

## MASTER'S THESIS

### The chemistry of osmium and ruthenium carbonyl clusters with functionalized alkyne and phosphine ligands

Ting, Fai Lung

*Date of Award:*  
2001

[Link to publication](#)

#### General rights

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent URL assigned to the publication

The Chemistry of Osmium and Ruthenium Carbonyl Clusters  
with Functionalized Alkyne and Phosphine Ligands

TING Fai Lung

A thesis submitted in partial fulfillment of the requirements  
for the degree of  
Master of Philosophy

September 2001

Hong Kong Baptist University

## Abstract

Reactions of several diyne ligands  $\text{HC}\equiv\text{CRC}\equiv\text{CH}$  ( $\text{R} = 2,7\text{-fluorenediyl R}_1, 2,7\text{-fluoren-9-onediyl R}_2, 4,4'\text{-di(tert-butyl)-2,2'-bithiazole-5,5'-diyl R}_3$  or  $2,2'\text{-bithiophene-5,5'-diyl R}_4$ ) with  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  in  $\text{CH}_2\text{Cl}_2$  at room temperature afforded the monomeric  $[\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-HC}_2\text{RC}\equiv\text{CH})]$  ( $\text{R} = \text{R}_1$  **1a**,  $\text{R}_2$  **2a**,  $\text{R}_3$  **3a** or  $\text{R}_4$  **4a**) and dimeric  $[\{\text{Os}_3(\text{CO})_9(\mu\text{-CO})\}_2(\mu_3\text{-}\eta^2\text{-HC}_2\text{RC}_2\text{H})]$  ( $\text{R} = \text{R}_1$  **1b**,  $\text{R}_2$  **2b**,  $\text{R}_3$  **3b** or  $\text{R}_4$  **4b**) complexes in moderate yields. New hexaruthenium carbonyl clusters  $[\{\text{Ru}_3(\mu\text{-H})(\text{CO})_9\}_2\{\mu_3\text{-}\eta^2, \eta^2\text{-C}_2\text{RC}_2\}]$  **5** and  $[\{\text{Ru}_3(\text{CO})_9(\mu\text{-CO})\}_2\{\mu_3\text{-}\eta^2\text{-HC}_2\text{RC}_2\text{H}\}]$  **6** ( $\text{R} = \text{R}_2$ ) have been prepared by treatment of  $\text{HC}\equiv\text{CRC}\equiv\text{H}$  with an equimolar amount of  $[\text{Ru}_3(\text{CO})_{12}]$  and  $[\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2]$ , respectively, in refluxing THF. Reactions of  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  with platinum bis(alkynyl) complexes *cis*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{L})]$  ( $\text{L} = \text{Me}_2\text{bipy}$ ,  $\text{Bu}^t_2\text{bipy}$ ) at room temperature readily gave the novel, spiked-triangular heterometallic cluster complexes  $[\text{Os}_3\text{Pt}(\text{CO})_9(\mu_4\text{-}\eta^2\text{-C}\equiv\text{CPh})(\eta^1\text{-C}\equiv\text{CPh})(\text{L})]$  ( $\text{L} = \text{Me}_2\text{bipy}$  **7** or  $\text{Bu}^t_2\text{bipy}$  **8**).

A novel phosphido-bridged complex  $[\text{Ru}_2(\text{CO})_6\{\mu\text{-P}(\overline{\text{C}(\text{CH})_3\text{O}})_2\}(\mu\text{-}\eta^1, \eta^2\text{-}\overline{\text{C}(\text{CH})_3\text{O}})]$  **9** was produced in good yield by the thermal reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with tri(2-furyl)phosphine. Complex **9** readily reacted with two equivalents of terminal alkynes  $\text{HC}\equiv\text{CR}$  ( $\text{R} = \text{Ph}$ , *p*- $\text{C}_6\text{H}_4\text{Me}$ , *p*- $\text{C}_6\text{H}_4\text{NO}_2$ ,  $\text{Fc}$ , *p*- $\text{C}_6\text{H}_4\text{Fc}$ ,  $(\text{C}_4\text{H}_2\text{S})\text{C}\equiv\text{CH}$  or

