Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Coordination Chemistry Reviews 248 (2004) 1329–1341

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Synthetic routes to homoleptic and heteroleptic ruthenium(II) complexes incorporating bidentate imine ligands

Leone Spiccia*, Glen B. Deacon, Christopher M. Kepert

School of Chemistry, Monash University, Victoria 3800, Australia

Received 28 December 2003; received in revised form 19 April 2004; accepted 22 April 2004
Available online 19 July 2004

Contents

Abstract

Ruthenium(II) complexes are finding applications in a variety of fields and, in particular, as photo-sensitisers in the conversion of solar energy into chemical or electrical energy where a major achievement has been the development of a dye sensitised solar cell (DSSC) by the Grätzel group. In order to optimise the performance of such devices there is a need to prepare complexes with tunable spectral and physico-chemical properties. Synthetic approaches have been developed which enable the rational synthesis of heteroleptic tris(diimine)ruthenium(II) complexes with the desired properties. In this review we focus on contributions made by our group which have led to the development of two approaches to such heteroleptic complexes both of which use $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ polymer as a key precursor. These approaches differ in that one requires conversion of $[\text{Ru}(\mathbf{L})(\text{CO})_2(\text{Cl})_2]$ into a triflate complex, $[\text{Ru}(\mathbf{L})(\text{CO})_2(\text{CF}_3\text{SO}_3)_2]$ followed by substitution of the triflate by a second diimine ligand ($\mathbf{L}^1$) to form $[\text{Ru}(\mathbf{L})(\mathbf{L}^1)(\text{CO})_2]^{2+}$ and chemical decarbonylation in the presence of a further diimine

---

Abbreviations: bpy, 2,2′-bipyridine; phen, 1,10-phenanthroline; H_2dcbpy, 2,2′-bipyridine-4,4′-dicarboxylic acid or 4,4′-dicarboxy-2,2′-bipyridine; tpy, 2,2′:6′,2″-terpyridine; H_3tctpy, 2,2′:6′,2″-terpyridine-4,4′,4″-tricarboxylic acid or 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine; tri(methoxycarbonyl)tpy, 4,4′,4″-trimethoxycarbonyl-2,2′:6′,2″-terpyridine; dpk, di(2-pyridyl) ketone; amp, 2-aminopyridine; biq, 2,2′-biquinoline; $(\text{EtO}_2\text{C})_2$bpy, 4,4′-di(ethoxycarbonyl)-2,2′-bipyridine; 4,4′-Me_2bpy, 4,4′-dimethyl-2,2′-bipyridine; 5,5′-Me_2bpy, 5,5′-dimethyl-2,2′-bipyridine; 4,7-Me_2phen, 4,7-dimethyl-1,10-phenanthroline; 5,6-Me_2phen, 5,6-dimethyl-1,10-phenanthroline; 2,9-Me_2phen, 2,9-dimethyl-1,10-phenanthroline; Hdpa, di(2-pyridyl)amine; $\text{bpyCH}_2\text{MV}^{2+}$, 1-((4′-methyl-2,2′-bipyridin-4-yl)methyl)-1′-methyl-4,4′bipyridinium; MebpyCOOH, 4′-methyl-2,2′-bipyridine-4-carboxylic acid; bpyCH_2PTZ, 10-((4′methyl-2,2′-bipyridin-4-yl)methyl)phenothiazine

* Corresponding author. Tel.: +61-3-99054526; fax: +61-3-99054597.
E-mail address: leone.spiccia@sci.monash.edu.au (L. Spiccia).

0010-8545/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2004.04.008

ligand (**L**^{2}) to [Ru(**L**)(**L**^{1})(**L**^{2})]$^{2+}$ while the other involves photodecarbonylation of [Ru(**L**)(CO)$_2$(Cl)$_2$] to produce [Ru(**L**)(CO)(Cl)$_2$]$_2$, which on sequential addition of two further diimine ligands finally yields [Ru(**L**)(**L**^{1})(**L**^{2})]$^{2+}$. These versatile methods, together with those developed by others, provide the synthetic tools needed to produce Ru(II) complexes with properties required for a particular application.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Homoleptic complex; Heteroleptic complex; Bidentate ligand; Ruthenium(II) complexes; Synthesis

1. Introduction

Since the luminescence of [Ru(bpy)$_3$]$^{2+}$ was first reported [1], tris(diimine) and related ruthenium complexes have been investigated extensively as model compounds for studies of photochemical processes [2–11] and as candidates for utilisation in practical applications such as molecular electronics [5,12,13] and light harvesting processes that mimic photosynthesis [5,14–25]. Attempts to optimise the performance of ruthenium imine complexes employed in these systems have initiated systematic studies into the effects of various modifications in co-ordination environment on physico-chemical properties [5,7–11,26,27]. Further investigation into the behaviour of such complexes in vitreous states [28] and monolith encapsulated forms [29], for example, has been stimulated by interests in their electronic and catalytic properties.

The potential of these complexes to act as photosensitisers in the conversion of solar energy to chemical or electrical energy has become an intensely scrutinised area of research [5,14,15,17–21,24,25,30,31]. Some of the initial efforts to harvest solar energy were focussed on the use of [Ru(bpy)$_3$]$^{2+}$ analogues to promote the conversion of water into dihydrogen and dioxygen, which could power fuel cells [32]. The combination of a high chemical, thermal and photochemical stability, reversible redox behaviour, substantial UV-visible light absorption and long lived metal to ligand charge transfer (MLCT) excited states indicated that such species were excellent candidates for this purpose [2,6,33]. A number of approaches were based on homogenous mixtures of components in solution [34–36]. Kalyanasundaram and Grätzel [37] were at the forefront of these developments, successfully integrating the production of dihydrogen and dioxygen. A methyl viologen quencher reduces protons to H_2 via a colloidal platinum catalyst whilst a colloidal ruthenium dioxide mediates the regeneration of the [Ru(bpy)$_3$]$^{2+}$ sensitiser and generation of O_2 (Fig. 1) [37].

In recent years, the most actively investigated aspect of solar energy conversion has been concerned with the design and optimisation of dye sensitised solar cells (DSSCs) (see for example refs. [15–19,23]). The assertion that [Ru(bpy)$_3$]$^{2+}$ could potentially be oxidatively quenched by electron transfer to the conduction band of a titanium dioxide electrode [32] was initially examined with the photodecomposition of water in mind [38]. Derivatised [Ru(bpy)$_3$]$^{2+}$ complexes were attached to the surface of the titanium dioxide electrode [39] in order to circumvent a slow response cathodic photocurrent caused by the generation of superoxide [40]. Subsequently, the Grätzel group reasoned that the concept could be incorporated into DSSCs, a revolutionary type of solar cell, which mimicked the "electron pump mechanism" of photosynthesis [14,15,23] by using a ruthenium based sensitiser in place of chlorophyll and a titanium dioxide semiconductor to perform functions analogous to biological membranes. A clever combination of components allows oxidative quenching of the excited sensitiser by the conduction band of the semiconductor and reduction of the oxidised sensitiser via an iodine/iodide couple (Fig. 2).

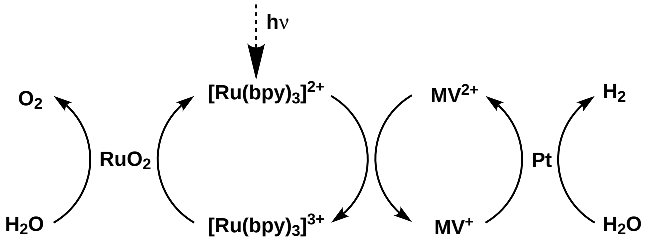


Fig. 1. Components used to carry out the photoassisted dissociation of water [37].

Refinement of DSSCs by, for example, improving the titania deposition methods [41–43], modification of the semiconductor surface to reduce charge recombination phenomena occurring at the solid–solution interface [44–47], a better choice of redox mediator to reduce the dye to its original state [15,48], and use of sensitisers with improved light absorption properties developed by modification of the ligand environment [15,49], has yielded devices with performances that compare favourably with those of conventional PV devices. This together with the possibility of cheaper production costs [50–52] has continued to stimulate research in this area, some of which is being reviewed in this volume. Our own purpose here is to detail the contribution

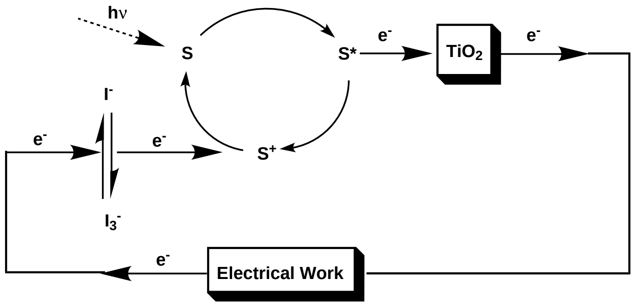


Fig. 2. Schematic of dye sensitised solar cell (DSSC) developed by Grätzel and co-workers.

made by our research group to the development of synthetic methods that enable the systematic incorporation of dissimilar diimine ligands into the Ru^{II} co-ordination sphere.

Whilst there is little doubt that the potential for efficient solar energy conversion has provided the major impetus for the investigation of properties of, in particular, Ru^{II} diimine complexes, it should be stressed that such complexes are attracting attention as pharmaceuticals [53–55], multi-electron transfer catalysts [8], as fluorescent and electrochemical sensing anion specific receptors [56], as catalysts for the water–gas shift reaction [57–59], hydroformylation [60], and reagents facilitating the reduction of carbon dioxide to carbon monoxide and formate (an important endeavour given the increasing atmospheric carbon dioxide concentrations and depletion of natural resources) [61–65].

2. Brief overview of photophysical properties of ruthenium(II) complexes

Variation of ligands has been demonstrated to have considerable effect on the efficiency of sensitisation by ruthenium(II) dyes adsorbed on semiconductor surfaces in photovoltaic cells [14,15,49] and the catalytic reduction of carbon dioxide [62,63]. The ligand combination in a sensitiser can tune the energy of the excited state [2,5,7,16,27,33,66,67], absorption [5,7,16,27,68] and excited-state lifetime [5,7,16,69] of the complex. The effectiveness of a photoelectric transducer is reliant upon the sensitiser having an excited state energy level conducive to quenching by the conduction band of the semiconductor substrate and the excited state being sufficiently long lived to allow electron transfer to this band [5,7,16]. Additionally, the combination of ligands comprising the Ru^{II} primary co-ordination sphere needs to be capable of facilitating the absorption of available light, giving rise to appropriate excited state [16,70]. These parameters need to be optimised in order to maximise cell efficiency [16,18].

