

Rhodium 1994

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1. Introduction

The chemistry of rhodium has continued to attract interest in 1994, an SCI search revealing in excess of 1000 references. Much of the work in this field is "organometallic" in nature and since such compounds are reviewed elsewhere in *Coord. Chem. Rev.*, the treatment herein is restricted to those compounds which I feel will be of particular interest to the coordination chemistry community. Such judgements are by their nature subjective, especially in a discipline with such ill-defined boundaries, and I apologise to all those research workers whose research does not feature here. While ignoring most compounds containing metal-carbon bonds, I have deliberately included the cyclometallated compounds of ligands containing pyridine units linked to potentially metallating aryl rings. The photophysics and synthesis of such species is inextricably linked to the continuing quest for light-harvesting analogues of ruthenium polypyridyl species and as such is one of the most active areas of modern coordination chemistry. A notable feature of this year's literature has been the

interest in the preparation and use of rhodium complexes in biological and medicinal situations; while these complexes are reviewed in the appropriate places in the text, readers are also guided to a review of the application of coordination compounds in chemotherapy which includes a review of some rhodium-based potential anti-cancer compounds [1].

The review follows the format established by the previous reviewer with di, tri and polynuclear complexes separated into an individual section at the end. I hope that this account will continue to provide readers with a broad overview of the year's rhodium coordination chemistry. Searches of both the SCI and the Cambridge Structural Data Base have been used in the construction of this article. Several papers which were published at the end of 1993 but not incorporated into the SCI until 1994 have been included in this review for the sake of completeness.

1.1. Rhodium(IV) and (V)

A UV-VIS spectroscopic study on RhF_3 has been reported and the spectra of this intensely coloured compound assigned and interpreted [2]. The compound Claus' blue, previously believed to contain rhodium(IV), has been spectroscopically identified as a rhodium(III) superoxo species [3].

1.2. Rhodium(III)

1.2.1. Complexes with halide and pseudo-halide ligands

The binding of rhodium(III) chloride with DNA has been investigated by circular dichroism [4]. The compound reacts with the DNA bases and induces conformational changes in the double-helical structure. Small amounts of the rhodium complex stabilise the B conformation of DNA while at higher rhodium concentrations the C conformation is induced.

1.2.2. Complexes with oxygen donor ligands

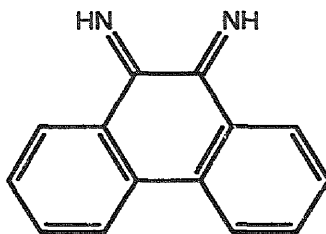
A range of rhodium(III) superoxide complexes have been prepared from Claus' blue which was shown to contain a $[\text{Rh}_2^{\text{III}}(\text{O}_2)]^{5+}$ core [3].

1.2.3. Complexes with sulfur donor ligands

The chemistry of dimethylsulfoxide with rhodium(III) chloride has been reinvestigated and the anionic species $\text{cis-}[\text{RhCl}_4(\text{dmsO})_2]^-$ isolated and structurally characterised [5]. Both dmsO molecules are *S*-bonded to the metal centre. Isomerisation of the complex to the *trans* isomer is promoted by light. This *trans* isomer is thermodynamically unstable and in dmsO solution reverts back to the *cis* isomer [6]. A crown thioether complex of rhodium(III) with the ligand tetrathiocyclodecane has been prepared [7]. Completion of the coordination sphere with 9,10-phenanthrenequinone diimine gives a metalointercalator.

1.2.4. Complexes with nitrogen donor ligands

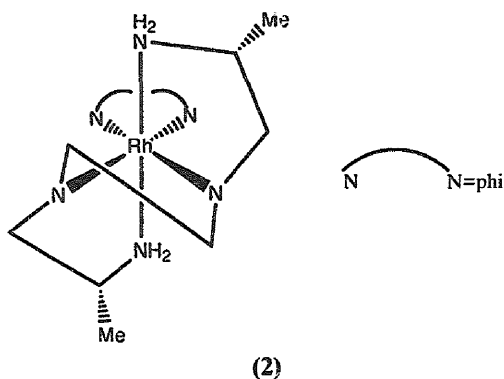
Much of the reported chemistry of rhodium(III) complexes with nitrogen donors is centred around polypyridine ligands and their analogues. Within this sphere Barton and co-workers have published a number of papers reporting their investigations into DNA intercalation by rhodium(III) complexes [7–12,14]. Much of this work centres around complexes of the ligand 9,10-phenanthrenequinonediimine (phi) which is illustrated in (1). The cationic complex $[\text{Rh}(\text{NH}_3)_4(\text{phi})]^{3+}$ has been prepared and its binding to a small duplex oligonucleotide strand $(\text{TGGCCA})_2$ monitored by 1D and 2D NMR spectroscopic techniques [8]. The NMR spectra support classical intercalative binding in the major groove and this binding is associated with upfield shifts of the resonances corresponding to the aromatic protons on the phi ligand. Molecular modelling studies based on the NMR spectroscopic results implicate π -stacking interactions between the phi ligand and the nucleotide bases together with hydrogen bonding interactions between the protons on the axial coordinated amines and guanine oxygen atoms on the nucleoside bases. In order to further probe the interaction of ancillary ligands with DNA, a range of cations of type $[\text{RhX}_4(\text{phi})]^{3+}$ were prepared; $\text{X} = (\text{en})_2$, (tren), tetraazacyclododecane or tetrathiaacyclododecane [7]. The cationic complexes $[\text{Rh}(\text{bpy})_2(\text{phi})]^{3+}$ and $[\text{Rh}(\text{bpy})(\text{phi})_2]^{3+}$ and substituted derivatives have been prepared [9]. The compounds again bind to the major groove of DNA via the phi ligand. On irradiation with UV light they promote DNA strand cleavage. The precise shape of the metal complex governs the complex-DNA recognition event; the introduction of bulky groups on the bipyridyl ligands can be used to target the complex towards specific base sequences. The selectivities are rationalised in terms of unfavourable steric interactions and favourable Van-der-Waals interactions.



