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THIOCARBONYL AND
SELENOCARBONYL COMPLEXES
OF IRIDIUM

A thesis presented to the
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for the degree of
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Keith G. Town
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ABSTRACT

The results to be described and discussed in this thesis concern synthesis and reactivity of iridium(I) and (III) complexes containing thiocarbonyl or selenocarbonyl ligands.

Chapter 1 comprises: a review of Vaska's compound, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and related species, covering syntheses, structure and bonding and reactions of this very widely studied moiety; and brief reviews of metal-thiocarbonyl syntheses and reactions and metal-selenocarbonyl chemistry. These three reviews background the themes developed in this work; of preparations and reactions, particularly ligand reactions, of thiocarbonyl and selenocarbonyl analogues of Vaska's compound and species derived from $\text{IrCl}(\text{CE})(\text{PPh}_3)_2$, E = S, Se.

A new synthesis of $\text{IrCl}(\text{CS})(\text{PPh}_3)_2$ is described in Chapter 2. The route employed involves preparation of dithioester complexes and facets of the reactivity of these species have been considered and a number of metallocycle derivatives prepared. Reductions of coordinated-thiocarbonyl groups have been considered; $\text{IrH}(\text{CS})(\text{PPh}_3)_3$ was transformed into $\text{IrH}_2(\text{SMe})(\text{PPh}_3)_3$ by treatment with hydrogen, while the thiocarbonyl cation complexes $[\text{IrClX}(\text{CO})(\text{CS})(\text{PPh}_3)_2]^+$ were treated with borohydride to afford thioformyl species. Iridium alkyl, thiocarbonyl complexes have been prepared, and transformed by reaction with dithiocarbamate ion to yield *monohapto*-thioacetyl derivatives.

The preparation of $\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$, the selenocarbonyl analogue of Vaska's compound is reported in Chapter 3. The synthesis utilizes carbon diselenide as the selenocarbonyl source, and involves a four-step conversion of a *dihapto*-carbon diselenide adduct complex to the iridium(I) selenocarbonyl species. Reactions of a range of iridium(I) complexes with carbon diselenide are described, including the preparation of a complex including three CSe_2 groups. Reactions of $\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$ have been studied and several iridium(I) and (III) selenocarbonyl compounds prepared. The ready reduction of $\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$ (in the presence of phosphine) by borohydride to give $\text{IrH}_2(\text{SeMe})(\text{PPh}_3)_3$ is described and comparisons are drawn between the relative reactivities of iridium thiocarbonyl and selenocarbonyl groups, in analogous species, with nucleophiles. It is concluded the Ir-CSe system is more reactive under similar conditions. Metallocycle derivatives of iridium selenocarbonyl, diselenomethylester complexes have been characterised.

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