(C<sub>4</sub>H<sub>2</sub>S)<sub>2</sub>C≡CH) by an interesting head-to-tail ynyl coupling with a furan group to form [Ru<sub>2</sub>(CO)<sub>4</sub>{μ-P( $\overline{C(CH)_3O}$ )<sub>2</sub>}{μ-η<sup>1</sup>,η<sup>1</sup>,η<sup>2</sup>,η<sup>3</sup>-(R)CC(H)C(R)C(H) $\overline{C(CH)_3O}$ }] (R = Ph **10**, *p*-C<sub>6</sub>H<sub>4</sub>Me **11**, *p*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> **12**, Fc **13**, *p*-C<sub>6</sub>H<sub>4</sub>Fc **14**, (C<sub>4</sub>H<sub>2</sub>S)<sub>2</sub>C≡CH **16** or (C<sub>4</sub>H<sub>2</sub>S)<sub>2</sub>C≡CH **17**) containing a novel furyl-substituted C<sub>4</sub> hydrocarbonyl chain. Reaction of **9** with a 1:1 mixture of ferrocenylacetylene and *p*-nitrophenylacetylene yielded an inseparable pair of isomers [Ru<sub>2</sub>(CO)<sub>4</sub>{μ-P( $\overline{C(CH)_3O}$ )<sub>2</sub>}{μ-η<sup>1</sup>,η<sup>1</sup>,η<sup>2</sup>,η<sup>3</sup>-(R<sub>1</sub>)CC(H)C(R<sub>2</sub>)C(H) $\overline{C(CH)_3O}$ }] (R<sub>1</sub> = *p*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, R<sub>2</sub> = Fc **15a**, R<sub>1</sub> = Fc, R<sub>2</sub> = *p*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> **15b**), of which one isomer has been structurally characterized.

Simple mono- and disubstitution products [Ru<sub>2</sub>(CO)<sub>5</sub>{P( $\overline{C(CH)_3O}$ )<sub>3</sub>}{μ-P( $\overline{C(CH)_3O}$ )<sub>2</sub>}{μ-η<sup>1</sup>,η<sup>2</sup>- $\overline{C(CH)_3O}$ }] **19a** and [Ru<sub>2</sub>(CO)<sub>4</sub>{P( $\overline{C(CH)_3O}$ )<sub>3</sub>}{μ-P( $\overline{C(CH)_3O}$ )<sub>2</sub>}{μ-η<sup>1</sup>,η<sup>2</sup>- $\overline{C(CH)_3O}$ }] **19b** were produced by the thermal reaction of **9** with tri(2-furyl)phosphine. Similar thermal substitution reactions also proceeded when **9** reacted with the diphosphines, namely bis(diphenylphosphido)methane (dppm), bis(diphenylphosphido)amine (dppa) or bis(diphenylphosphido)methylamine (dppma), affording [Ru<sub>2</sub>(CO)<sub>4</sub>{μ-P( $\overline{C(CH)_3O}$ )<sub>2</sub>}{μ-η<sup>1</sup>,η<sup>2</sup>- $\overline{C(CH)_3O}$ }(μ-L)] (L = dppm **20**, dppa **21** or dppma **22**) in good yields. Upon reaction with bis(diphenylphosphido)ferrocene (dppf), a mixture of [{Ru<sub>2</sub>(CO)<sub>5</sub>{μ-P( $\overline{C(CH)_3O}$ )<sub>2</sub>}{μ-η<sup>1</sup>,η<sup>2</sup>- $\overline{C(CH)_3O}$ }]<sub>2</sub>(η<sup>1</sup>,η<sup>1</sup>-dppf)] **23a** and polymeric [Ru<sub>2</sub>(CO)<sub>4</sub>{μ-P( $\overline{C(CH)_3O}$ )<sub>2</sub>}{μ-η<sup>1</sup>,η<sup>2</sup>- $\overline{C(CH)_3O}$ }(η<sup>1</sup>,η<sup>1</sup>-dppf)]<sub>n</sub> **23b** was obtained in which the dppf was found to bridge two identical μ-phosphido Ru<sub>2</sub> units.

