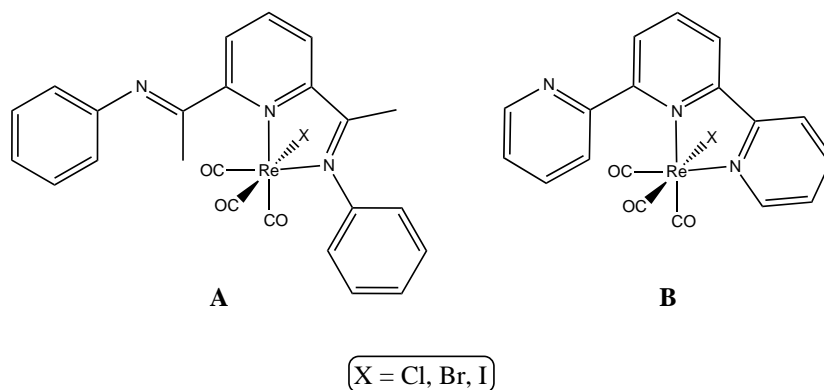


Figure 1.1 Two common *fac*-[L₂Re(CO)₃X] complexes with tridentate σ -donor ligands: L = bis(imino)pyridine (**A**) and 2,2':6',2''-terpyridine (**B**)

Further development of this chemistry has been restricted by the limited structural and electronic variability of the common pseudo-octahedral *fac*-[L₂ReX(CO)₃] (L₂ = */alpha*-diimine) products. While these systems continue to receive considerable attention, studies detailing the coordination chemistry of the meridionally-coordinated tridentate triimine Re^I dicarbonyl core are quite limited.⁵² For example, while κ_3 -(terpy)Re(CO)₂Cl was initially reported in 1988,⁵³ closer analysis of the reported analytical data (including ¹H NMR) indicate that this compound is more likely κ_2 -LRe(CO)₃Cl. A more recent report for this compound provides spectroscopic details of this species as well as the preliminary report for the generation of [(κ_3 -(terpy)Re(CO)₂L)]⁺ cations (L = PPh₃, PEt₃, NC₅H₅, and NCCH₃).⁵⁴ Finally, the ¹H NMR data for (κ_3 -(terpy)Re(CO)₂Br) has been reported.³⁷

In order to fully exploit the potential of this versatile family of compounds, the limits imposed by the bidentate coordination need to be addressed. Furthermore, it would appear that, on the basis of the tridentate ligands that have been investigated, the

concerted effort to produce the tridentate species has been unsuccessful. Attracted by this challenge we sought to synthesize, crystallographically authenticate, and investigate the photophysical properties of low-valent rhenium pincer complexes displaying an N,N',N''-chelated terpyridine array.

We recently reported the conversion of bidentate bis(imino)pyridine complexes 2,6-{2,6-Me₂C₆H₃N=CPh}₂(NC₅H₃)Re(CO)₃X (X = Cl, Br) into tridentate pincer ligand compounds, 2,6-{2,6-Me₂C₆H₃N=CPh}₂(NC₅H₃)Re(CO)₂X (X = Cl, Br).⁵² This transformation was performed in the solid-state by controlled heating of these bidentate species above 200°C in a tube furnace under a flow of nitrogen gas giving excellent yields ($\geq 95\%$). These compounds defined a new coordination environment for Re^I carbonyl chemistry where the metal center is supported by a planar, tridentate pincer coordinated bis(imino)pyridine ligand.

Complexes of 2,2':6',2''-terpyridine (terpy) are of interest due to the conceptual relationship to established bis(imino)pyridine compounds.^{55,56} Herein, we provide rational synthetic procedures to these novel species as well as their characterization and analysis of their visible electronic transitions. These results will broaden the accessibility of such compounds for investigation and application. This report for the unconventional but accessible synthesis of tridentate pincer complexes promises to enhance the versatile chemistry of Re^I and yield new venues for exploration.

This thesis will be a discussion of the development of chemistry of Re^I complexes, their characterization, and comparison of structural and photo-physical properties to computed values. Further exploration of the CO₂ reduction by photo-catalysis of these new complexes will be analyzed. This thesis will also take a more detailed look at specifics of the mechanisms proposed for current Re^I diimine catalysts, and propose new geometries for prior mechanistic steps based on experimental, computational, and

literature review work.