(1)

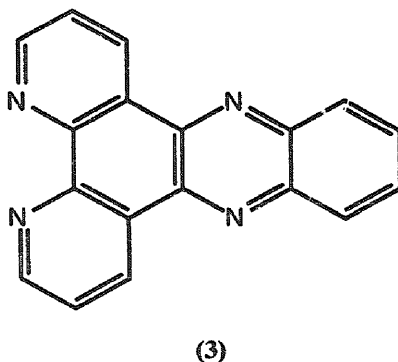
These two approaches to obtaining additional interactions through designed ancillary ligands (hydrogen-bonding via amines and the introduction of steric substituents) were combined in a survey of the compound shown in (2) and its isomers [10,11]. Six isomers were prepared and purified by HPLC. A preliminary communication of the binding studies suggests that, once again, steric clashes provide selectivity in the binding [11]. Further control of sequence specificity has been achieved by attaching short, thirteen residue polypeptides onto a derivative of $[\text{Rh}(\text{phen})(\text{phi})_2]^{3+}$ [12]. This complex binds via the phi ligand in the major groove

of DNA and acts as a UV photosensitiser promoting DNA cleavage, the polypeptide chain directing the complex to a specific DNA sequence.



Dichloro bisphenanthroline rhodium(III) and trisphenanthroline rhodium(III) salts have also been investigated by researchers at Purdue for use as photosensitisers in the degradation and inactivation of infectious DNA from phages S31 and G4 [13]. With both salts, only slight sensitisation is observed.

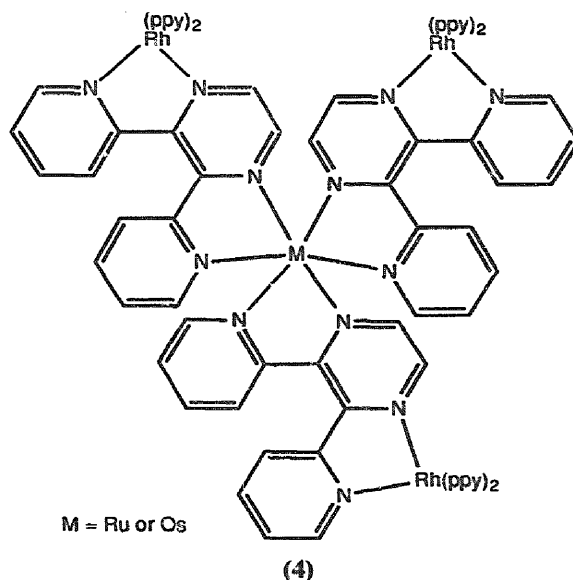
In collaboration with the Barton group, Turro and co-workers have investigated, by luminescence quenching experiments, photo-induced electron transfer between intercalated complexes [14]. The complex cations $[\text{Rh}(\text{phen})(\text{phi})_2]^{3+}$ and $[\text{Ru}(\text{phen})_2(\text{dppz})]^{3+}$ were prepared (dppz = dipyridophenazine, illustrated in (3)) and studied in the presence of DNA. Comparison with non-intercalative acceptor species suggests that electron transfer between the intercalators does indeed take place via the DNA helix.



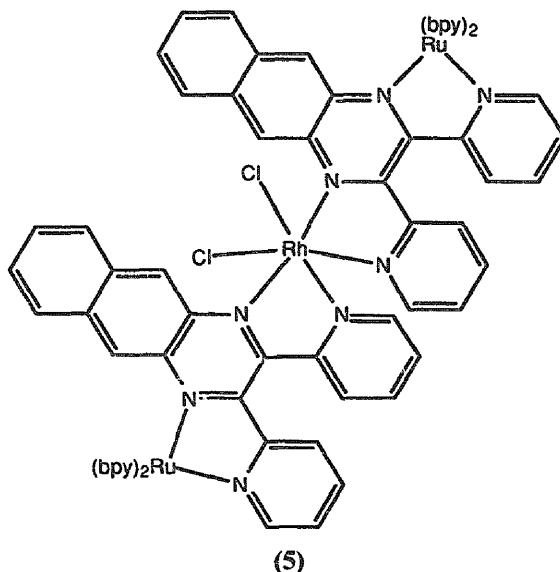
The photophysical properties of rhodium(III) polypyridyl species continue to attract attention and tris ligand complexes of the cyclometallating ligand ppyH has been prepared by treating the complex $[\text{RhL}_2\text{Cl}]_2$ with silver(I) triflate in the presence of a thirty fold excess of HL at 110°C (L = ppy). Heating the mixture under

reflux for 24 hours gave the desired complex, which was purified on Sephadex LH20, in about 50% yield [15]. Mixed ligand complexes were not prepared. The ligands are arranged about the metal ion with the nitrogen donors in a *fac* arrangement as confirmed by solution ^1H NMR spectroscopic studies. The excited state properties were investigated at 9 K in polymethacrylate. The lowest excited state for the complex $[\text{Rh}(\text{ppy})_3]$ is a ligand centred $^3\pi\text{-}\pi^*$ state. The short observed luminescent lifetime reflects mixing of CT character into the $^3\pi\text{-}\pi^*$ lowest excited states.

Balzani and co-workers have incorporated the photo-active $[\text{Rh}(\text{ppy})_2(\text{bpy})]^+$ unit into a supramolecular, light-harvesting dendrimeric system [16]. They have prepared tetranuclear systems in which three of these fragments are arranged about a ruthenium(II) or osmium(II) centre and linked together using the bridging ligand 2,3-bis(2-pyridyl)pyrazine. The complexes are shown in (4). The compounds contain four chiral octahedral centres and the products are therefore obtained as a mixture of diastereoisomers. On irradiation of both compounds, photoexcitation leads to emission from the central atom (ruthenium or osmium). Energy is channelled from the rhodium centres into the centre of the dendrimer. The absorption and electrochemical properties of the complexes are also reported.