In simple terms, if we assume that $[Ru(diimine)_3]^{2+}$ complexes approximate an octahedral ligand field (although more correctly $[Ru(bpy)_3]^{2+}$ possesses D_3 symmetry), then we might regard the full t_{2g} orbitals as the highest occupied molecular orbitals (HOMO). Due to a strong crystal field, the lowest unoccupied molecular orbital (LUMO) in these complexes is a vacant π-antibonding orbital [6]. Therefore, the lowest energy electronic transition is a metal to ligand charge transfer which can be considered as metal centre oxidation and ligand reduction [2,5]. Stabilization of the excited state is enhanced by delocalisation of the electron over π-bonding orbitals of the acceptor ligand [71]. An important feature of the heteroleptic tris(diimine) Ru^{II} complexes, which differentiates them from the homoleptic species, is the increased number of π^* levels into which an excited electron may be promoted [68,72]. Experimental comparisons of the energy of the absorption maxima with the difference between in the potentials for ruthenium oxidation and ligand reduction, and a correlation of the reduction potential of the free ligand with that of the corresponding complex revealed a linear relationship between the energy of light required for MLCT and the energy gap between the Ru^{II} t_{2g} set and the lowest lying π^* orbital [6,16,72–74]. The importance of ligand selection in photoelectric and photocatalytic applications has led to strategies for optimisation of various properties by judicious choice of ligands. For example, incorporation of three inequivalent ligands with π^* levels that allow the overlap of absorptions corresponding to $t_{2g} \rightarrow \pi^*$ transitions to each ligand would cause the complex to absorb all visible light, which could be termed a “black absorber” [27,68].

Although the dependence of the excited state properties of Ru^{II} complexes on ligand environment is well established [75], most studies have been confined to homoleptic complexes ($[Ru(\mathbf{L})_3]^{2+}$) and heteroleptic complexes of type $[Ru(\mathbf{L})_2(\mathbf{L}^1)]^{2+}$ and $[Ru(\mathbf{L})_2X_2]$ (**L** and $\mathbf{L}^1$ are inequivalent diimines and X is an anion such as a halide or pseudohalide) [2,6,24], and only recently has the successful separation of stereochemical and geometrical isomers of mixed ligand mononuclear and polynuclear Ru^{II} complexes been reported [76–83] opening up exciting opportunities for the detailed examinations of the dependence of the spectroscopic, photophysical and electrochemical properties on structural features of the isomers. The focus of study on $[Ru(\mathbf{L})_2(\mathbf{L}^1)]^{2+}$ and $[Ru(\mathbf{L})_2X_2]$ complexes has arisen largely because of difficulties associated with the synthesis and purification of heteroleptic complexes with three dissimilar diimine ligands, $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$ (**L**, $\mathbf{L}^1$ and $\mathbf{L}^2$ are inequivalent diimines). One of the synthetic challenges tackled in our laboratory has been the development of versatile synthetic methods to such complexes. After a brief outline of the general synthetic methods to homoleptic $[Ru(\mathbf{L})_3]^{2+}$ and heteroleptic $[Ru(\mathbf{L})_2(\mathbf{L}^1)]^{2+}$ complexes and dyes most commonly used in DSSCs, synthetic strategies to heteroleptic $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$ complexes are reviewed in more detail.

3. Synthetic methods

3.1. Homoleptic ruthenium(II) diimine complexes

The synthesis of the homoleptic $[Ru(bpy)_3]Cl_2$, first reported in 1936, involved prolonged heating of a mixture of $RuCl_3{\cdot}xH_2O$ and excess of 2,2′-bipyridine, according to [84]:

$$2\,RuCl_3 \cdot xH_2O + 8\,bpy \rightarrow 2[Ru(bpy)_3]Cl_2 + xH_2O + C_{20}H_{14}N_4 + 2\,HCl \qquad (1)$$

A more versatile method involving reduction of $RuCl_3{\cdot}xH_2O$ with sodium phosphinate or phosphinic acid in the presence of a diimine ligand was subsequently used to prepare $[Ru(diimine)_3]^{2+}$ complexes incorporating an array of substituted 2,2′-bipyridines and 1,10-phenanthrolines [85–92].

A later preparation involves reaction of the versatile $[Ru(CO)_2Cl_2]_n$ with 2,2′-bipyridine and trimethylamine-*N*-oxide in 2-methoxyethanol [93].

$$[Ru(CO)_2Cl_2]_n + 3n\,\text{bpy} + 2n\,Me_3NO \xrightarrow{MeOCH_2CH_2OH} n[Ru(bpy)_3]Cl_2 + 2n\,Me_3N + 2n\,CO_2 \quad (2)$$

The method, which can be applied to heteroleptic complexes (outlined below), is capable of generalisation.

A method involving conversion of $[Ru(C_6H_6)Cl_2]^{2+}$ [94] to heteroleptic complexes might well be modified to yield homoleptic complexes.

$$[Ru(C_6H_6)Cl_2]_2 + 6L \xrightarrow{h\nu,\ MeCN} 2[RuL_3]Cl_2 + 2C_6H_6 \quad (3)$$

Chiral tris(diimine) ruthenium complexes have been prepared by a prolonged reaction and the method appears generally applicable [95].

$$RuCl_3 \xrightarrow[3L]{MeOH/AcOH} [RuL_3]Cl_2 \quad (4)$$

3.2. Heteroleptic ruthenium(II) diimine complexes $[Ru(\mathbf{L})_2(\mathbf{L}^1)]^{2+}$

The development of a synthetic methodology to heteroleptic tris(diimine) complexes of type $[Ru(\mathbf{L})_2(\mathbf{L}^1)]^{2+}$ was a major advance providing access to an array of complexes. One route involved the reaction of a ruthenium(III) complex, $[Ru(\mathbf{L}^1)Cl_3]$, with an excess of a different diimine, **L** [91].

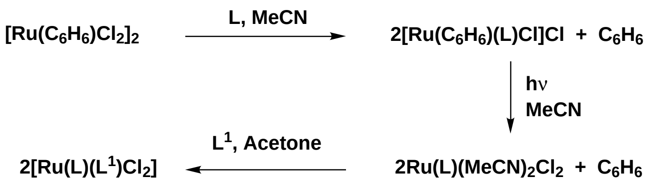
$$[Ru(\mathbf{L}^1)Cl_3] \xrightarrow{L,\Delta} [Ru(\mathbf{L})_2(\mathbf{L}^1)]^{2+} \quad (5)$$

A facile, widely used, route involves reaction of $[Ru(\mathbf{L})_2Cl_2]$ with a second diimine in an appropriate medium [95–97].

$$[Ru(\mathbf{L})_2Cl_2] + \mathbf{L}^1 \rightarrow [Ru(\mathbf{L})_2(\mathbf{L}^1)]Cl_2 \quad (6)$$

Syntheses of $[Ru(\mathbf{L})_2Cl_2]$ required for this reaction were initially unsatisfactory and included thermal decomposition of $[Ru(bpy)_3]Cl_2$ [96] and $(\mathbf{L}H)[Ru(\mathbf{L})Cl_4]$ [96,98] (**L**H = protonated diimine) and a photochemical process involving irradiation of $[Ru(bpy)_3]\mathbf{X}_2$ or $[Ru(bpy)_3]Cl_2$ [99].

A most convenient synthesis of such complexes entails the direct reaction of $RuCl_3{\cdot}xH_2O$ with slightly more than two molar equivalents of a diimine ligand in DMF in which the solvent acts as a reductant, converting Ru^{III} to Ru^{II} [95,100]. A minor amount of the monocarbonyl complex $[Ru(bpy)_2(CO)Cl]^+$ may also be formed, presumably by the thermal decarbonylation of the solvent [101], but in the context of $[Ru(\mathbf{L})_2(\mathbf{L}^1)]^{2+}$ syntheses such an impurity is not problematic. Further reaction with another diimine ligand then produces the desired $[Ru(\mathbf{L})_2(\mathbf{L}^1)]^{2+}$ complex [95]. Another approach to give the unsymmetrical dichlorides involves the reaction sequence in Scheme 1 [94].



Scheme 1.

Reaction of $[Ru(\mathbf{L})_2(CO)_2]^{2+}$ (**L** = phen or bpy) [102,103] and optically resolved *cis*-$[Ru(bpy)_2(CO)_2]^{2+}$ [11,80,104] with a different bipyridine nucleophile ($\mathbf{L}^1$) and Me_3NO yields $[Ru(\mathbf{L})_2(\mathbf{L}^1)]^{2+}$. The method has also been used to yield geometric isomers of complexes containing two molecules of the same unsymmetrical bidentate ligand [103]. More simply, $[Ru(bpy)(CO)_2Cl_2]$ reacts with Me_3NO and phen to give $[Ru(bpy)(phen)_2]^{2+}$ [93], a reaction capable of being generalised.

$$[Ru(bpy)(CO)_2Cl_2] + 2phen + 2Me_3NO \rightarrow [Ru(bpy)(phen)_2]Cl_2 + 2CO_2 + 2Me_3N \quad (7)$$

The dimethyl sulfoxide complex $[Ru(DMSO)_4Cl_2]$, formed by reacting $RuCl_3{\cdot}xH_2O$ with DMSO, has also proved a convenient synthon for the preparation of heteroleptic complexes with two diimine ligands. Addition of a bidentate ligand, **L**, to $[Ru(DMSO)_4Cl_2]$ in a non-donor solvent replaces two DMSO ligands and forms $[Ru(\mathbf{L})(DMSO)_2Cl_2]$ [105]. The lability of the DMSO and chloride ligands allows their replacement by a bidentate ligand, $\mathbf{L}^1$, yielding $[Ru(\mathbf{L})(\mathbf{L}^1)_2]^{2+}$ [106,107]. As will be described later, this method has been developed to a stage where heteroleptic complexes containing three dissimilar diimine ligands, $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$, can be prepared [108,109]. In addition, the reaction of $[Ru(\mathbf{L})_2(DMSO)Cl]^+$ with a different diimine ligand, $\mathbf{L}^1$, gave $[Ru(\mathbf{L})_2(\mathbf{L}^1)]^+$ with retention of stereochemistry [110–112].

3.2.1. Dyes applied in DSSCs

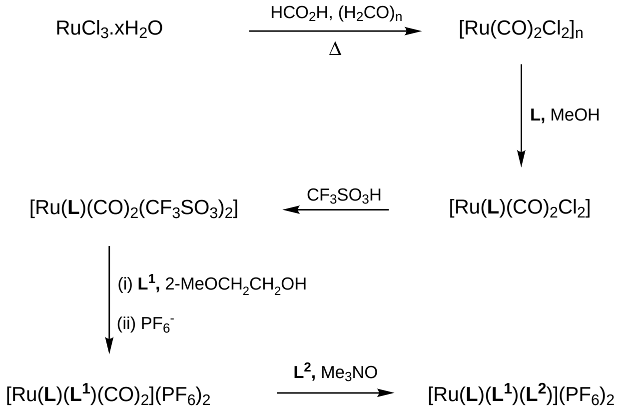
A plethora of Ru^{II} complexes have been screened for their ability to act as photosensitisers in DSSCs (see for example [16]). Rather than exhaustively reviewing the synthesis of such complexes, our attention here focuses on the most frequently used Ru^{II} dye sensitisers, these methods being representative of a wider variety of approaches used. The complex associated with the breakthrough discovery of DSSCs was $[Ru(H_2dcbpy)_2(NCS)_2]$, where H_2dcbpy = 4,4′-dicarboxy-2,2′-bipyridine [15]. The synthesis of this complex follows the typical path for bis(diimine)Ru thenium(II) complexes, i.e., reaction of the ligand with $RuCl_3{\cdot}xH_2O$ at high temperatures in DMF produces $[Ru(H_2dcbpy)_2(Cl)_2]$ (commonly called N3), which is treated with an excess of a thiocyanate salt also in DMF to yield the product. The product contained small amounts of the tris(diimine) complex, $[Ru(H_2dcbpy)_3]Cl_2$, and the **S**-bound thiocyanate linkage isomers, $[Ru(H_2dcbpy)_2(\mathbf{N}CS)(\mathbf{S}CN)]$ and $[Ru(H_2dcbpy)_2(\mathbf{S}CN)_2]$. Purification was achieved by slowly precipitating the dye by acidifying an alkaline solution to pH 3.3 [113]. Moreover, procedures have been developed which allow the isolation of two tetrabutylammonium salts, viz. $(Bu_4N)_4[Ru(dcbpy)_2(NCS)_2]$ and $(Bu_4N)_2[Ru(Hdcbpy)_2(NCS)_2]$ [114] and these led to improvements in cell performance over N3 [115].