When the reactions were carried out using bis(diphenylphosphido)ethane (dppe) or bis(diphenylphosphido)propane (dppp), compounds  $[\text{Ru}_2(\text{CO})_5\{\mu\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_2\}\{\mu\text{-}\eta^1,\eta^1,\eta^1\text{-C}_6\text{H}_4\text{PPh}(\text{CH}_2)_n\text{PPh}_2\}]$  ( $n = 2$  **24** or  $3$  **25**) were isolated as the thermodynamic products, in which both P atoms chelate to one Ru centre to afford five- (for **24**) and six-membered (for **25**) ruthenacycles, accompanied by orthometallation reaction and reductive elimination of furan. As the length of the methylene segment between PPh<sub>2</sub> groups is increased for bis(diphenylphosphido)butane (dppb) and bis(diphenylphosphido)pentane (dpppe), cyclometallation is not favoured in either case. Instead,  $[\{\text{Ru}_2(\text{CO})_5\{\mu\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_2\}\{\mu\text{-}\eta^1,\eta^2\text{-}\overline{\text{C}(\text{CH}_3)_3\text{O}}\}\}_2(\eta^1,\eta^1\text{-L})]$  ( $L = \text{dppb}$  **26a** or dpppe **27a**) and  $[\text{Ru}_2(\text{CO})_4\{\mu\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_2\}\{\mu\text{-}\eta^1,\eta^2\text{-}\overline{\text{C}(\text{CH}_3)_3\text{O}}\}(\eta^1,\eta^1\text{-L})]_n$  ( $L = \text{dppb}$  **26b** or dpppe **27b**) were obtained with the product yield depending on the stoichiometry of the reactants. Another novel diruthenium complex  $[\text{Ru}_2(\text{CO})_5\{\mu\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_2\}\{\mu\text{-}\eta^1,\eta^1,\eta^2\text{-C}_{14}\text{H}_8\text{PPh}_2\}]$  **28** was also obtained through the thermal treatment of **9** with (9-anthracenyl)diphenylphosphine.

Two phosphine-disubstituted isomers  $[(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}\{\text{P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_3\}_2]$  **29a** and **29b**, a  $\mu$ -phosphido tetraruthenium cluster  $[(\mu\text{-H})_2\text{Ru}_4(\text{CO})_7(\mu\text{-CO})\{\text{P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_3\}_2\{\mu\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_2\}\{\mu\text{-}\eta^2\text{-}\overline{\text{C}(\text{CH}_3)_3\text{O}}\}]$  **30** and two  $\mu_3$ -phosphinidene tetraruthenium clusters  $[(\mu\text{-H})_2\text{Ru}_4(\text{CO})_{12}\{\mu_3\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})\}]$  **31** and  $[(\mu\text{-H})_2\text{Ru}_4(\text{CO})_{10}\{\text{P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_3\}_2\{\mu_3\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})\}]$  **32** have been synthesised by reaction of tri(2-furyl)phosphine with  $[(\mu\text{-}$

$\text{H})_4\text{Ru}_4(\text{CO})_{12}]$  in THF under reflux. Reaction of (9-anthracenyl)diphenylphosphine with  $[(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{12}]$  under similar conditions afforded the new compound  $[\text{HRu}(\text{CO})_3(\text{PPh}_2\text{C}_{14}\text{H}_8)][(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{11}(\text{PPh}_2\text{C}_{14}\text{H}_9)]$  33.

# *Table of Contents*

Declaration	i
Abstract	ii
Acknowledgement	vi
Table of Contents	vii
List of Tables	xi
List of Figures	xi
List of Schemes	xiv
List of Chart	xvi
List of Abbreviations	xvii
List of Symbols	xix
<b>Chapter 1 Introduction</b>	<b>1</b>
1.1 Significance of Chemical Research in Transition Metal Clusters	1
1.2 Structure and Bonding in Transition Metal Clusters	4
1.3 Characterization Methods	6
1.4 Alkyne-Transition Metal Chemistry	13
1.4.1 Alkyne-Transition Metal Coordination Modes	13
1.4.1.1 Mononuclear Alkyne Complexes	13
1.4.1.2 Dinuclear Alkyne Complexes	14
1.4.1.3 Polynuclear Alkyne Complexes	16
1.4.2 Synthesis of Transition Metal-Alkyne Complexes	18
1.4.2.1 Thermolysis	18
1.4.2.2 Chemical Activation	20
1.4.2.3 Photochemical Activation	22
1.4.2.4 Condensation, Substitution and Ligand Exchange Reactions	23
1.4.2.5 Other Method	24