Chapter 2

New Geometries for Re^I

2.1 Section Title

2.2 Section Title

2.3 Section Title

2.4 Section Title

2.4.1 Subsection

SubSubSection

SubSubSection

2.4.2 Subsection

Chapter 3

Photocatalysis of CO₂

Text

3.1 Section

3.1.1 Subsection

3.1.2 Subsection

3.1.3 Subsection

SubSubSection

SubSubSection

SubSubSection

3.2 Section

3.3 Section

3.3.1 Subsection

Chapter 4

Mechanism of CO₂ Reduction

Text

4.1 Section

4.1.1 Subsection

4.1.2 Subsection

4.1.3 Subsection

SubSubSection

SubSubSection

SubSubSection

4.2 Section

4.3 Section

4.3.1 Subsection

Chapter 5

Conclusions

5.1 Section

5.1.1 Subsection

5.1.2 Subsection

5.1.3 Subsection

SubSubSection

SubSubSection

SubSubSection

5.2 Section

5.3 Section

5.3.1 Subsection

Bibliography

1. Zeise, W. C. *J. Physik und Chemie (Schweigger)* **1831**, *62*, 393–441.
2. Hunt, L. B. *Platinum Metals Review* **1984**, *28*, 76–83.
3. Griess, J. P.; Martius, C. A. *Compt rendus*. **1861**, *53*, 922–925.
4. Birnbaum, K. *Ann. Chem. (Liebig)* **1868**, *145*, 67–77.
5. Small, B. L.; Brookhart, M. *Journal of the American Chemical Society* **1998**, *120*, 7143–7144.
6. Small, B. L.; Brookhart, M.; Bennett, A. M. A. *Journal of the American Chemical Society* **1998**, *120*, 4049–4050.
7. J. P. Britovsek, G.; C. Gibson, V.; J. McTavish, S.; A. Solan, G.; J. P. White, A.; J. Williams, D.; J. P. Britovsek, G.; S. Kimberley, B.; J. Maddox, P. *Chem. Commun.* **1998**, 849–850.
8. Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *Journal of the American Chemical Society* **1999**, *121*, 8728–8740.
9. Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chemical Reviews* **2007**, *107*, PMID: 17488059, 1745–1776.
10. Boudier, A.; Breuil, P.-A. R.; Magna, L.; Olivier-Bourbigou, H.; Braunstein, P. *Chem. Commun.* **2014**, *50*, 1398–1407.
11. Dudle, B.; Rajesh, K.; Blacque, O.; Berke, H. *Journal of the American Chemical Society* **2011**, *133*, 8168–8178.
12. Jain, K. R.; Herrmann, W. A.; Kühn, F. E. *Coordination Chemistry Reviews* **2008**, *252*, Chiral Catalysis, 556–568.
13. Kuninobu, Y.; Takai, K. *Chemical Reviews* **2011**, *111*, 1938–1953.
14. Bartholoma, M.; Valliant, J.; Maresca, K. P.; Babich, J.; Zubieta, J. *Chem. Commun.* **2009**, 493–512.
15. Schibli, R.; Schubiger, A. **2002**, *29*, 1529–1542.

16. Coogan, M.; Fernández-Moreira, V.; Kariuki, B.; Pope, S.; Thorp-Greenwood, F. *Angewandte Chemie International Edition* **2009**, *48*, 4965–4968.
17. Giordano, P. J.; Wrighton, M. S. *Journal of the American Chemical Society* **1979**, *101*, 2888–2897.
18. Sacksteder, L.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorganic Chemistry* **1990**, *29*, 4335–4340.
19. Caspar, J. V.; Meyer, T. J. *The Journal of Physical Chemistry* **1983**, *87*, 952–957.
20. Yam, V. W.-W. *Chem. Commun.* **2001**, 789–796.
21. Feliz, M.; Rodriguez-Nieto, F.; Ruiz, G.; Wolcan, E. *Journal of Photochemistry and Photobiology A: Chemistry* **1998**, *117*, 185–192.
22. Ruiz, G.; Wolcan, E.; Féliz, M. *Journal of Photochemistry and Photobiology A: Chemistry* **1996**, *101*, 119–125.
23. Lin, R.; Fu, Y.; Brock, C. P.; Guarr, T. F. *Inorganic Chemistry* **1992**, *31*, 4346–4353.
24. Hino, J. K.; Della Ciana, L.; Dressick, W. J.; Sullivan, B. P. *Inorganic Chemistry* **1992**, *31*, 1072–1080.
25. Walters, K. A.; Kim, Y.-J.; Hupp, J. T. *Inorganic Chemistry* **2002**, *41*, 2909–2919.
26. Striplin, D.; Crosby, G. *Coordination Chemistry Reviews* **2001**, *211*, 163–175.
27. Martin, T. A.; Ellul, C. E.; Mahon, M. F.; Warren, M. E.; Allan, D.; Whittlesey, M. K. *Organometallics* **2011**, *30*, 2200–2211.
28. Abel, E. W.; Wilkinson, G. *J. Chem. Soc.* **1959**, 1501–1505.
29. Kirkham, W. J.; Osborne, A. G.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc.* **1965**, 550–553.
30. Zingales, F.; Sartorelli, U.; Trovati, A. *Inorganic Chemistry* **1967**, *6*, 1246–1248.
31. Gamelin, D. R.; George, M. W.; Glyn, P.; Grevels, F.-W.; Johnson, F. P. A.; Klotzbuecher, W.; Morrison, S. L.; Russell, G.; Schaffner, K.; Turner, J. J. *Inorganic Chemistry* **1994**, *33*, 3246–3250.
32. Martí, A. A.; Mezei, G.; Maldonado, L.; Paralitici, G.; Raptis, R. G.; Colón, J. L. *European Journal of Inorganic Chemistry* **2005**, *2005*, 118–124.
33. Morse, D. L.; Wrighton, M. S. *Journal of the American Chemical Society* **1976**, *98*, 3931–3934.
34. Giordano, P. J.; Fredericks, S. M.; Wrighton, M. S.; Morse, D. L. *Journal of the American Chemical Society* **1978**, *100*, 2257–2259.
35. Granifo, J.; Bird, S. J.; Orrell, K. G.; Osborne, A. G.; Šik, V. *Inorganica Chimica Acta* **1999**, *295*, 56–63.