Another efficient dye, termed the 'black dye' because of its excellent light absorption over most of the visible region, incorporates a terpyridine tridentate ligand, 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine (H_3tctpy) [49,70]. To facilitate purification the ligand was first converted into the trimethyl ester and then refluxed with $RuCl_3{\cdot}xH_2O$ under argon in an $EtOH/CH_2Cl_2$ mixture to form $[Ru(tri(methoxycarbonyl)terpy)Cl_3]$. Further reaction with an excess of ammonium thiocyanate, at reflux in DMF, followed by hydrolysis with triethylamine produces the dye which was isolated as $\{(C_2H_5)_3NH\}[Ru(H_3tctpy)(\mathbf{N}CS)_3]$. The product was found to be predominantly a mixture of linkage isomers, viz., 60% **N**-bonded isomer (preferred for DSSCs), 20% **N**- and **S**-bonded isomers and 10% **S**-bonded isomer. Chromatographic purification and crystallisation as an alkylammonium salt, $\{(C_4H_9)_4N\}_{4-y}[Ru(H_y tctpy)(\mathbf{N}CS)_3]$ was followed by detailed spectroscopic, structural and photochemical investigations [70].

3.3. Synthetic strategies to heteroleptic tris(diimine) ruthenium(II) complexes, $[Ru(L)(L^1)(L^2)]^{2+}$.

3.3.1. Syntheses based on $[Ru(CO)_2Cl_2]_n$

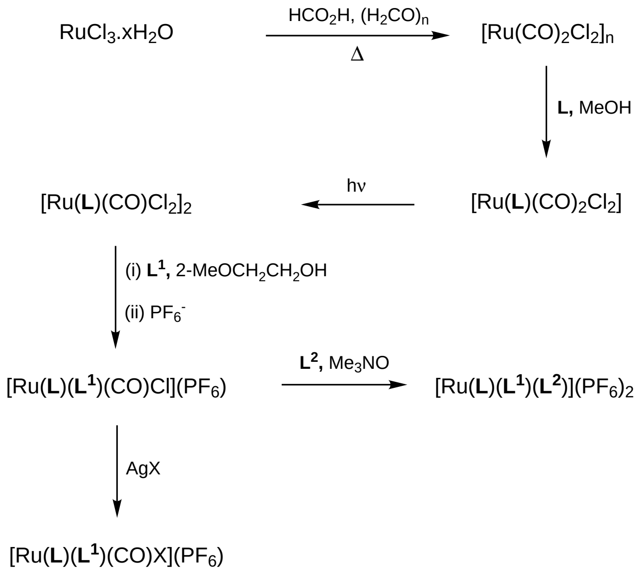
Heteroleptic tris(diimine) Ru(II) complexes of type $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$, where **L**, $\mathbf{L}^1$ and $\mathbf{L}^2$ are dissimilar bidentate ligands, have been reported from the early 1980's, the first example involving use of $[Ru(CO)_2Cl_2]_2$ as initial synthon [102]. The dicarbonyldichlororuthenium(II) polymer, $[Ru(CO)_2Cl_2]_n$ is readily prepared from commercial hydrated $RuCl_3$ [116,117]. The ease of cleavage of this polymer and the contrasting lability and chemistry of the chloro and carbonyl ligands has provided excellent scope for the synthesis of mixed ligand complexes. We have been developing $[Ru(CO)_2Cl_2]_n$ as a synthon for heteroleptic $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$ complexes [72,102,118–125]. Preparations described by other workers follow later.



Scheme 2. Triflate route to heteroleptic$[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$ complexes.

Two routes to $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$ complexes based on $[Ru(CO)_2Cl_2]_n$ are described in Schemes 2 and 3 and both initially involve the conversion of $[Ru(CO)_2Cl_2]_n$ into $[Ru(\mathbf{L})(CO)_2Cl_2]$ [93,118,119]. From this common product, the two routes diverge with one following the path of exchange of the chloro ligands by triflate [118,120,126,127] followed by substitution of this relatively labile anion by a diimine ligand [93,118] while in the other photodecarbonylation of $[Ru(\mathbf{L})(CO)_2Cl_2]$ yields a dinuclear product [128] which is subjected to cleavage by a strongly binding ligand. For both routes, the final step involved chemical decarbonylation with Me_3NO in the presence of a third diimine ligand [72,102,125,126]. Pakkanen and co-workers [129–133] have prepared $[Ru(\mathbf{L})(CO)_2Cl_2]$ complexes using $[Ru(CO)_3Cl_2]_2$ as starting material. These synthetic developments provide considerable scope for designing and then preparing complexes with tunable physicochemical properties.

3.3.1.1. $[Ru(CO)_2Cl_2]_n$. The reaction of $RuCl_3{\cdot}xH_2O$ with formic acid in the presence of excess paraformaldehyde results in the reduction of Ru(III) to Ru(II) and formation of $[Ru(CO)_2Cl_2]_n$, [72,118] which was isolated as a pale yellow powder [72,116–118]. Possible redox processes



Scheme 3. Photochemical decarbonylation route to heteroleptic $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$ complexes.

responsible for the formation of the product are shown below:

$$\text{reduction}: \mathrm{RuCl_3(\cdot}x\mathrm{H_2O)} + 2\mathrm{HCOOH} + \mathrm{e^-} \\ \rightarrow \frac{1}{n}[\mathrm{Ru(CO)_2Cl_2}]_n + 2\mathrm{H_2O} + \mathrm{Cl^-} + (x\mathrm{H_2O})$$

$$\text{oxidation}: \mathrm{HCOOH} + \frac{1}{n}(\mathrm{CH_2O})n \\ \rightarrow 2\mathrm{CO} + \mathrm{H_2O} + 2\mathrm{H^+} + 2\mathrm{e^-}$$

$$\text{overall}: 2\mathrm{RuCl_3}(x\mathrm{H_2O}) + 5\mathrm{HCOOH} + \frac{1}{n}(\mathrm{CH_2O})_n \\ \rightarrow \frac{2}{n}[\mathrm{Ru(CO)_2Cl_2}]_n + 5\mathrm{H_2O} + 2\mathrm{HCl} + 2\mathrm{CO} + (x\mathrm{H_2O}) \tag{8}$$

The generation of excess carbon monoxide provides an explanation for the presence of the dinuclear tricarbonyl impurity, $[\mathrm{Ru(CO)_3Cl_2}]_2$, in the product, a compound which exhibits carbonyl stretching at ~2138 $\mathrm{cm^{-1}}$ [72,116] and is thought to be related to the production of HCl during the reaction. This proposal is supported by an increase in yield observed on deliberate addition of HCl. For the $[\mathrm{Ru(CO)_2Cl_2}]_n$ polymer, the twin terminal ν(CO) IR absorptions indicate that the structure consists of a "kinked-chain" (Fig. 3) with *cis*- and *trans*-bridging chlorides and *cis*-terminal carbonyls, analogous to that proposed for $[\mathrm{Mo(NO)_2Cl_2}]_n$ [134].

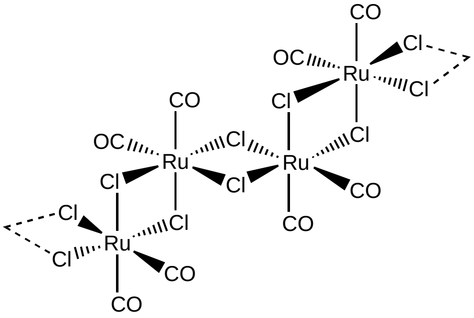


Fig. 3. Proposed "kinked-chain" structure of $[\mathrm{Ru(CO)_2Cl_2}]_n$.

3.3.1.2. *[Ru(**L**)(CO)$_2$Cl$_2$].* Polymeric $[\mathrm{Ru(CO)_2Cl_2}]_n$ reacts readily with bidentate diimine ligands in an alcohol solvent to give (bidentate)dicarbonyldichlororuthenium(II) complexes, $[\mathrm{Ru}(\mathbf{L})\mathrm{(CO)_2Cl_2}]$ (where **L** includes 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 5,5′-dimethyl-2,2′-bipyridine, 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, di(2-pyridyl) ketone, 2,2′-biquinoline and 2-aminomethylpyridine) [72,93,118,119,126,135].

$$\frac{1}{n}[\mathrm{Ru(CO)_2Cl_2}]_n \xrightarrow{\mathbf{L},\mathrm{MeOH}} [\mathrm{Ru}(\mathbf{L})\mathrm{(CO)_2Cl_2}] \tag{9}$$

These complexes are excellent precursors to mixed ligand complexes by virtue of differences in the reactivity of the carbonyl and chloride ligands; variation in their ability to be displaced by other ligands and physical processes (e.g. photolabilisation [128]) facilitating the selective addition of ligands [72]. Pakkanen and co-workers [129–133] have developed an alternative procedure which converts $[\mathrm{Ru(CO)_3Cl_2}]_2$ into $[\mathrm{Ru}(\mathbf{L})\mathrm{(CO)_2Cl_2}]$ complexes that can then also be subjected to the procedure outlined in Scheme 2. This work also indicates that the presence of this compound as an impurity in $[\mathrm{Ru(CO)_2Cl_2}]_n$ does not affect the outcome of reaction 9.

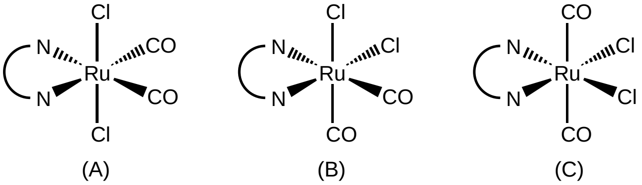


Fig. 4. Geometric isomers of $[\mathrm{Ru}(N\text{–}N)\mathrm{(CO)_2Cl_2}]$ where *N–N* is a symmetrical diimine ligand. (A) *cis*-CO, *trans*-Cl; (B) *cis*-CO, *cis*-Cl; (C) *trans*-CO, *cis*-Cl.

