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SYNTHESIS, CHARACTERISATION, X-RAY CRYSTALLOGRAPHY ANALYSIS, AND THERMOLYSIS STUDY OF TRIRUTHENIUM CARBONYL CLUSTER DERIVATIVES OF PHOSPHINE AND ARSINE LIGANDS

HUSNA IZZATI BINTI MUHAMMAD NOR AZHARAN

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ABSTRACT

Triruthenium metal carbonyl clusters bearing bidentate and monodentate phosphine/arsine ligands continue to expand as an interesting research area due to their potential application in catalysis as well as its unique bonding modes. However, there is a lack of studies on the structure and the reactivity of $Ru_3(CO)_8(\mu\text{-L–L})_2$ and $Ru_3(CO)_9(\mu\text{-(L–L)})(L)$ where [L–L = bidentate; L = monodentate phosphine/arsine ligands] complexes involving bidentate diphosphine ligands with more than one methylene group. Most previous research has focused on bidentate ligands with short backbones, such as dppm and dpam, and no crystallographic or thermolysis studies reported for longer chain ligands (dppe, dppp, or dppb) on $Ru_3(CO)_8(\mu\text{-L–L})_2$ and $Ru_3(CO)_9(\mu\text{-(L–L)})(L)$ types. This gap limits the understanding of how ligand chain length affects cluster transformation, bonding, and reactivity. It is also fundamentally important to observe the transformation and activation of these ligands on the triruthenium cluster *via* thermolysis reactions. In this study, all synthesized structures are new, except $Ru_3(CO)_8(\mu\text{-dppe})_2$ (**2.1c**), which was previously reported without a crystal structure. Single crystal X-ray diffraction data for six complexes of $Ru_3(CO)_8(\mu\text{-L–L})_2$ and $Ru_3(CO)_9(\mu\text{-(L–L)})(L)$ types were successfully obtained and supported with spectroscopic data: $Ru_3(CO)_8(\mu\text{-dppe})_2$ (**2.1c**), $Ru_3(CO)_8(\mu\text{-dppp})(dppp)$ (**2.3a**), $Ru_3(CO)_9(\mu\text{-dppe})(PPh_3)$ (**3.1a**), $Ru_3(CO)_9(\mu\text{-dppp})(PPh_3)$ (**3.2a**), $Ru_3(CO)_9(\mu\text{-dpam})(AsPh_3)$ (**4.1a**), and $Ru_3(CO)_9(\mu\text{-dppp})(AsPh_3)$ (**4.2a**). The structural analysis of each of the complexes has been discussed. Compound (**2.1c**) shows a common bridging mode of the dppe ligands across the Ru–Ru bond. However, a unique feature is observed in (**2.3a**), where one dppp ligand bridge to Ru–Ru bond, while the other one chelates a single Ru atom in a $\mu_1\text{-}\eta^2$ coordination mode. The crystal structure of (**2.3a**) exhibits a Star-of-David disorder involving the triangular Ru atoms. Thermolysis of compound (**2.3a**) yielded a new compound $Ru_3(CO)_6(\mu\text{-}Ph_2P(CH_2)_3P(C_6H_4))(dppp)(\mu\text{-H})_2$ (**5.1a**). The presence of two bridging hydride ligands in (**5.1a**) was verified by ^1H NMR spectroscopy at -10.31 ppm and -16.44 ppm. Thermolysis of compounds (**3.1a**) and (**3.2a**) yielded the complexes $Ru_3(CO)_5(\mu_2\text{-CO})(\mu_3\text{-PPh}(CH_2)_2PPh)(\mu_3\text{-}C_6H_4)(\mu_2\text{-}PPh_2)$ (**5.2b**), and $Ru_3(CO)_6(\mu_2\text{-}PPh_2)(\mu_2\text{-PPh}(CH_2)_3PPh_2)(\mu_4\text{-}C_6H_4)$ (**5.3a**), respectively. All thermolysis products exhibited a consistent pattern of ligand rearrangement, including dephenylation and orthometallation, both of which contribute to the formation of new complexes. These transformations commonly result in orthometallated species as major thermolysis products. In contrast, compound (**5.2b**) features an open triruthenium core with the formation of a phenyl acyl ligand. Overall, this study presents nine new crystal structures and offers fundamental insights into ligand transformations involving P–C bond cleavage and C–H bond activation, highlighting their impact on the triruthenium cluster framework. For future studies, the formation of new thermolysis compounds could be further explained in detail through mechanistic investigations. Moreover, potential applications, such as catalytic studies, could be explored and supported by theoretical calculations using Density Functional Theory (DFT).

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CHAPTER 1
INTRODUCTION

1.1 Transition Metal Carbonyl Cluster Chemistry

Transition metals are elements found in the *d*-block of the periodic table and play a crucial role in coordination chemistry, which investigates the structure, bonding, and reactivity of their complexes (Winter, 2015). Numerous advancements and research have been conducted regarding the interest in exploring the fascination of transition metal clusters (Kirakci et al., 2023; Rahaman et al., 2021). Metal atoms in clusters exhibit diverse coordination modes, and this coordination geometry around the metal centre influences the properties and reactivity of the cluster. The transition metals in group 7-10 clusters exhibit coordination with π-acceptor ligands, particularly with emphasis on carbonyl ligands (Dyson & McIndoe, 2000).

The transition metal carbonyl clusters are made of three or more metal atoms, where each of the atoms is chemically bonded with the other metal atoms in the group, and bonded to the π-acceptor ligands, which consist of the carbonyl group. These metals are in low oxidation states and are known as π-acceptor clusters or low oxidation state clusters (Dyson & McIndoe, 2000; Cesari et al., 2021). Transition metal carbonyl has grown in popularity after it was discovered that the ligands can coordinate to more than one metal centre and significantly impact the structure of the ligands, spectroscopic characteristics, and reactivity. The replacement of CO in metal cluster carbonyls by phosphines, arsines, and related ligands are common (Bruce et al., 1988a; Huda et al., 2025; Raithby, 2024).

The bonding mode of metal clusters with carbonyl ligands are an interesting part of transition metal cluster chemistry. Carbonyl ligands are composed of a carbon atom that is triple bonded to an oxygen atom (C≡O). When these ligands coordinate to transition metal clusters, they commonly do so by donating electron density from the lone pair of electrons from the oxygen atoms to the metal centre (Pradier et al., 2011). This results in the development of metal-carbonyl bonds, which give rise to unique bonding properties. Carbonyl is the most essential ligand in transition metal carbonyl cluster chemistry due to its ability to stabilize metals in low oxidation states and its