Related bridging ligands such as 2,3-bis(2-pyridyl)quinoxaline and 2,3-bis(2-pyridyl)benzoquinoxaline have been used by Brewer and co-workers to assemble heterotrimetallic systems about a central rhodium centre [17]. The complexes (5) are prepared in high yield (95%) using a building-block strategy similar to that adopted by Balzani. The terminal ruthenium polypyridyl units act as light harvesting units and the central rhodium centre as a reaction centre at which the harvested energy may be used to drive a chemical reaction. On irradiation, one



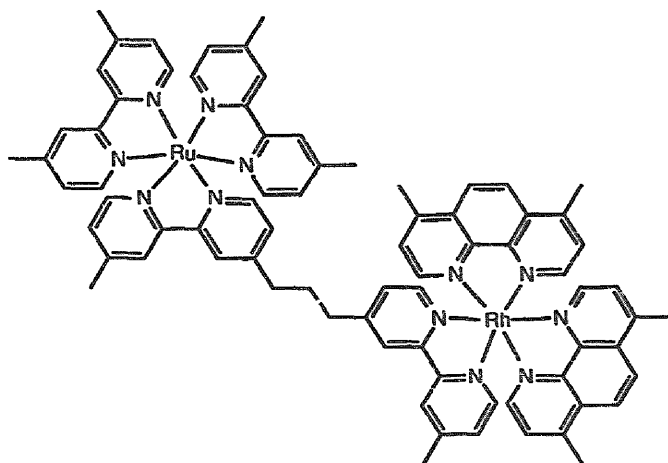
electron is transferred from each ruthenium(II) centre into the bridging ligands. The central rhodium fragment may then be used to deliver these two electrons, stored on the bridging ligands to a substrate. The properties of the supramolecule may be tuned by varying the bridging ligands. A simpler dimetallic complex (6) has also been reported. Irradiation of either chromophore leads to a Ru(III)Rh(II) excited state [18]. Rate constants for the forward and reverse electron transfer processes have been evaluated.

A general review of the work of von Zelewsky in the area of ruthenium and rhodium polypyridyl complexes has also appeared [19].

Compounds of type $[\text{Rh}(\text{bpy})_2\text{X}_2]^{3+}$ bearing pyrrole substituents on the bpy groups have been incorporated into films by electropolymerisation of the pyrrole substituents [20].

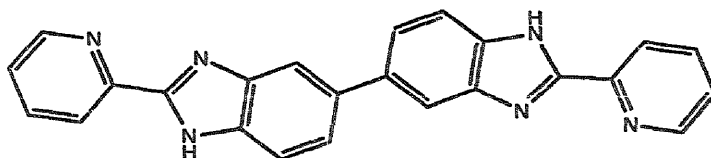
Sauvage and co-workers have prepared a series of compounds in which rhodium(III) terpyridyl species are covalently attached through the 4'-positions to porphyrins [21,22]. The photophysical properties of the systems with both free base porphyrins and their zinc complexes have been reported. Introduction of a phenylene spacer between the porphyrin unit and the rhodium(III) polypyridyl leads to a decrease in the electronic coupling and electron transfer rates. The compounds are proposed as multicomponent photosynthetic systems. Rhodium porphyrin complexes have also been used for the molecular recognition of nitrogen containing bases [23].

Haga and co-workers have investigated the chemistry of rhodium(III) with a bis-benzimidazole substituted bpy ligand (7) [24]. Both a mononuclear rhodium(III) and a mixed-metal dinuclear rhodium(III)/ruthenium(II) complex have been prepared and their electrochemical and spectroscopic properties reported. The effect of



(6)

pH (i.e. altering the protonation state of the benzimidazole units) on the complexes' properties are described. In the complex cation $[\text{Ru}(\text{bpy})_2(7)\text{Rh}(\text{bpy})_2]^{3+}$ no emission is observed due to intramolecular electron transfer from the ruthenium excited state to the rhodium(III) centre. In contrast, the monodeprotonated complex emits on excitation of the ruthenium chromophore. Preferential deprotonation at the site adjacent to the rhodium(III) centre leads to a negative potential shift in the reduction potential and the electron transfer does not take place.

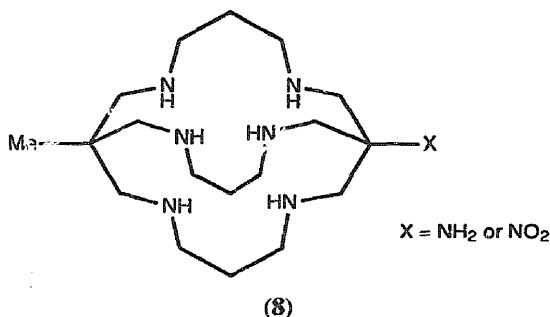


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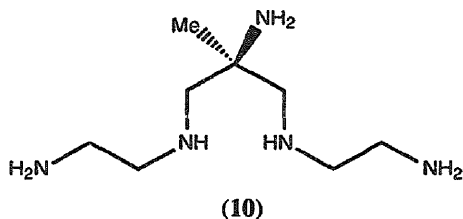
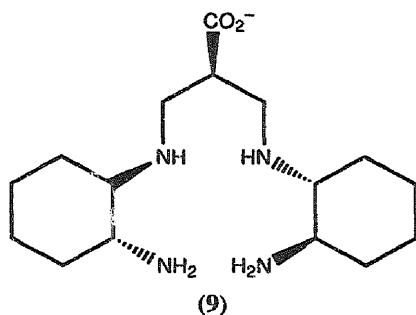
The synthesis and characterisation of rhodium(III) complexes of cryptate ligands (8) have been reported [25]. Metal centred phosphorescence was observed at 77 K.

The rhodium(III) phthalocyanine complex anion $[\text{Rh}(\text{pc})(\text{OH})_2]^-$ has been prepared and its electronic spectrum reported [26]. The effect on the electronic spectra of replacing the axial ligands with phenolate, benzenethiolate and benzeneselenate ligands has also been reported [27]. An electrochemical investigation of a number of rhodium(III) phthalocyanine complexes has been undertaken [28]. The first reduction process can be ligand or metal centred and this is determined by the two axial ligands that complete the *pseudo*-octahedral coordination sphere of the metal centre.