For a symmetric bidentate ligand, such a reaction can result in any one of three geometric isomers (see Fig. 4). On the basis of the IR spectrum, which exhibited symmetric (ν_{sym}) and antisymmetric (ν_{asym}) stretching vibrations attributable to *cis*-carbonyls and a far IR spectrum with only one Ru–Cl stretching absorption, the structure of the complexes with L = bpy, phen, biq, dpk [118,119,136] was assigned as having the *cis*-dicarbonyl-*trans*-dichloro configuration (**A**). The NMR spectra showed same number of signals as the free ligand indicating a symmetrically co-ordinated ligand, consistent with isomer (**A**). Pakkanen and co-workers [129–133], on the other hand have found that the *cis*-dicarbonyl-*cis*-dichloro isomer (B) is formed when $[\mathrm{Ru(CO)_3Cl_2}]_2$ is used as starting material.

Likewise, the 2-aminomethylpyridine derivative, $[\mathrm{Ru(amp)(CO)_2Cl_2}]$, the only complex to form as one of the other geometric isomers when $[\mathrm{Ru(CO)_2Cl_2}]_n$ is used, has a *cis*-arrangement of carbonyls and chlorides (**B** in Fig. 4). A difference in reactivity between a diimine and an imine/amine can not explain this finding. The 1,2-diaminoethane complex adopts a *cis*-dicarbonyl *trans*-dichloro-1,2-diaminoethane configuration corresponding to structure (**A**) [136]. It was argued that the longer reaction time necessary to cleave $[\mathrm{Ru(CO)_2Cl_2}]_n$ with amp resulted in the formation of the thermodynamically stable product (isomer **B**).

An unexpected product was isolated from the reaction of $[\mathrm{Ru(CO)_2Cl_2}]_n$ with dpk for which delocalisation of electron density [137] can give rise to further chemistry. Storage of a methanolic solution of $[\mathrm{Ru(dpk)(CO)_2Cl_2}]$ in the dark resulted in the addition of methanol to co-ordinated dpk and crystallised a product with structure shown in Fig. 5 [138]. The deprotonated ketal formed from this addition, methoxydi(2-pyridyl)methoxide, co-ordinates facially such that the ketal oxygen is *trans*- to the chloride and the pyridyl nitrogens are *trans*- to the carbonyls (Fig. 5). This

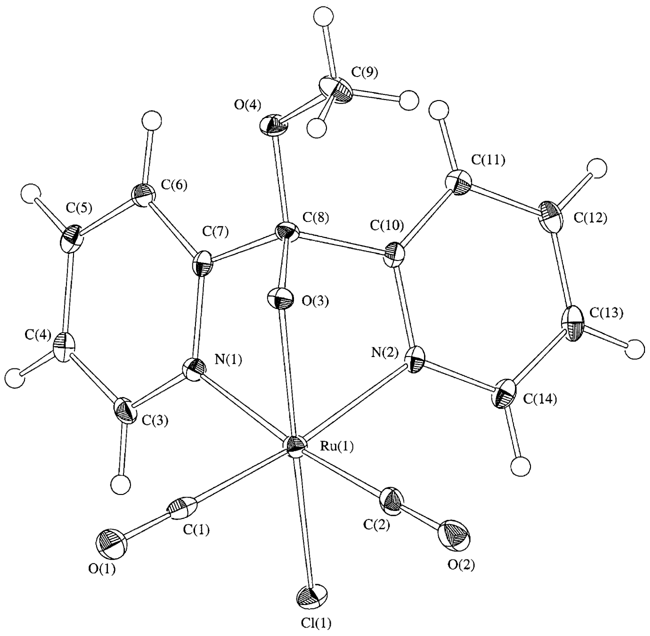


Fig. 5. Structure of product obtained on addition of methanol to dpk in $[Ru(dpk)(CO)_2Cl_2]$ [138].

chemistry has precedent in that nucleophilic attack on metal bound dpk has been reported for first row transition metal complexes [137,139] and Cr(III) and Ru(II) bis(diol) complexes formed on addition of water have been structurally characterised [140].

3.3.1.3. Chemical decarbonylation of $[Ru(\mathbf{L})(CO)_2Cl_2]$. Despite initially being thought inert to further substitution, subsequent investigation showed that both the carbonyl and the chloride ligands in $[Ru(\mathbf{L})(CO)_2Cl_2]$ are susceptible to replacement under appropriate conditions. For example, on treatment with the decarbonylation agent trimethylamine N-oxide (Me_3NO) in pyridine, $[Ru(\mathbf{L})(CO)_2Cl_2]$ complexes were found to undergo monodecarbonylation to yield the monocarbonyl pyridine complexes, $[Ru(\mathbf{L})(CO)(py)Cl_2]$ [121]. A related chemical decarbonylation has been used to give $[Ru(bpy)_2Cl(py)]^+$ [141]. A useful reaction from the point of view of obtaining photoactive Ru(II) dye for use in DSCCs was the reaction of such complexes with an inequivalent diimine ligand and trimethylamine N-oxide. As noted earlier, total decarbonylation was achieved by reaction of $[Ru(\mathbf{L})(CO)_2Cl_2]$ and $[Ru(\mathbf{L})(CO)(py)Cl_2]$ with Me_3NO in the presence of an excess of a bidentate ligand $\mathbf{L}^1$ in 2-methoxyethanol [93,102]. This provided another facile route for the synthesis of the heteroleptic complexes $[Ru(\mathbf{L})(\mathbf{L}^1)_2]^{2+}$ in good yield. The chloride ligands were also found to be displaced by reaction with silver carboxylates in a solution of the corresponding acid yielding the analogous carboxylate complex, $[Ru(\mathbf{L})(CO)_2(RCO_2)_2]$ [118]. For example,

$$[Ru(phen)Cl_2(CO)_2] + 2\,AgO_2CCH_3 \rightarrow [Ru(phen)(CO)_2(CH_3CO_2)_2] + 2AgCl \qquad (10)$$

3.3.1.4. Triflate route (Scheme 2). An observation, which led to the development of a versatile synthesis of $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$, was the finding that the chloride ligands in $[Ru(\mathbf{L})(CO)_2Cl_2]$ were vulnerable to displacement by trifluoromethanesulphonate ($CF_3SO_3^-$). Three methods were used to achieve chloride substitution. Firstly, reaction of the bis(acetato) complex, $[Ru(phen)(CO)_2(CH_3CO_2)_2]$, with CF_3SO_3H yielded the corresponding $[Ru(phen)(CO)_2(CF_3SO_3)_2]$ derivative, but this method failed for the analogous bpy complex. In acetonitrile, analogous reactions yielded bis(acetonitrile) complexes [118]:

$$[Ru(\mathbf{L})(CH_3CO_2)_2(CO)_2] + 2CF_3SO_3H \rightarrow [Ru(\mathbf{L})(CO)_2(MeCN)_2](CF_3SO_3)_2 + 2CH_3CO_2H \qquad (11)$$

These might well be used as intermediates to give $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$ in view of Freedman's use of the corresponding chlorides [94].

More generally, heating $[Ru(\mathbf{L})(CO)_2Cl_2]$ (e.g., where $\mathbf{L}$ is bpy and Me_2bpy) with triflic acid either neat or dissolved in high boiling point organic solvent, thereby removing the HCl produced, drives the reaction to completion. The reaction temperature of 110 °C represented a balance between achieving reasonable rates whilst minimising the decomposition of the complexes [72,127]. In cases where the ligands were susceptible to acid hydrolysis, eg., $[Ru((EtO_2C)_2bpy)(CO)_2Cl_2]$, a complex with ester groups, reaction with silver triflate at reflux in dichloromethane was used [72]. The yields of the triflate complexes varied considerably from high (80%) to poor (25%) [72,118,127]. The products were found to be stable for long periods providing all traces of triflic acid were removed and the complexes were dried thoroughly prior to storage. The analytical data, including two ν(CO) absorptions and multiple ν(SO) absorptions indicated that the *cis*-carbonyl, *cis*-triflato isomer is formed [72,118] indicative of thermal isomerization given that the reactant has *trans*-dichloro stereochemistry. $[Ru(phen)(CO)_2(CF_3SO_3)_2]$, however, was obtained with *trans*-triflato groups from the *trans*-diacetatoruthenium(II) precursor [118].

The triflate groups are susceptible to facile substitution by bidentate ligands under quite mild conditions (e.g., refluxing ethanol in the presence of a dissimilar diimine ligand, $\mathbf{L}^1$), resulting in the formation of the dicarbonyl complexes $[Ru(\mathbf{L})(\mathbf{L}^1)(CO)_2]^{2+}$, which were isolated as PF_6^- salts in yields ranging from 30 to 80% [72,118,120,127]. The NMR and IR spectra for these complexes were again consistent with a *cis*-disposition of the carbonyl ligands. Triflato labilization has also been used in the synthesis of *trans*-$[RuL_2AB]$complexes [142] and 'black' absorbers [68].

Exploitation of $[Ru(\mathbf{L})(\mathbf{L}^1)(CO)_2]^{2+}$ as a synthon for tris(diimine) complexes incorporating three dissimilar ligands, $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$, was achieved by chemical decarbonylation with Me_3NO in the presence of an excess of a third bidentate ligand, $\mathbf{L}^2$, in 2-methoxyethanol [72,102,126]. Interestingly, in the case of complexes containing the esterified ligand $(EtO_2C)_2$bpy, a transesterification reaction took place through which the ethyl group was replaced by $–CH_2CH_2OMe$ from the 2-methoxyethanol solvent, requiring a change of solvent to 1,2-dimethoxyethane [72]. A notable feature of the reaction was the dependence of the rate of decarbonylation on the two bidentate ligands, **L** and $\mathbf{L}^1$. This was faster for ligands with electron withdrawing groups in keeping with the view that Me_3NO assisted decarbonylations occur by oxygen atom transfer to the carbonyl. A mechanistic rationale has been based on the expectation that a decrease in the electron density on the metal centre, caused by the electron withdrawing substituent, will make the carbonyl more prone to nucleophilic attack [72].