1.5	The Chemistry of Transition Metal Clusters with Phosphorus Ligands	26
1.5.1	Phosphido ( $\mu$ -PR <sub>2</sub> ) Bridges	27
1.5.2	Phosphinidene Bridges and Caps ( $\mu_3$ -PR, $\mu_4$ -PR)	29
1.5.3	Triply-Bridging 'Naked' Phosphides	31
1.5.4	Semi-Interstitial and Interstitial Phosphido Clusters	33
	References	36
<b>Chapter 2</b>	<b>The Chemistry of Triosmium and Triruthenium Carbonyl Clusters Containing Functionalized Alkyne Ligands</b>	<b>41</b>
2.1	Synthesis and Structural Characterization of Triosmium and Triruthenium Carbonyl Clusters with Functionalized Diynes	41
2.1.1	Introduction of Transition Metal–Diene Clusters	41
2.1.2	Synthesis of Diynes	47
2.1.3	Synthesis and Characterization of Osmium–Diene Complexes	50
2.1.4	Synthesis and Characterization of Ruthenium–Diene Complexes	56
2.2	Synthesis and X-ray Structures of Osmium-Platinum Heterometallic Clusters from the Reaction between [Os <sub>3</sub> (CO) <sub>10</sub> (NCMe) <sub>2</sub> ] and <i>cis</i> -Platinum Bis(alkynyl) Complexes	61
2.2.1	Introduction	61
2.2.2	Results and Discussion	62
2.3	Summary of Spectroscopic Data for Complexes 1 – 8	71
	References	74
<b>Chapter 3</b>	<b>Synthesis, Characterization and Reactivity Studies of Phosphido-Bridged Dinuclear Ruthenium Carbonyl Complexes</b>	<b>77</b>
3.1	Introduction	77
3.2	Synthesis of [Ru <sub>2</sub> (CO) <sub>6</sub> { $\mu$ -P( $\overline{\text{C}(\text{CH}_3)_3\text{O}}_2$ )}( $\mu$ - $\eta^1, \eta^2$ - $\overline{\text{C}(\text{CH}_3)_3\text{O}}$ )] <b>9</b>	80



3.3	Reactivity of Novel Phosphido-Bridged Dinuclear Ruthenium Carbonyl Cluster towards Terminal Alkynes	85
3.3.1	Reaction of <b>9</b> with some Terminal Alkynes	85
3.3.2	Reaction of <b>9</b> with Ferrocene-containing Alkynes	87
3.3.3	Reaction of <b>9</b> with Terminal Diyne Ligands	89
3.3.4	Proposed Mechanism for the Alkyne Coupling	92
3.3.5	Crystal Structures for Complexes <b>10</b> – <b>17</b>	96
3.3.6	Reactivity of <b>17</b> towards $[\text{Co}_2(\text{CO})_8]$	108
3.4	Reactivity of Novel Phosphido-Bridged Dinuclear Ruthenium Carbonyl Cluster towards Phosphines. Substitution, Polymerization, Cyclometallation and Elimination Reactions	110
3.4.1	Reaction of <b>9</b> with Tri(2-furyl)phosphine	112
3.4.2	Reaction of <b>9</b> with some Diphosphines $\text{PPh}_2\text{EPPH}_2$	117
3.4.3	Reaction of <b>9</b> with (9-Anthracenyl)diphenylphosphine	138
3.5	Summary of Spectroscopic Data for Complexes <b>9</b> – <b>28</b>	142
	References	148
<b>Chapter 4</b>	<b>The Chemistry of Tetraruthenium Carbonyl Clusters Containing Functionalized Phosphines</b>	<b>156</b>
4.1	General Background of Tetraruthenium Carbonyl Clusters containing Phosphido and Phosphinidene group	156
4.2	Reaction of Tetraruthenium Carbonyl Cluster $[(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{12}]$ with Tri(2-furyl)phosphine	163
4.2.1	Spectroscopic and Structural Characterization of <b>29a</b> and <b>29b</b>	165
4.2.2	Spectroscopic and Structural Characterization of <b>30</b>	170
4.2.3	Spectroscopic and Structural Characterization of <b>31</b> and <b>32</b>	174
4.3	Reaction of Tetraruthenium Carbonyl Cluster $[(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{12}]$ with (9-Anthracenyl)diphenylphosphine	179
4.4	Summary of Spectroscopic Data for Complexes <b>29</b> – <b>33</b>	185
	References	186

<b>Chapter 5</b>	<b>Concluding Remark and Future Work</b>	<b>190</b>
<b>Chapter 6</b>	<b>Experimental Section</b>	<b>194</b>
6.1	General Experimental	194
6.2	Experimental Procedures	196
6.2.1	Experimental for Chapter 2	196
6.2.2	Experimental for Chapter 3	200
6.2.3	Experimental for Chapter 4	213
References		215
<b>Appendices</b>		<b>217</b>
<b>Curriculum Vitae</b>		