The ligand (9) reacts with rhodium(III) to give a complex cation $[\text{Rh}(9)\text{Cl}]^{2+}$



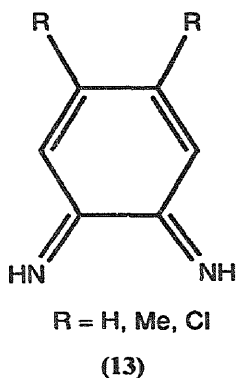
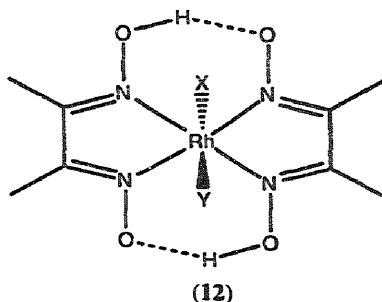
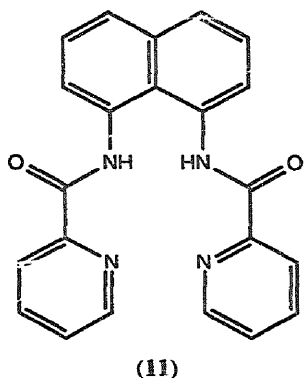
in which the ligand behaves as a quinquedentate ligand [29]. In contrast, the ligand (10) reacts with rhodium(III) to give a neutral complex *fac*-[Rh(10)Cl₃] which has been crystallographically characterised [30]. The ligand behaves as a tridentate ligand with the central three amines coordinated and the terminal amines non-coordinated. Extended reflux over a period of weeks is required to effect conversion to a complex containing a quinquedentate ligand.



Ligand (11) exhibits a variety of coordination modes. The neutral amide ligand acts as a bis-didentate ligand giving oligomeric complexes with rhodium(III) while the doubly deprotonated ligand behaves as a tetradentate ligand giving complexes in which an octahedral coordination sphere is completed by two axial ligands [31].

Several X-ray crystallographic studies of rhodium(III) oxime complexes of type (12) have been undertaken. A comparison of the structures for $X = \text{py}$ and $Y = \text{I}$ or Cl reveals a more elongated rhodium-pyridine bond in the iodo compound [32]. A crystal structure of the compound with $X = \text{PPh}_3$ and $Y = \text{Et}$ has also been reported [33].

Interactions of a range of 1,4-diimine ligands (13) with a {Cp*Rh^{III}} fragment have been investigated. The complexes have been characterised by X-ray techniques and their electrochemical and absorption properties reported [24].



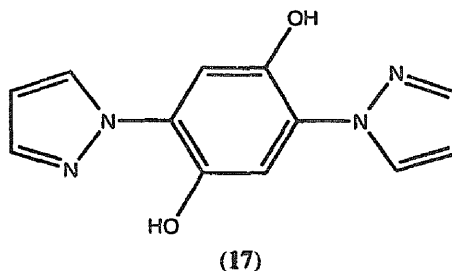
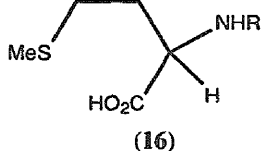
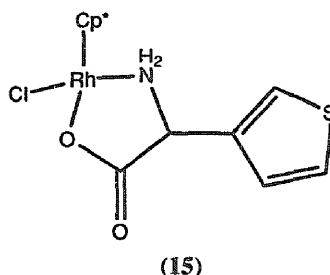
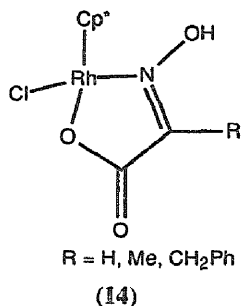
1.2.5. Complexes with phosphorus donor ligands

Phosphine dissociation rate constants for a range of rhodium(III) complexes have been determined [35].

1.2.6. Complexes with ligands with mixed donor atoms

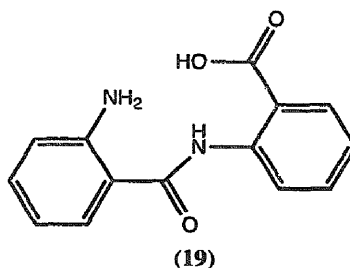
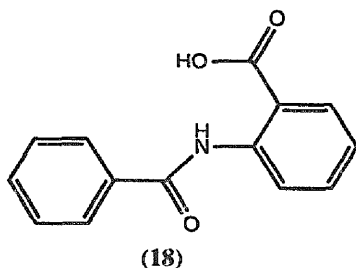
A variety of complexes of rhodium(III) with amino acids have been prepared by Beck and co-workers such as those shown in (14) [36]. The same workers have also investigated the reaction of 2-(3-thienyl)glycine with rhodium(III) and have characterised a complex (15) containing the ligand in an *N,O* didentate bonding mode [37]. In the course of their studies these workers have also investigated complexation of the ligand (16). This ligand acts as a tridentate *N,O,S*-bonded ligand and this bonding mode has been structurally characterised in the cation $[\text{Cp}^*\text{Rh}(\text{16})]^+$ [38].

The behaviour of the ligand (17) (H_2L) towards rhodium(III) species has been reported. The ligand can potentially act either as a neutral (H_2L), monoanionic (HL^-) or dianionic (L^{2-}) ligand. "Complexes" of all three types have been reported and characterised, although in the case of the neutral ligand (H_2L) there are no metal-ligand bonds and instead clathrates are formed. Similarly, in the complexes

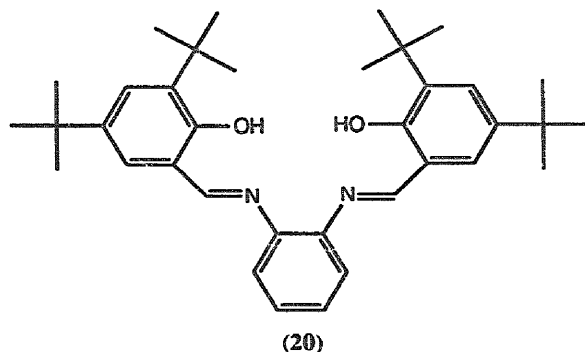


containing the monoanionic ligand (HL^-) only one metal ion binds to the ligand and the other binding site, bearing the proton, is left uncoordinated [39].

Complexes of rhodium(III) with the ligands (18) and (19) have been prepared and characterised [40]. Ligand (18) behaves as a monoanionic didentate N,O donor while ligand (19) is a tridentate N_2O ligand.



A complex of formula $[Rh(20-2H)(C_4H_9)]$ has been structurally characterised [41]. The metal centre is in a square pyramidal environment with the ligand (20) in the plane and a butyl group in the axial position. This dark purple compound is stable in solution in the dark but is light sensitive. Exposure to light in the presence of dihydrogen leads to the formation of a hydride species and the liberation of butane.