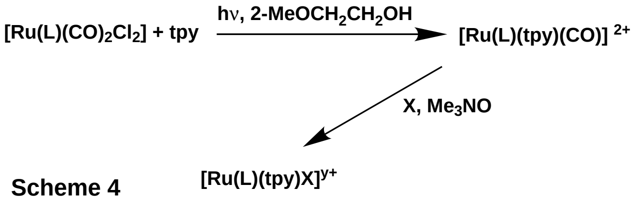
In cases where the ligand can be oxidised by Me_3NO, an alternative strategy has been developed whereby $[Ru(\mathbf{L})(\mathbf{L}^1)(CO)_2]^{2+}$ is treated with Me_3NO in MeCN or pyridine to give $[Ru(\mathbf{L})(\mathbf{L}^1)(A)_2]^{2+}$ (where A = MeCN or py) and then the unidentate ligands are displaced by the oxidisable bidentate ligand [143].

$$[Ru(\mathbf{L})(\mathbf{L}^1)(CO)_2]^{2+} \xrightarrow[Me_3NO]{A} [Ru(\mathbf{L})(\mathbf{L}^1)(A)_2]^{2+} \xrightarrow[-2A]{L^2} [Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$$

A strategy for selective removal of one carbonyl ligand was also developed providing a new route to bridged diruthenium complexes [143]. In addition, the dicarbonylruthenium(II) intermediate route has been used to give homochiral (Δ_3/Λ_3) and heterochiral ($\Delta_2\Lambda_3/\Delta/\Lambda_2$) complexes with two ruthenium(II) ions bridged by 1,4,5,8,9,12-hexaazatriphenylene [144]. Enantiomers of both forms were isolated and identified. Decarbonylation of Δ- and Λ-$[Ru(\mathbf{L})_2(CO)_2]^{2+}$ (**L** = phen, bpy or 4,4′-Me_2bpy)in the presence of **L** gave $[Ru(\mathbf{L})_3]^{2+}$ with retention of configuration [145]. Conversion of $[Ru(\eta^2 - tpy)(CO_2)X_2]$(X = Cl, Br) into $[Ru(\eta^3 - tpy)COX_2]$ with Me_3NO is extremely facile [146].

3.3.1.5. Photodecarbonylation route (Scheme 3). In the development of the photodecarbonylation route to tris(diimine) complexes, it was recognised that irradiation of ruthenium(II)-polypyridyl-carbonyl complexes has been used to perform photosubstitution reactions. Irradiation of $[Ru(bpy)(CO)_2Cl_2]$ in the presence of terpyridine had been used to prepare $[Ru(bpy)(tpy)(CO)]^{2+}$ [145] and chemical decarbonylation then used to synthesise complexes incorporating other monodentate ligands (Scheme 4, [145]).

Photolysis of $[Ru(bpy)(CO)_2Cl_2]$ in acetonitrile (λ = 366 nm) was found to promote an initial substitution reaction forming $[Ru(bpy)(CH_3CN)(CO)Cl_2]$ before slower decarbonylation to the bis(acetonitrile) complex [147]. The potential of this photodecarbonylation reaction to produce an extensive range of mixed ligand Ru^{II} complexes added impetus to our studies.



Scheme 4.

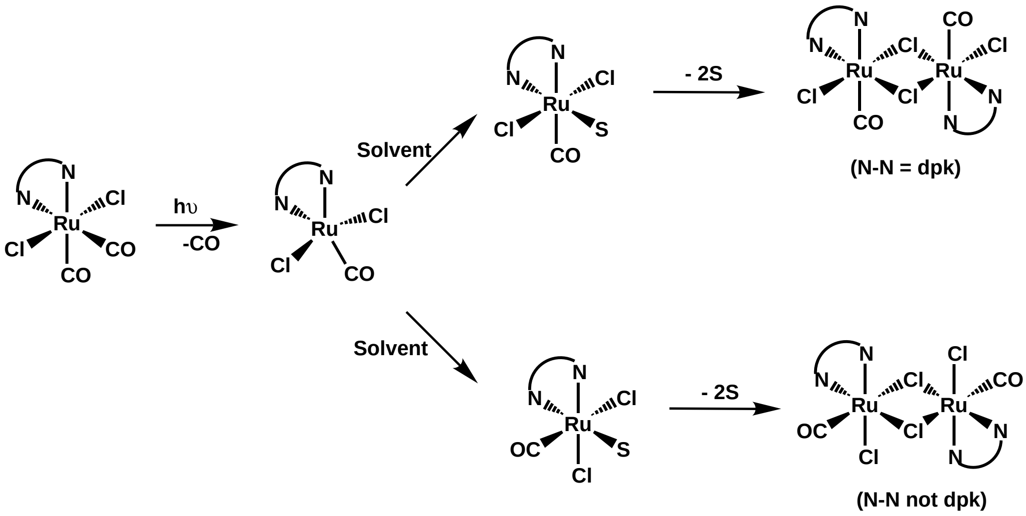
Irradiation of $[Ru(\mathbf{L})(CO)_2Cl_2]$ (where **L** is a diimine ligand) in CH_2Cl_2 with visible light was found to result in monodecarbonylation and yielded very insoluble monocarbonyl complexes:

$$2[Ru(\mathbf{L})(CO)_2Cl_2] \xrightarrow{h\nu} [Ru(\mathbf{L})(CO)Cl_2]_2 + 2\,CO \qquad (12)$$

The elimination of the strongly π-accepting carbonyl induces a weaker ligand field and results in a red-shift of the charge transfer transitions and causes the disappearance of two ν(CO) stretching absorptions (at 2050–2060 cm^{-1} and 1990–2010 cm^{-1}). The products with **L** = bpy, 4,4′-Me_2bpy, 5,5′-Me_2bpy, phen, 4,7-Me_2phen, 2,9-Me_2phen) exhibited a single ν(CO) stretching band at ca.1950 cm^{-1} suggestive of similar structures, while for **L** = dpk a ν(CO) absorption at 1985 cm^{-1} indicated a different structure (Scheme 5). The lowering of ν(CO) from those for the dicarbonyl precursors, $[Ru(\mathbf{L})(CO)_2Cl_2]$, is indicative of an increased bond order between the carbonyl and metal centre and thus a diminished likelihood of further decarbonylation, an important property which confers long term stability and ease of storage—a desirable quality in a potential synthon.

Irradiation of *cis*-dicarbonyl-*trans*-dichloro(di(2-pyridyl)-amine)ruthenium(II) and $[Ru(amp)(CO)_2Cl_2]$ in poorly coordinating solvents did not culminate in the isolation of well-defined, reproducible compounds [138]. Decomposition appeared to occur upon photolysis. One explanation was based on the possibility that an excited state involved in the decarbonylation is stabilised by favourable delocalisation of electrons on bpy, phen, dpk and their derivatives in resonance forms which cannot be achieved in the cases of di(2-pyridyl)amine (Hdpa) or amp. This may indicate that the photochemical decarbonylation of $[Ru(\mathbf{L})(CO)_2Cl_2]$ to $[Ru(\mathbf{L})(CO)_2Cl]_2$ is limited to cases where the ligand involved has a π-system which can effectively stabilise the excited state. In terms of the synthesis of heteroleptic complexes, however, this should not prove to be a major synthetic limitation since the amp or Hdpa ligands can be added in later steps of the overall preparation.

3.3.1.6. $[Ru(\mathbf{L})(\mathbf{L}^1)(CO)Cl]^+$. Monocarbonyl complexes with two identical diimine ligands, $[Ru(\mathbf{L})_2(CO)Cl]^+$, are often generated either by carbonylation of $[Ru(\mathbf{L})_2Cl_2]$ with carbon monoxide [62] or as side-products in the synthesis of dichlorobis(bidentate)ruthenium(II) ($[Ru(\mathbf{L})_2Cl_2]$) com-



Scheme 5.

plexes, arising from the decarbonylation of DMF [101]. The development of a facile synthetic route to $[Ru(\mathbf{L})(CO)Cl_2]_2$ dimers (Scheme 5), involving photodecarbonylation of $[Ru(\mathbf{L})(CO)_2Cl_2]$ [128], allowed us to access a family of ideal precursors to Ru(II) complexes containing dissimilar diimine ligands ($\mathbf{L}$ and $\mathbf{L}^1$), viz., $[Ru(\mathbf{L})(\mathbf{L}^1)(CO)Cl]^+$. A convenient synthesis of these complexes, which avoided inefficiencies arising from the possible low yields of the triflate complexes [72,126,127], was developed which involved the reaction of $[Ru(\mathbf{L})(CO)Cl_2]_2$ with an excess of a bidentate ligand ($\mathbf{L}^1$) in a suitable solvent (e.g. 2-methoxyethanol) followed by precipitation as hexafluorophosphate or perchlorate salts (X) [128].

$$[Ru(\mathbf{L})(CO)Cl_2]_2 + \mathbf{L}^1 \xrightarrow{MX} 2[Ru(\mathbf{L})(\mathbf{L}^1)(CO)Cl]X + Cl^- \tag{13}$$

Three geometric isomers are possible for $[Ru(\mathbf{L})(\mathbf{L}^1)(CO)Cl]^+$ two *cis* (I and II) and one *trans* isomer (Fig. 6), complicating structural assignment. The spectroscopic data (particularly the NMR spectra) indicated a major and minor product both of which were concluded to be *cis*-isomers from the number of NMR resonances (viz. 16 aromatic resonances were observed for each rather that the eight expected for a *trans* isomer). Molecular structure determinations then confirmed that the major product was always that produced by substitution of the dichloride bridge in the $[Ru(\mathbf{L})(CO)Cl_2]_2$ precursors (Scheme 6, N''–N'' ≠ dpk) by the incoming diimine ligand, $\mathbf{L}^1$. For the majority of complexes investigated, this meant that the product formed depended on the order of addition of the diimine ligands, with the second incoming ligand always having a nitrogen *trans* to the carbonyl. However, the NMR spectra of these complexes indicate that, although one *cis*-isomer clearly predominates, some of the second *cis*-isomer is also formed indicating that some rearrangement occurs.

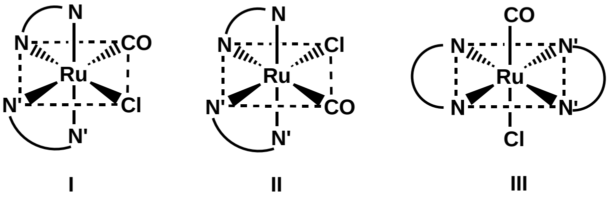
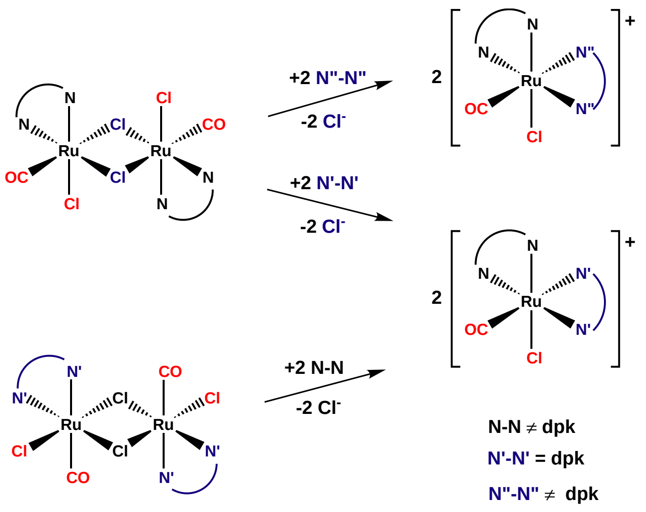


Fig. 6. Geometric isomers of $[Ru(\mathbf{L}^1)(\mathbf{L}^2)(CO)Cl]^+$; $\mathbf{L}^1$, $\mathbf{L}^2$ = symmetrical bidentate ligands.