36. Orrell, K. G.; Osborne, A. G.; Šik, V.; da Silva, M. W.; Hursthouse, M. B.; Hibbs, D. E.; Malik, K. A.; Vassilev, N. G. *Journal of Organometallic Chemistry* **1997**, *538*, 171–183.
37. Abel, E. W.; Dimitrov, V. S.; Long, N. J.; Orrell, K. G.; Osborne, A. G.; Pain, H. M.; Sik, V.; Hursthouse, M. B.; Mazid, M. A. *J. Chem. Soc., Dalton Trans.* **1993**, 597–603.
38. Gong, X.; Ng, P. K.; Chan, W. K. *Advanced Materials* **1998**, *10*, 1337–1340.
39. Lo, K. K.-W.; Louie, M.-W.; Zhang, K. Y. *Coordination Chemistry Reviews* **2010**, *254*, 18th International Symposium on the Photochemistry and Photophysics of Coordination Compounds Sapporo, 2009, 2603–2622.
40. Lin, T.-P.; Chen, C.-Y.; Wen, Y.-S.; Sun, S.-S. *Inorganic Chemistry* **2007**, *46*, 9201–9212.
41. Slone, R. V.; Yoon, D. I.; Calhoun, R. M.; Hupp, J. T. *Journal of the American Chemical Society* **1995**, *117*, 11813–11814.
42. D. Beer, P.; Timoshenko, V.; Maestri, M.; Passaniti, P.; Balzani, V. *Chem. Commun.* **1999**, 1755–1756.
43. Beer, P. D.; Hayes, E. J. *Coordination Chemistry Reviews* **2003**, *240*, 35 Years of Synthetic Anion Receptor Chemistry 1968–2003, 167–189.
44. Amoroso, A. J.; Arthur, R. J.; Coogan, M. P.; Court, J. B.; Fernandez-Moreira, V.; Hayes, A. J.; Lloyd, D.; Millet, C.; Pope, S. J. A. *New J. Chem.* **2008**, *32*, 1097–1102.
45. Amoroso, A. J.; Coogan, M. P.; Dunne, J. E.; Fernandez-Moreira, V.; Hess, J. B.; Hayes, A. J.; Lloyd, D.; Millet, C.; Pope, S. J. A.; Williams, C. *Chem. Commun.* **2007**, 3066–3068.
46. Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536–538.
47. Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helvetica Chimica Acta* **1986**, *69*, 1990–2012.
48. Takeda, H.; Ishitani, O. *Coordination Chemistry Reviews* **2010**, *254*, Inorganic Reaction Mechanisms A Tribute to Ralph Pearson on the occasion of his 90th birthday, 346–354.
49. Christensen, P.; Hamnett, A.; Muir, A. V. G.; Timney, J. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1455–1463.
50. Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414–1416.
51. Caulton, K. G. *European Journal of Inorganic Chemistry* **2012**, *2012*, 435–443.
52. Jurca, T.; Chen, W.-C.; Michel, S.; Korobkov, I.; Ong, T.-G.; Richeson, D. S. *Chemistry – A European Journal* **2013**, *19*, 4278–4286.

53. Juris, A.; Campagna, S.; Bidd, I.; Lehn, J. M.; Ziessel, R. *Inorganic Chemistry* **1988**, *27*, 4007–4011.
54. Black, D. R.; Hightower, S. E. *Inorganic Chemistry Communications* **2012**, *24*, 16–19.
55. Russell, S. K.; Darmon, J. M.; Lobkovsky, E.; Chirik, P. J. *Inorganic Chemistry* **2010**, *49*, PMID: 20143847, 2782–2792.
56. Tondreau, A. M.; Atienza, C. C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J. *Science* **2012**, *335*, 567–570.