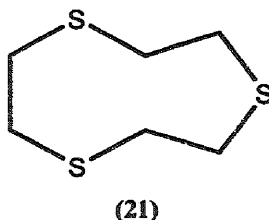
1.3. Rhodium(II)

Mechanistic studies on the substitution of the water ligands in hexaaquarhodium(II) salts by salicylaldoxime have been undertaken. The reaction is first order in both [substrate] and [ligand]. The kinetic data support an associative mechanism [42].

1.4. Rhodium(I)

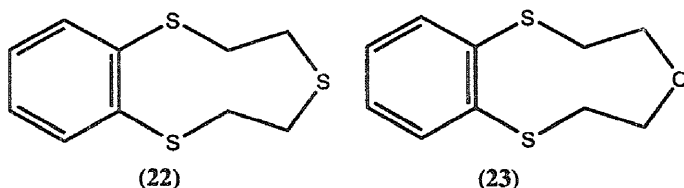
1.4.1. Complexes with sulfur donor ligands

The coordination chemistry of rhodium(I) with sulfur ligands has been dominated by the chemistry of macrocyclic ligands. Schröder and Halcrow have studied the reaction of a variety of rhodium(I) alkene starting materials with the potentially tridentate macrocycle 1,4,7-trithiacyclononane (9S3) (21). The ligand binds in a facial capping manner presenting six electrons to the metal ion and might therefore be thought of as a neutral analogue of the cyclopentadiene class of ligands. Three complexes containing the metal in a five-coordinate environment were reported and structurally characterised. In each case the macrocycle acts as an S_3 chelating ligand and the two remaining coordination sites are filled by alkene ligands [43].



Jenkins and Loeb have investigated the chemistry of the related ligand (Ph9S3) shown in (22). The chemistry appears to be structurally analogous and they have isolated and crystallographically identified a five coordinated species [44]. The phenyl ring restricts the movement of this macrocycle and this is reflected in the chemistry

of the complexes $[\text{Rh}(\text{L})(\text{cod})]^+$ ($\text{L} = 9\text{S}3$ or $\text{Ph}9\text{S}3$). The related macrocycle $\text{Ph}9\text{S}2\text{O}$ (**23**) was also prepared. This macrocycle acts only as a didentate S_2 ligand and the crystal structure reveals a four coordinate square planar rhodium(I) centre [44].



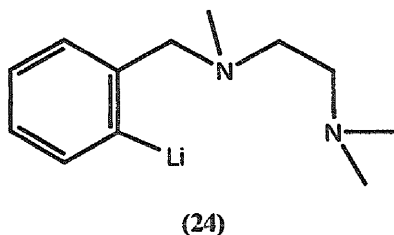
Rhodium(I) carbonyl complexes of thiourea, 1,3-diphenyl-2-thiourea and dithi-zone have been prepared [45].

1.4.2. Complexes with nitrogen donor ligands

While the work on complexes with sulfur donors has centred around the theme of macrocycles, the chemistry with nitrogen donors has proved to be more varied. The reaction of rhodium(I) compounds with trispyrazolylboranes has been reported. The reaction proceeds with degradation of the ligand to give a pyrazole/pyrazolate complex [46].

A wide variety of rhodium(I) carbonyl compounds with substituted pyridine ligands have been prepared [45]. The preparation of $[\text{RhCp}^*(\text{LL})]$ compounds ($\text{LL} = \alpha$ -diimine) has been investigated. These compounds are readily oxidised [47].

Transmetalation between a rhodium(I) compound and the lithio complex of a potentially tridentate N_2C donor ligand (**24**) yields a square planar N,C coordinated species $[\text{RhL}(\text{cod})]$. Substitution of the olefin ligand with monodentate carbon monoxide or phosphite ligands gives species which are fluxional in solution, the ligand switching between the didentate and tridentate modes [48].



Square planar complexes, prepared via ligand exchange reactions, of a chelating didentate isonitrile have been characterised [49]. Square planar rhodium(I) complexes of *N*-isocyanodialkylamines CNNR_2 ($\text{R} = \text{Et}$, $i\text{Pr}$) have also been prepared and characterised [50]. Spectroscopic analysis [51] of the rhodium(I) complex of *p*-methylphenylisocyanide (**L**) at room temperature implicates the presence of a mixture of oligomers of formula $[\text{Rh}(\text{L})_4]_n^+$.

1.4.3. Complexes with phosphorus donor ligands

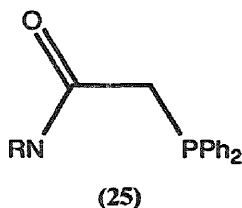
Addition of pyridine to Wilkinson's catalyst $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ gives a series of compounds in which the pyridine molecules displace the chloro and/or phosphine ligand(s). These species have been shown to be effective catalysts for the reductive coupling of aldehydes [52]. Addition of triethylamine to the same compound gives compounds which are effective catalysts for 2-propanol dehydrogenation [53].

Phosphine addition to rhodium(I) 2-quinaldinate (quin) complexes give complexes of type $[\text{Rh}(\text{quin})(\text{PR}_3)_2]$ proceeds via a five coordinate intermediate in an associative mechanism [54]. A complex in which a diphosphine ligand is added to a rhodium(I) 2-quinaldinate (quin) complex has been structurally characterised and reveals that the diphosphine bridges two metal centres [55].

1.4.4. Complexes with ligands with mixed donor atoms

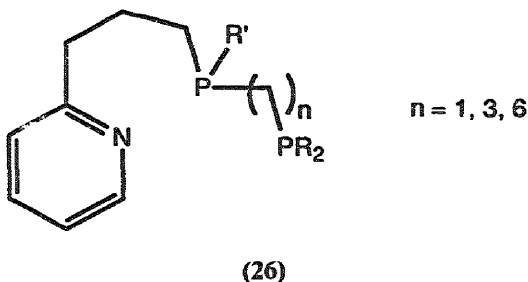
Rhodium(I) carbonyl complexes of anionic *N,O*-donor ligands have been prepared and evaluated as catalysts for styrene hydroformylation [56]. Rhodium(I) complexes of *S,P*-donor ligands perform the same function [57].