An interesting situation arises when di (2-pyridyl) ketone is used as a ligand because the structure of $[Ru(\mathbf{dpk})(CO)Cl_2]$ is different from those of all the other $[Ru(\mathbf{L})(CO)Cl_2]_2$ complexes (Scheme 6, bottom structure LHS) in that the carbonyl is trans to an imine nitrogen rather than a chloride (Scheme 6, top structure LHS). As a consequence, the same major product is obtained regardless of whether **dpk** is added to $[Ru(\mathbf{L})(CO)Cl_2]_2$ (where $\mathbf{L} \neq \mathbf{dpk}$) or $\mathbf{L}$ was added to $[Ru(\mathbf{dpk})(CO)Cl_2]$.



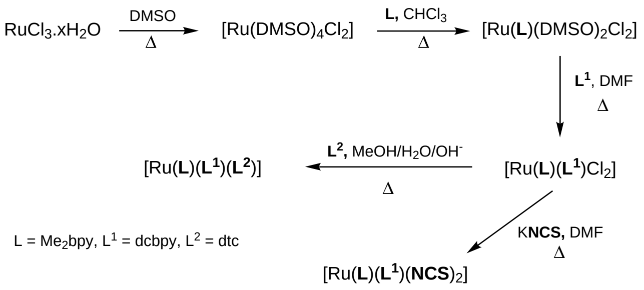
Scheme 6.

The synthesis of **dpk** complexes is, however, complicated by the fact that the solvent 2-methoxyethanol adds to **dpk** leading to intractable mixtures. As noted earlier, similar chemistry was observed when decarbonylation of $[Ru(CO)_2Cl_2]_n$ was carried out in methanol in the presence of dpk in an effort to produce $[Ru(dpk)(CO)_2Cl_2]$. (Fig. 5).

3.3.1.7. $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$. A convenient synthesis of heteroleptic tris(diimine)Ru(II) complexes, $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$ cations has been developed which involves reaction of $[Ru(\mathbf{L})(\mathbf{L}^1)(CO)Cl]^+$ with a dissimilar bidentate diimine ligand ($\mathbf{L}^2$) in the presence of trimethylamine-*N*-oxide as decarbonylating agent and isolation of the products as either hexafluorophosphate or perchlorate salts [$\mathbf{L} \neq \mathbf{L}^1 \neq \mathbf{L}^2 =$ 2,2′−bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (4,4′-Me_2bpy), 5,5′-dimethyl-2,2′-bipyridine (5,5′-Me_2bpy), 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen), 5,6-dimethyl-1,10-phenanthroline (5,6-Me_2phen), di(2-pyridyl)amine (Hdpa) and 2,2′:6′,2″-terpyridine (tpy)]. This is the final step of the versatile route for the production of mixed ligand Ru(II) complexes, detailed in Scheme 3 [124]. Clean ES mass spectra with characteristic isotopic distribution patterns (viz., peaks at *m/z* 304 → 351 for the 2+ cation and 1+ cation-anion ion pairs at *m/z* 760 → 847) and the ^{1}H NMR and COSY spectra confirmed the formation of the $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$ cations. The spectra showed no evidence of products of type $[Ru(\mathbf{L})_2(\mathbf{L}^1)]^{2+}$, $[Ru(\mathbf{L})_2(\mathbf{L}^2)]^{2+}$, $[Ru(\mathbf{L})(\mathbf{L}^1)_2]^{2+}$ and $[Ru(\mathbf{L})(\mathbf{L}^2)_2]^{2+}$. In the case of the Hdpa complexes, deprotonation of Hdpa occurs during the electrospray mass spectrometry analysis and led to signals attributable to singly charged complexes, $[Ru(\mathbf{L})(\mathbf{L}^1)(dpa)]^+$. The X-ray structure of these complexes indicated that the isomer formed was that expected if reaction proceeded without rearrangement by direct substitution of the carbonyl and chloro ligands in $[Ru(\mathbf{L})(\mathbf{L}^1)(CO)Cl]^+$.

3.3.2. Syntheses based on $[Ru(DMSO)_4Cl_2]$

Apart from being low yielding in some cases, the triflate route to heteroleptic complexes $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$ proved less effective when the imine ligands in question incorporate anionic groups (eg., carboxylates and phosphonates). As this is also the case for the decarbonylation route, there has been a need to develop effective synthetic methods that allow such ligands to be incorporated into Ru(II) complexes. Methods based on the $[Ru(DMSO)_4Cl_2]$ synthon, conveniently prepared by reacting ruthenium(III) trichloride with neat DMSO, have been reported quite recently [108,109]. Scheme 7 describes this procedure, which as yet has not been applied extensively. Reaction of $[Ru(DMSO)_4Cl_2]$ complex with a diimine ligand, **L**, in a low boiling point solvent, $CHCl_3$, produced $[Ru(\mathbf{L})(DMSO)_2Cl_2]$ [108]. Protic solvents or high boiling point aprotic solvents resulted in a mixture of mono- and bis- complexes and their use has to be avoided. For symmetrical disubstituted diimine ligands, the presence of six resonances in the ^{1}H NMR spectrum of the product indicated that the two imine nitrogen as are trans to two different ligands, i.e., DMSO and Cl^-, hence the all *cis* isomer is obtained.



Scheme 7. $[Ru(DMSO)_4Cl_2]$ route to heteroleptic ruthenium (II) complexes.

Subsequently, reaction of $[Ru(\mathbf{L})(DMSO)_2Cl_2]$ with a second diimine ligand, dcbpy ($\mathbf{L}^1$), in DMF at high temperature successfully substituted the remaining DMSO ligands and produced the heteroleptic complex, $[Ru(\mathbf{L})(\mathbf{L}^1)Cl_2]$ [108], linking with other strategies (see below). Substitution of the chloride ligands was achieved in two ways. Firstly, reaction in DMF with an excess of KNCS at high temperature gave $[Ru(\mathbf{L})(\mathbf{L}^1)(SCN)_2]$, an analogue of the well studied N3 dye, $[Ru(\mathbf{L}^1)_2(SCN)_2]$. Secondly, $[Ru(\mathbf{L})(DMSO)_2Cl_2$ was reacted with sodium diethyldithiocarbamate (dtc) under alkaline conditions in a mixture of MeOH and water to yield $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]$. These complexes show similar visible light absorption profile to the N3 dye but, importantly, some light was absorbed over the whole visible region, an important feature for any dye for use in DSSCs.

Following a similar approach, Meyer and co-workers [109] prepared a $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ complex in which all three biyridyl ligands were asymmetric. In a one-pot procedure, $[Ru(DMSO)_4Cl_2]$ was used a precursor and was first reacted with $bpyCH_2MV^{2+}$ (1-((4′-methyl-2,2′-bipyridin-4-yl)methyl)-1′-methyl-4,4′bipyridinium) and MebpyCOOH (4′-methyl-2,2′-bipyridine-4-carboxylic acid) at reflux in ethanol. The third ligand $bpyCH_2PTZ$ (10-((4′methyl-2,2′-bipyridin-4-yl)methyl)phenothiazine) was then added and the incorporation of the ligand into the complex followed by UV-visible spectrophotometry. Purification by cation-exchange chromatography and precipitation from acidic solution as a PF_6^- salt yielded $[Ru(MebpyCOOH)(bpyCH_2MV)(bpyCH_2PTZ)](PF_6)_4$ in reasonable yield (19%) which could exist as one of eight geometric isomers. The order of addition of the ligands was important as it was found that when $bpyCH_2PTZ$ ligand was added first, the homoleptic tris complex $[Ru(bpyCH_2PTZ)_3]^{2+}$ formed. Cyclic voltammetry revealed that the complex exhibits rich electrochemistry with five reversible or quasi-reversible redox processes occurring at +1.31, +0.81, −0.34, −0.75 and −1.38 V. Excitation of the main MLCT band at 464 nm induced efficient intramolecular electron transfer and resulted in the formation a charge separated state, $[Ru(MebpyCOOH)(bpyCH_2MV^{\bullet+})(bpyCH_2PTZ^{\bullet-})]^{4+}$.

3.3.3. Other synthetic methods

The route from $[Ru(C_6H_6)Cl_2]_2$ to unsymmetrical dichlororuthenium species (Scheme 1) can be continued to give unsymmetrical tris(heteroleptic) complexes [94]:

$$[Ru(\mathbf{L})(\mathbf{L}^1)Cl_2] \xrightarrow[EtOH/H_2O,NH_4PF_6]{L^2} [Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)](PF_6)_2 + 2Cl^- \quad (14)$$

Although only used for two examples it has potential for further development.

A conceptually simple route [95] involves reaction of $RuCl_3$ with successive different ligands in DMF/LiCl under increasingly vigorous conditions to give $[Ru(\mathbf{L})(\mathbf{L}^1)Cl_2]$ with a final step, replacement of chlorides with a further ligand in EtOH or $MeOH/H_2O/CH_3CO_2H$. Three examples involving different 4′4′-disubstituted 2,2′-bipyridine ligands illustrated the method but the need for HPLC purification as well as recrystallization may limit its attractiveness.

Thummel et al. [148] reported that the reaction of $[Ru(\mathbf{L})Cl_3]$, where $\mathbf{L}$ = bpy with a 2, 21-biquinoline derivative ($\mathbf{L}^1$) in refluxing ethanol gave $[Ru(\mathbf{L})(\mathbf{L}^1)Cl_2]$, which was further reacted with a bi-1,8-naphthyridine to yield $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$, and precipitated on addition of a PF_6^- salt. An ingenious synthesis, which hinges on the substitution of one sterically hindered biquinoline ligand in $[Ru(bpy)(biq)_2]^{2+}$ by acetonitrile followed by displacement of acetonitrile with a dissimilar diimine ligand, has given rise to a number of complexes though these are restricted to having biquinoline as one of the ligands [149]. These routes take advantage of the steric bulk of 2,2′-biquinoline with the von Zelewsky method elegantly using it to generate a more general synthesis. A similar approach has been used, by Sauvage and co-workers [150], to prepare elaborate $[Ru(\mathbf{L})_2(\mathbf{L}^1)]^{2+}$ complexes with irradiation used to labilise the sterically congested ligand.

All of these latter methods follow the $[Ru(\mathbf{L})(\mathbf{L}^1)Cl_2]$ strategy and differ mainly in the route to these synthons, as well as some differences in the conditions for introduction of $\mathbf{L}^2$.

Regardless of which method is used to prepare $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$ complexes, trace amounts of more symmetrical impurities, e.g., $[Ru(\mathbf{L})(\mathbf{L}^1)_2]^{2+}$, $[Ru(\mathbf{L})_2(\mathbf{L}^2)]^{2+}$, may be present at levels not detectable by spectroscopic and electrochemical methods. Their detection requires specialised cation exchange chromatographic analysis (e.g., see, [103,109,144,151]).