Phosphorus-nitrogen donor ligands have also been prepared and their coordination chemistry with rhodium(I) investigated. The complexes of phosphine-imine ligands act as good alkene hydrogenation catalysts but also promote isomerisation [58]. Rhodium(I) complexes of the phosphinamido ligand (25) have also been prepared and characterised [59].

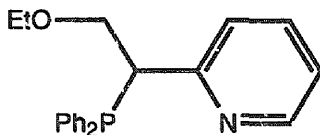


Complexes of the potentially tridentate ligands (26) have been prepared and structurally characterised. The metal centre occupies a distorted square planar coordination environment and is bound to the three donor atoms of the ligand. The coordination shell is completed by a chloride ligand [60].

The coordination chemistry of the ligand (27) has been investigated. While the

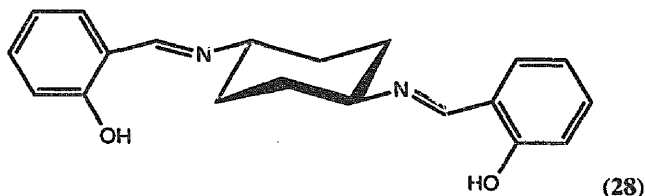


ligand behaves as a facially coordinating tridentate ligand with octahedral metal ions with rhodium(I) a square planar complex $[\text{Rh}(\text{cod})(27)]^+$ is obtained in which the oxygen atom is non-coordinated. Dimeric compounds in which the P and O donor atoms bridge the two metals have also been prepared [12a].



(27)

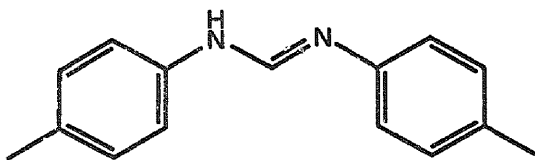
The bisrhodium complex $[\text{Rh}_2(\text{CO})_4\text{L}]$ of the doubly deprotonated ligand (28) has been shown to behave as a calamitic mesomorphic material. The compound exhibits smectic A behaviour but has a smaller mesophase range than the analogous iridium compound [62].



(28)

1.5. Di-, tri- and polynuclear compounds

A number of compounds containing a central $\text{Rh}_2(\text{OAc})_4$ core with a variety of terminal ligands have been prepared. The complex with terminal ligands (29) has been structurally characterised [63]. The terminal ligand binds in a monodentate fashion via the imine nitrogen. Structural determination of a compound containing *O*-bonded ethanol ligands has also been reported [64]. Substituent effects in these complexes have also been examined [65].



(29)

The $\text{Rh}_2(\text{OAc})_4$ core can also be incorporated into polymeric arrays by reaction with polynucleating multi-monodentate ligands. Thus reaction with 2-amino-methylpyridine [66] or tetracyanoethylene [67] gives rise to coordination polymers. The former compound is a linear polymer in which H-bonding between the amine

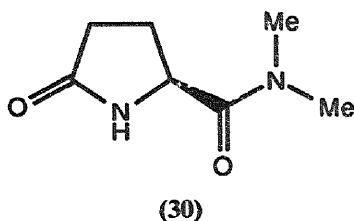
groups and the carboxylate oxygens is observed. The tetracyanide ethylene compounds contains infinite chains with interstitial sites in which organic solvent molecules reside.

The carboxylate groups may also be replaced in the core. Reaction with bpy and phen [68] leads to a series of compounds of unknown structure of formula $\text{Rh}_2(\text{LL})_n$ (LL = bpy or phen). Reaction of guanine bases with the $\text{Rh}_2(\text{OAc})_4$ core leads to the displacement of two adjacent acetate groups [69]. This compound has implications for potential anti-tumour drugs. Coordination of pyrazole derivatives [70] and ferrocene based *N* and *P* donor chelates [71] have also been reported together with an investigation of the electronic structure of diimine containing compounds [72]. The catalytic hydroformylation activity of dimers containing bridging pyrazolato has been investigated. Increased activity when compared to monorhodium compounds is observed [73]. Dimetallic compounds containing bridging imidazole ligands have also been reported [74].

Rhodium porphyrin compounds are often found as dimers and both homo rhodium-rhodium and hetero rhodium-indium dimers have been reported. The rhodium-rhodium dimer is tightly bound both through a rhodium(II)-rhodium(II) interaction and π -stacking interactions [75]. A new synthetic approach to these compounds has also been reported [76]. The rhodium-indium bond is proposed, from its reactivity, to be polarised towards rhodium(I)-indium(III) [77]. Rhodium complexes of octa-ethyltetraazaporphyrins have also been prepared [78].

The spectroscopic and photophysical properties of rhodium dimers containing diisocyanomethane ligands has been reported [79]. Molecular calculations are used to rationalise and predict the observed eclipsed and staggered conformations in these compounds. An investigation of the correlation between the metal-metal separation and force constant in dinuclear rhodium compounds has been undertaken [80].

A compound of formula $[\text{Rh}_2(\text{30-H})_4(\text{MeCN})_2]$ has been prepared [81]. Structural characterisation shows the ligand to bind in an anionic bridging mode through the nitrogen and oxygen of the pyrrolidone moiety.



Isomerisation processes in a chloro bridged complex have been studied by NMR spectroscopy [82]. High yielding routes to dimeric chloro-bridged rhodium phosphine compounds have been described [83].

A wide range of phosphine bridged rhodium(I) compounds have been prepared [84]. Rhodium-manganese dimers containing sulfide and thiolato bridges have also been reported [85]. A range of trimeric rhodium containing systems with ligand (**1**), phenanthrenquinonediiimine, have been synthesised and characterised [86].

References

- [1] P. Kopfmaier, *Eur. J. Clinical Pharm.* 47 (1994) 1.
- [2] E.G. Hope, *Polyhedron* 12 (1993) 2977.
- [3] I.J. Ellison, R.D. Gillard, M. Moszner, M. Wilgocki and J.J. Ziolkowski, *J. Chem. Soc., Dalton Trans.*, (1994) 2531.
- [4] A. Koutsodimou, N. Katsaros, D. Kovalademertzi, *Transition Metal Chem.* 19 (1994) 260.
- [5] E. Alessio, A.S.O. Santi, P. Faleschini, M. Caligaris and G. Mestroni, *J. Chem. Soc., Dalton Trans.*, (1994) 1849.
- [6] E. Alessio, A.S.O. Santi, P. Faleschini, M. Caligaris and G. Mestroni, *J. Chem. Soc., Dalton Trans.*, (1994) 1849.
- [7] A.H. Crotz, L.Y. Kuo, J.K. Barton, *Inorg. Chem.* 32 (1993) 5963.
- [8] J.G. Collins, T.P. Shields, J.K. Barton, *J. Am. Chem. Soc.* 116 (1994) 9840.
- [9] A. Sitlani, J.K. Barton, *Biochemistry* 33 (1994) 12100.
- [10] A.H. Crotz, J.K. Barton, *Inorg. Chem.* 33 (1994) 1940.
- [11] A.H. Crotz, B.P. Hudson, J.K. Barton, *J. Am. Chem. Soc.* 115 (1993) 12577.
- [12] N.Y. Sardesai, K. Zimmermann, J.K. Barton, *J. Am. Chem. Soc.* 116 (1994) 7502.
- [13] T. Mohammad, I. Tessman, H. Morrison, M.A. Kennedy, S.W. Simmons, *Photochem. and Photobiol.* 59 (1994) 189.
- [14] C.J. Murphy, M.R. Arkin, N.D. Ghatlia, S. Bossmann, N.J. Turro, J.K. Barton, *Proc. Natl. Acad. USA* 91 (1994) 5315.
- [15] M.G. Columbo, T.C. Brunold, T. Reidener, H.U. Gudel, M. Fortsch, H.B. Burgi, *Inorg. Chem.* 33 (1994) 545.
- [16] S. Serroni, A. Juris, C. Campagna, M. Venturi, G. Denti, V. Balzani, *J. Am. Chem. Soc.* 116 (1994) 9086.
- [17] S.M. Molnar, G.E. Jensen, L.M. Vogler, S.W. Jones, L. Laverman, J.S. Bridgewater, M.M. Richter, K.J. Brewer, *J. Photochem. and Photobiol. A* 80 (1994) 315.
- [18] M.T. Delli, C.A. Bignozzi, A. Harriman, J.R. Schoonover, F. Scandola, *J. Am. Chem. Soc.* 116 (1994) 3768.
- [19] A. von Zelewsky, *Chimia* 48 (1994) 331.
- [20] I.M.F. De Olivera, J.C. Moutet, *J. Electroanal. Chem.* 361 (1993) 203.
- [21] J.-P. Collin, A. Harriman, V. Heitz, F. Odobel, J.-P. Sauvage, *J. Am. Chem. Soc.* 116 (1993) 5679.
- [22] F. Odobel, J.-P. Sauvage, A. Harriman, *Tetrahedron Lett.* 34 (1993) 8113.
- [23] Y. Kuroda and H. Ogoshi, *Synlett*, (1994) 319.
- [24] M. Haga, T. Ano, T. Ishizaki, K. Kano, K. Nozaki and T. Onho, *J. Chem. Soc., Dalton Trans.*, (1994) 263.
- [25] R.J. Geue, M.B. McDonnell, A.W.H. Mau, A.M. Sargeson and A.C. Willis, *J. Chem. Soc., Chem. Commun.*, (1994) 667.
- [26] G. Ostendorp, S. Sievertsen, H. Homborg, *Z. Anorg. Allg. Chem.* 620 (1994) 279.
- [27] S. Sievertsen, G. Ostendorp, H. Homborg, *Z. Anorg. Allg. Chem.* 620 (1994) 290.
- [28] T. Nyokong, *J. Chem. Soc., Dalton Trans.*, (1994) 1359.
- [29] T.W. Hambley, G.A. Lawrance, M. Maeder and G. Wei, *J. Chem. Soc., Dalton Trans.*, (1994) 355.
- [30] T.W. Hambley, G.A. Lawrance, M. Maeder, K.J. Molloy, M. Rossignoli, *Aust. J. Chem.* 47 (1994) 829.
- [31] E. Mannessizoupa, T.F. Zafiropoulos, S.P. Perlepes, *Z. Naturforsch, Teil B* 49 (1994) 111.
- [32] S. Geremia, R. Dreoa, L. Ranaccio, G. Tauzher, L. Antolini, *Inorg. Chim Acta* 216 (1994) 125.
- [33] V. Kettmann, M. Dunajjurco, D. Steinborn, M. Ludwig, *Acta Crystallogr., Sect. C* 50 (1994) 1239.
- [34] C. Paek, J.J. Ko, J.K. Uhm, *J. Korean Chem. Soc.* 15 (1994) 980.
- [35] L.A. Bengtsson, B.T. Heaton, J.A. Iggo, C. Jacob, G.L. Monks, J. Ratnam and A.K. Smith, *J. Chem. Soc., Dalton Trans.*, (1994) 1857.
- [36] R. Lampeka, S. Berge, R. Kramer, K. Polborn, W. Beck, *Z. Naturforsch, Teil B* 49 (1994) 225.
- [37] E. Schuhmann, C. Robl, W. Beck, *Z. Naturforsch, Teil B* 49 (1994) 1569.
- [38] Y.L. Zhou, B. Wagner, K. Polborn, K. Sunkel, W. Beck, *Z. Naturforsch, Teil B* 49 (1994) 1193.