4. Conclusion

Ruthenium(II) complexes continue to attract attention from a number of perspectives, of which their ability to act as photo-sensitisers in the conversion of solar energy into chemical or electrical energy, is most intensely studied. Much of this activity has been stimulated by the contributions made by Professor Grätzel and his research group. With these developments has come the need for synthetic methods capable of producing complexes with tunable physico-chemical properties, such as light absorption. Herein, we have detailed our contribution to the development of methods that enable the rationale synthesis of heteroleptic tris(diimine)ruthenium(II) complexes, and place them in the wider context of those made by other research groups. Two approaches, developed in our laboratories, are based on the use of $[Ru(CO)_2Cl_2]_n$ polymer as a key precursor. The first approach involves the isolation of a triflate complex, $[Ru(\mathbf{L})(CO)_2(CF_3SO_3)_2]$, which is reacted with a second diimine ligand ($\mathbf{L}^1$) to form $[Ru(\mathbf{L})(\mathbf{L}^1)(CO)_2]^{2+}$. Subsequent chemical decarbonylation and reaction with a further diimine ligand ($\mathbf{L}^2$) gives $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$. The second approach circumvents the need to isolate the triflato complexes and instead uses photodecarbonylation of $[Ru(\mathbf{L})(CO)_2(Cl)_2]$ to produce $[Ru(\mathbf{L})(CO)(Cl)_2]_2$, which can be converted into $[Ru(\mathbf{L})(\mathbf{L}^1)(CO)Cl]^+$ by reaction with a second diimine ligand and then with a third diimine ligand under decarbonylation conditions to produce $[Ru(\mathbf{L})(\mathbf{L}^1)(\mathbf{L}^2)]^{2+}$. These versatile methods add to the synthetic tools available for production of ruthenium(II) complexes with properties required for a particular application.

Acknowledgements

GBD and LS would like to acknowledge the tremendous contributions that a number of very talented research students and post-doctoral fellows have made to the development of our research on ruthenium synthetic chemistry, and the financial support provided by Monash University.

References

[1] J.P. Paris, W.W. Brandt, J. Am. Chem. Soc. 81 (1959) 5001.
[2] K. Kalyanasundaram, Coord. Chem. Rev. 46 (1982) 159.
[3] M.K. Nazeeruddin, M. Grätzel, K. Kalyanasundaram, R.B. Girling, R.E. Hester, J. Chem. Soc., Dalton Trans. (1993) 323.
[4] T.E. Keyes, F. Weldon, E. Müller, P. Péchy, M. Grätzel, J.G. Vos, J. Chem. Soc. Dalton Trans. (1995) 2705.
[5] V. Balzani, A. Juris, M. Venturi, Chem. Rev. 96 (1996) 759.
[6] A. Juris, F. Barigelletti, S. Campagna, V. Balzani, P. Belser, A. von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.
[7] V. Balzani, A. Juris, Coord. Chem. Rev. 211 (2001) 97.
[8] V. Balzani, F. Scandola, Supramolecular Photochemistry, Horwood, Chichester, 1991.
[9] K. Kalyanasundaram, Photochemistry of polypyridine and porphyrin complexes, Academic Press, London, 1992.
[10] D.M. Roundhill, Photochemistry and photophysics of metal complexes, Plenum, New York, 1994.
[11] F.R. Keene, Coord. Chem. Rev. 166 (1997) 121.
[12] A. Harriman, R. Ziessel, J. Chem. Soc., Chem. Commun. (1996) 1707.

[13] H.C.-Y. Bettega, M. Hissler, J.-C. Moutet, R. Ziessel, Chem. Mater. 9 (1997) 3.
[14] M. Grätzel, Coord. Chem. Rev. 111 (1991) 167.
[15] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.
[16] K. Kalyanasundaram, M. Grätzel, Coord. Chem. Rev. 77 (1998) 347.
[17] A. Hagfeldt, M. Grätzel, Acc. Chem. Res. 33 (2000) 269.
[18] M. Grätzel, Prog. Photovolt. Res. Appl. 8 (2000) 171.
[19] M. Grätzel, J. Photochem. Photobiol C: Photochem. Rev. 4 (2003) 145.
[20] L. Sun, L. Hammarstrom, B. Akermark, S. Styring, Chem. Soc. Rev. 30 (2001) 36.
[21] H. Durr, S. Bossmann, Acc. Chem. Res. 34 (2001) 905.
[22] D. Burdinski, E. Bothe, K. Wieghardt, Inorg. Chem. 39 (2000) 105.
[23] B. O'Regan, M. Grätzel, Nature (Lond.) 335 (1991) 737.
[24] A. Hagfeldt, M. Grätzel, Chem. Rev. 95 (1995) 49.
[25] C.A. Bignozzi, J.R. Schoonover, F. Scandola, Prog. Inorg. Chem. 44 (1997) 1.
[26] S. Fanni, T.E. Keyes, C.M. O'Conner, H. Hughes, R. Wang, J.G. Vos, Coord. Chem. Rev. 208 (2000) 77.
[27] P.A. Anderson, F.R. Keene, T.J. Meyer, J.A. Moss, G.F. Strouse, J.A. Treadway, Dalton Trans. (2002) 3820.
[28] K.M. Marness, H. Masui, R.M. Wrighton, R.W. Murray, J. Am. Chem. Soc. 119 (1997) 3987.
[29] K.F. Mongey, J.G. Vos, B.D. McCraith, C.M. McDonagh, C. Coates, J.J. McGarvey, J. Mater. Chem. 7 (1997) 3987.
[30] S. Ruile, O. Kohle, P. Péchy, M. Grätzel, Inorg. Chim. Acta 261 (1997) 129.
[31] K. Kalyanasundaram, M. Grätzel, Coord. Chem. Rev. 77 (2000) 347.
[32] C. Creutz, N. Sutin, Proc. Natl. Acad. Sci. U.S.A. 72 (1975) 2858.
[33] A. Juris, S. Campagna, V. Balzani, G. Gremaud, A. von Zelewsky, Inorg. Chem. 27 (1988) 3652.
[34] J.-M. Lehn, J.-P. Sauvage, Nouv. J. Chem. 1 (1977) 449.
[35] J.-M. Lehn, J.-P. Sauvage, R. Ziessel, Nouv. J. Chem. 3 (1979) 423.
[36] K. Kalyanasundaram, J. Kiwi, M. Grätzel, Helv. Chim. Acta 61 (1978) 2720.
[37] K. Kalyanasundaram, M. Grätzel, Angew. Chem., Int. Edn. (Engl.) 18 (1979) 701.
[38] W.D.K. Clark, N. Sutin, J. Am. Chem. Soc. 99 (1977) 4676.
[39] S. Anderson, E.C. Constable, M.P. Dare-Edwards, J.B. Goodenough, A. Hamnett, K.R. Seddon, R.D. Wright, Nature (Lond.) 280 (1979) 571.
[40] A. Hamnett, M.P. Dare-Edwards, R.D. Wright, K.R. Seddon, J.B. Goodenough, J. Phys. Chem. 83 (1979) 3280.
[41] D. Matthews, A. Kay, M. Grätzel, Aust. J. Chem. 47 (1994) 1869.
[42] C.J. Barbe, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, J. Am. Ceram. Soc. 80 (1997) 3157.
[43] J. Takahashi, H. Itoh, S. Motai, S. Shimada, J. Mater. Sci. 38 (2003) 1695.
[44] Y. Diamant, S.G. Chen, O. Melamed, A. Zaban, J. Phys. Chem. B 107 (2003) 1977.
[45] A. Kay, M. Grätzel, Chem. Mater. 14 (2002) 2930.
[46] A. Zaban, S.G. Chen, S. Chappel, B.A. Gregg, Chem. Commun. (2000) 2231.
[47] B.A. Gregg, F. Pichot, S. Ferrere, C.L. Fields, J. Phys. Chem. B 105 (2001) 1422.
[48] H. Nusbaumer, S.M. Zakeeruddin, J.-E. Moser, M. Grätzel, Chem. Eur. J. 9 (2003) 3756.
[49] M.K. Nazeeruddin, P. Péchy, M. Grätzel, J. Chem. Soc., Chem. Commun. (1997) 1705.
[50] J. Halme, Dye sensitised nanostructured and organic photovoltaic cells, M.Sc. Thesis, Helsinki University of Technology, 2002.
[51] A. Kay, M. Grätzel, Sol. Energy Mater. Sol. Cells 44 (1996) 99.
[52] K. Zwiebel, Sol. Energy Mater. Sol. Cells 59 (1999) 1.
[53] P. Lincon, B. Norden, J. Chem. Soc., Chem. Commun. (1996) 2145.
[54] C.S. Allardyce, P.J. Dyson, Platinum Met. Rev. 45 (2001) 62.
[55] J. Reedijk, Curr. Opinion. Chem. Biol. 3 (1999) 236.
[56] P.D. Beer, J. Chem. Soc., Chem. Commun. (1996) 689.
[57] D.J. Cole-Hamilton, J. Chem. Soc., Chem. Commun. (1980) 1213.
[58] K. Tanaka, M. Morimoto, T. Tanaka, Chem. Lett. (1983) 901.
[59] J.G. Haasnoot, W. Hinrichs, O. Weir, J.G. Vos, Inorg. Chem. 25 (1986) 4140.
[60] P. Hirva, T. Venäläinen, T.A. Pakkanen, J. Mol. Catal. 148 (1994) 722.
[61] H. Ishida, K. Tanaka, T. Tanaka, Organometallics 6 (1987) 181.
[62] H. Ishida, K. Fujiki, T. Ohba, K. Ohkubo, K. Tanaka, T. Terada, T. Tenaka, J. Chem. Soc., Dalton Trans. (1990) 2155.
[63] J.M. Lehn, R. Ziessel, J. Organomet. Chem. 382 (1990) 157.
[64] H. Nagao, T. Mizukawa, K. Tanaka, Inorg. Chem. 33 (1994) 3415.
[65] C.D. Sauthier, A. Deronzier, R. Ziessel, Inorg. Chem. 33 (1994) 2961.
[66] K. Kalyanasundaram, M. Grätzel, M. Nazeeruddin, J. Chem. Soc., Dalton Trans. (1991) 343.
[67] D.P. Rillema, C.B. Blanton, R.J. Shaver, D.C. Jackman, M. Boldaji, S. Bundy, L.A. Worl, T.J. Meyer, Inorg. Chem. 31 (1992) 1600.
[68] P.A. Anderson, G.F. Strouse, J.A. Treadway, F.R. Keene, T.J. Meyer, Inorg. Chem. 33 (1994) 3863.
[69] J.P. Collin, R. Kayhanian, J.-P. Sauvage, G. Calogero, F. Barigelletti, A. de Lian, J. Fischer, J. Chem. Soc., Chem. Commun. (1997) 775.
[70] M.K. Nazeeruddin, P. Péchy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, B.C.A.M. Grätzel, J. Am. Chem. Soc. 123 (2001) 1613.
[71] G.F. Strouse, J.R. Schoonover, R. Duesing, S. Boyde, W.E. Jones, T.J. Meyer, Inorg. Chem. 34 (1995) 473.
[72] P.A. Anderson, G.B. Deacon, K.H. Haarmann, F.R. Keene, T.J. Meyer, D.A. Reitsma, B.W. Skelton, G.F. Strouse, N.C. Thomas, J.A. Treadway, A.H. White, Inorg. Chem. 34 (1995) 6145.
[73] H.B. Ross, M. Boldaji, D.P. Rillema, C.B. Blanton, R.P. White, Inorg. Chem. 28 (1989) 1013.
[74] A.B.P. Lever, E.S. Dodsworth, Electrochemistry, charge transfer spectroscopy and electronic structure, Inorganic Electronic Structure and Spectroscopy, vol. II, Wiley, New York, 1999, p. 227.
[75] R.J. Watts, G.A. Crosby, J. Am. Chem. Soc. 93 (1971) 3184.
[76] B.T. Patterson, F.M. Foley, D. Richards, F.R. Keene, Dalton Trans. (2003) 709.
[77] C. Richardson, P.J. Steel, D.M. D'Alessandro, P.C. Junk, F.R. Keene, J. Chem. Soc., Dalton Trans. (2002) 2775.
[78] D.M. D'Alessandro, L.S. Kelso, F.R. Keene, Inorg. Chem. 40 (2001) 6841.
[79] L.H. Uppadine, F.R. Keene, P.D. Beer, J. Chem. Soc., Dalton Trans. (2001) 2188.
[80] T.J. Rutherford, P.A. Pellegrini, J. Aldrich-Wright, P.C. Junk, F.R. Keene, Eur. J. Inorg. Chem. 1998 (1998) 1677.
[81] B.T. Patterson, F.R. Keene, Inorg. Chem. 37 (1998) 645.
[82] N.C. Fletcher, P.C. Junk, D.A. Reitsma, F.R. Keene, J. Chem. Soc., Dalton Trans. (1998) 133.
[83] T.J. Rutherford, F.R. Keene, Inorg. Chem. 36 (1997) 2872.
[84] F.H. Burstal, J. Chem. Soc., Chem. Commun. (1936) 173.
[85] E.A. Seddon, K.R. Seddon, The Chemistry of Ruthenium, Elsevier, 1984.
[86] F.P. Dwyer, J.E. Humpoletz, R.S. Nyholm, J. Proc. R. Soc. (NSW) 80 (1946) 212.
[87] F.P. Dwyer, J. Proc. R. Soc. (NSW) 83 (1949) 134.
[88] J.D. Miller, R.H. Prince, J. Chem. Soc. A (1966) 1048.
[89] G.M. Bryant, J.E. Fergusson, H.K.J. Powell, Aust. J. Chem. 24 (1971) 257.
[90] C.T. Lin, W. Böttcher, M. Chou, C. Creutz, N. Sutin, J. Am. Chem. Soc. 98 (1976) 6536.
[91] S. Anderson, K.R. Seddon, J. Chem. Res. (S) (1979) 74.
[92] J.A. Broomhead, C.G. Young, Inorg. Synth. 21 (1982) 127.
[93] N.C. Thomas, G.B. Deacon, Inorg. Synth. 25 (1989) 107.

[94] D.A. Freedman, J.K. Evju, M.K. Pumije, K.R. Mann, Inorg. Chem. 40 (2001) 5711.
[95] D. Husek, Y. Inoue, S.R.L. Everitt, H. Ishida, M. Kumeda, M.G.B. Drew, Inorg. Chem. 39 (2000) 308.
[96] F.P. Dwyer, H.A. Goodwin, E.C. Gyarfas, Aust. J. Chem. 16 (1963) 544.
[97] P.J. Steel, E.C. Constable, J. Chem. Soc., Dalton. Trans. (1990) 1389.
[98] C.F. Lui, N.C. Lui, J.C. Bailar Jr, Inorg. Chem. 3 (1964) 1197.
[99] W.M. Wallace, P.E. Hoggard, Inorg. Chem. 18 (1979) 2934.
[100] B.P. Sullivan, D.J. Salmon, T.J. Meyer, Inorg. Chem. 17 (1978) 3334.
[101] J.M. Clear, J.M. Kelly, C.M. O'Connell, J.G. Vos, C.J. Cardin, J. Chem. Soc., Chem. Commun. (1980) 750.
[102] D.St.C. Black, G.B. Deacon, N.C. Thomas, Inorg. Chim. Acta 65 (1982) L75.
[103] T.J. Rutherford, D.A. Reitsma, F.R. Keene, J. Chem. Soc., Dalton Trans. (1994) 3659.
[104] T.J. Rutherford, P. Quagliotto, F.R. Keene, Inorg. Chem. 34 (1995) 3857.
[105] I.P. Evans, A. Spencer, G. Wilkinson, J. Chem. Soc., Dalton Trans. (1972) 204.
[106] O. Johansson, M. Borgstrom, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarstrom, L. Sun, B. Akermark, Inorg. Chem. 42 (2003) 2908.
[107] S.M. Zakeeruddin, M. Nazeeruddin, R. Humphry-Baker, P. Pechy, P. Quagliotto, C. Barolo, G. Viscardi, M. Graetzel, Langmuir 18 (2002) 952.
[108] S.M. Zakeeruddin, M.K. Nazeeruddin, R. Humphry-Baker, M. Grätzel, Inorg. Chem. 37 (1998) 5251.
[109] K.A. Maxwell, M. Sykora, J.M. De Simone, T.J. Meyer, Inorg. Chem. 39 (2000) 71.
[110] D. Hesek, Y. Inoue, S.R.L. Everitt, H. Ishida, M. Kuneida, M.G.B. Drew, Chem. Commun. (1999) 403.
[111] D. Hesek, Y. Inoue, S.R.L. Everitt, H. Ishida, M. Kuneida, M.G.B. Drew, Tetrahedron: Asymmetry 9 (1998) 4089.
[112] D. Hesek, Y. Inoue, S.R.L. Everitt, H. Ishida, M. Kuneida, M.G.B. Drew, J. Chem. Soc., Dalton Trans. (1999) 3701.
[113] M. Nazeeruddin, M. Grätzel, D.P. Rillema, Inorg. Synth. 32 (2002) 185.
[114] M.K. Nazeeruddin, S.M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.-H. Fischer, M. Grätzel, Inorg. Chem. 38 (1999) 6298.
[115] M.K. Nazeeruddin, R. Humphry-Baker, P. Liska, M. Graetzel, J. Phys. Chem. B 107 (2003) 8981.
[116] R. Colton, R.H. Farthing, Aust. J. Chem. 20 (1967) 1283.
[117] M.J. Clear, W.P. Griffiths, J. Chem. Soc., A (1969) 372.
[118] D.St.C. Black, G.B. Deacon, N.C. Thomas, Aust. J. Chem. 35 (1982) 2445.
[119] N.C. Thomas, G.B. Deacon, Synth. React. Inorg. Met. -Org. Chem. 16 (1986) 85.
[120] D.St.C. Black, G.B. Deacon, N.C. Thomas, Transition Met. Chem. 5 (1980) 317.
[121] D.St.C Black, G.B. Deacon, N.C. Thomas, Inorg. Chim. Acta 54 (1981) L143.
[122] C.M. Kepert, G.B. Deacon, L. Spiccia, Inorg. Chim. Acta 355C (2003) 211.
[123] P. Pearson, C.M. Kepert, G.B. Deacon, L. Spiccia, A.C. Warden, B.W. Skelton, A.H. White, Inorg. Chem. 43 (2004) 683.
[124] C.M. Kepert, N. Sahely, G.B. Deacon, L. Spiccia, G.D. Fallon, B.W. Skelton, A.H. White, Inorg. Chem. 43 (2004) 2818.
[125] C.M. Kepert, G.B. Deacon, L. Spiccia, B.W. Skelton, A.H. White, Dalton Trans. (2004) 1766.
[126] G.F. Strouse, P.A. Anderson, J.R. Schoonover, T.J. Meyer, F.R. Keene, Inorg. Chem. 31 (1992) 3004.
[127] D.St.C. Black, G.B. Deacon, N.C. Thomas, Polyhedron 2 (1983) 409.
[128] G.B. Deacon, C.M. Kepert, N. Sahely, B.W. Skelton, L. Spiccia, N.C. Thomas, A.H. White, J. Chem. Soc., Dalton Trans. (1999) 275.
[129] M. Haukka, J. Kiviaho, M. Ahlgrén, T.A. Pakkanen, Organometallics 14 (1995) 825.
[130] P. Homanen, M. Haukka, T.A. Pakkanen, J. Pursiainen, R.H. Laitinen, Organometallics 15 (1996) 4081.
[131] P. Homanen, M. Haukka, S. Luukkannen, M. Ahlgrén, T.A. Pakkanen, Eur. J. Inorg. Chem. (1999) 101.
[132] M. Haukka, P. Hirva, S. Luukkannen, M. Kallinen, M. Ahlgrén, T.A. Pakkanen, Inorg. Chem. 38 (1999) 3182.
[133] E. Eskelinen, S. Luukkannen, M. Haukka, M. Ahlgrén, T.A. Pakkanen, Dalton Trans. (2000) 2745.
[134] F.A. Cotton, B.F.G. Johnson, Inorg. Chem. 3 (1964) 1609.
[135] J.V. Kingston, J.W.S. Jamieson, G. Wilkinson, J. Inorg. Nucl. Chem. 29 (1967) 133.
[136] N.C. Thomas, Ph.D. Thesis, Monash University, 1983.
[137] M.C. Feller, R. Robson, Aust. J. Chem. 21 (1968) 2919.
[138] C.M. Kepert, Novel Synthetic Pathways to Complexes of Ruthenium Incorporating Inequivalent Diimine Ligands, Ph.D. Thesis, Monash University, 1999.
[139] M.C. Feller, R. Robson, Aust. J. Chem. 23 (1970) 1997.
[140] S. Sommerer, W.P. Jensen, R.A. Jacobson, Inorg. Chim. Acta 172 (1990) 3.
[141] E.C. Constable, J.M. Holmes, Inorg. Chim. Acta 126 (1987) 195.
[142] B.J. Coe, D.A. Friesen, D.W. Thompson, T.J. Meyer, Inorg. Chem. 35 (1996) 4575.
[143] J.A. Treadway, T.J. Meyer, inorg. Chem. 38 (1999) 2267.
[144] T.J. Rutherford, O. Van Gijte, A. Kirsch-De Mesmaeker, F.R. Keene, Inorg. Chem. 36 (1997) 4465.
[145] N.C. Fletcher, F.R. Keene, J. Chem. Soc., Dalton. Trans. (1998) 2293.
[146] G.B. Deacon, V.M. Patrick, B.W. Skelton, N.C. Thomas, A.H. White, Aust. J. Chem. 37 (1984) 929.
[147] L. Ruiz-Ramirez, T. Stephenson, J. Chem. Soc., Dalton Trans. (1974) 1640.
[148] R.P. Thummel, F. Lefoulon, S. Chirayil, Inorg. Chem. 26 (1987) 3072.
[149] A. von Zelewsky, G. Gremaud, Helv. Chim. Acta 71 (1988) 1108.
[150] A.-C. Laemmel, J.P. Collin, J.-P. Sauvage, Eur. J. Inorg. Chem. (1999) 383.
[151] F.R. Keene, M.R. Snow, P.J. Stephenson, E.R.T. Tiekink, Inorg. Chem. (1988) 2040.