- [39] P. Cornago, C. Escolastico, M.D.S. Maria, R.M. Claramunt, D. Carmona, M. Esteban, L.A. Oro, C. Focesfoces, A.L. Llamassaiz, J. Elguero, *J. Organometal. Chem.* 467 (1994) 293.
- [40] B.K. Kumar, V. Ravinder, G.B. Swamy, S.J. Swamy, *Ind. J. Chem., A* 33 (1994) 136.
- [41] D.J. Anderson, R. Eisenberg, *Inorg. Chem.* 33 (1994) 5378.
- [42] A.K. Ghosh, G.S. De, *Ind. J. Chem., A* 33 (1994) 929.
- [43] A.J. Blake, R.O. Gould, M.A. Halcrow and M. Schröder, *J. Chem. Soc., Dalton Trans.*, (1994) 2197.
- [44] H.A. Jenkins, S.J. Loeb, *Organometallics* 13 (1994) 1840.
- [45] D.K. Dutta, M.M. Singh, *Transition Metal Chem.* 19 (1994) 290.
- [46] M. Cano, J.A. Campo, J.V. Heras, E. Pinilla, C. Rivas, A. Monge, *Polyhedron* 13 (1994) 2463.
- [47] R. Reinhardt, W. Kaim, *Z. Anorg. Allg. Chem.* 619 (1993) 1998.
- [48] I.C.M. Wehmanooeyvaar, G.M. Kapteijn, D.M. Grove, W.I.J. Smeets and A.L. Spek, *J. Chem. Soc., Dalton Trans.*, (1994) 703.
- [49] K. Sakata, T. Fujitsu, H. Tajiri, M. Masatsuga, M. Hasimoto, *Synth. React. Inorg. Met.,-Org. Chem.* 24 (1994) 1509.
- [50] W.P. Fehlhammer, R. Metzner, W. Sperber, *Chem. Ber.* 127 (1994) 631.
- [51] H. Schumann, H. Hemling, V. Ravindar, Y. Badrieh, J. Blum, *J. Organometal. Chem.* 469 (1994) 213.
- [52] B.T. Heaton, J.A. Iggo, C. Jacob, J. Nadarajah, M.A. Fontaine, R. Messere and A.F. Noels, *J. Chem. Soc., Dalton Trans.*, (1994) 2875.
- [53] T. Matsubara, Y. Saito, *J. Mol. Catal.* 92 (1994) 1.
- [54] M. Cano, J.V. Heras, M.A. Lobo, E. Pinilla, *Polyhedron* 13 (1994) 1575.
- [55] M. Cano, J.V. Heras, M.A. Lobo, E. Pinilla, A. Monge, *Polyhedron* 13 (1994) 1563.
- [56] W.Z. Chen, Y. Xu, S.J. Liao, *Transition Metal Chem.* 19 (1994) 418.
- [57] S. Gladiali, A. Dore, D. Fabbri, *Tetrahedron Asym.* 5 (1994) 1143.
- [58] D.J. Law, R.G. Cavell, *J. Mol. Cat.* 91 (1994) 175.
- [59] T. Satyanarayana, K.V. Reddy, *Transition Metal Chem.* 19 (1994) 373.
- [60] A. Hessler, J. Fischer, S. Kucken, O. Stetzler, *Chem. Ber.* 127 (1994) 481.
- [61] M. Alvarez, N. Lugan and R. Mathieu, *J. Chem. Soc., Dalton Trans.*, (1994) 2755.
- [62] P. Berdague, J. Courtieu and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1994) 1313.
- [63] F. Nicolo, G. Bruno, S. Loschiavo, M.S. Sinicropi, P. Piriano, *Inorg. Chim., Acta* 223 (1994) 145.
- [64] F.A. Cotton, L.M. Daniels, P.A. Kibala, M. Matusz, W.J. Roth, W. Schwotzer, W.N. Wang, B.X. Zhong, *Inorg. Chim. Acta* 221 (1994) 9.
- [65] M.C. Pirrung, A.T. Morehead, *J. Am. Chem. Soc.* 116 (1994) 8991.
- [66] C.A. Crawford, E.F. Day, W.E. Streib, J.C. Huffman, G. Christou, *Polyhedron* 13 (1994) 2933.
- [67] F.A. Cotton, Y. Kim, J. Lu, *Inorg. Chim. Acta* 215 (1994) 1.
- [68] S. Lochiavo, M.S. Sinicropi, G. Tresoldi, C.G. Arena and P. Piriano, *J. Chem. Soc., Dalton Trans.*, (1994) 1517.
- [69] K.R. Dunbar, J.H. Matonic, V.P. Saharan, C.A. Crawford, G. Christou, *J. Am. Chem. Soc.* 116 (1993) 2201.
- [70] B. Viossat, N.H. Dung, J.C. Daran, J.C. Lancelot, *Acta Crystallogr., Sect. C* 49 (1993) 2084.
- [71] E.J. Kim, T.J. Kim, *J. Korean Chem. Soc.* 15 (1994) 990.
- [72] L. Catanec and F.P. Pruchnik, *J. Chem. Soc., Dalton Trans.*, (1994) 3261.
- [73] N. Schumann, H. Hemling, V. Ravindar, Y. Badrieh, J. Blum, *J. Organometal. Chem.* 469 (1994) 213.
- [74] F. Bonati, L.A. Oro, M.T. Pinollis, C. Tejel, *J. Organometal. Chem.* 465 (1994) 267.
- [75] S. Lee, M. Mediati and B. Wayland, *J. Chem. Soc., Chem. Commun.*, (1994) 2299.
- [76] K.S. Chan, Y.B. Leung, *Inorg. Chem.* 33 (1994) 3187.
- [77] D. Lux, D. Daphnomilli, A.G. Coutsolelos, *Polyhedron* 13 (1994) 2367.
- [78] Y.P. Ni, J.P. Fitzgerald, P. Carroll, B.B. Wayland, *Inorg. Chem.* 33 (1994) 2029.
- [79] V.M. Miskowski, S.F. Rice, H.B. Gray, R.F. Dallinger, S.J. Milder, M.G. Hill, C.L. Extrom, K.R. Mann, *Inorg. Chem.* 33 (1994) 3735.
- [80] P.D. Harvey, F. Shafiq, R. Eisenberg, *Inorg. Chem.* 33 (1994) 2799.
- [81] M.P. Doyle, W.R. Winchester, S.H. Simonsen, R. Ghosh, *Inorg. Chim. Acta* 220 (1994) 193.
- [82] G. Giordano, E. Rotondo, *Polyhedron* 13 (1994) 2507.

- [83] P. Binger, J. Haas, G. Glaser, R. Goddard, C. Kruger, *Chem. Ber.* 127 (1994) 1927.
- [84] W. Keim, P. Kraneburg, G. Dahmen, G. Deckers, U. Englert, K. Linn, T.P. Spaniol, G. Raabe, C. Kruger, *Organometallics* 13 (1994) 3558.
- [85] L.S. Wang, R. McDonald, M. Cowie, *Inorg. Chem.* 33 (1994) 3735.
- [86] S.S. Chern, G.H. Lee and S.M. Peng, *J. Chem. Soc., Dalton Trans.*, (1994) 1645.