

Mono- and dinuclear rhodium(I) complexes containing the ligand 3,5-bis(pyridin-2-yl)-1,2,4-triazole

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Abstract

Reactions of $[\text{RhClL}_2]$ ($\text{L}_2 = \text{diolefin}$ or $(\text{CO})(\text{PPh}_3)$) with the deprotonated form of the ligand 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt) gave neutral, mononuclear complexes $[\text{Rh}(\text{L}_2)(\text{bpt})]$. Cationic, mono- and dinuclear species of formulae $[\text{Rh}(\text{L}_2)(\text{Hbpt})]^+$, $[\{\text{RhL}_2\}_2(\text{bpt})]^+$ and $[\{\text{RhL}_2\}_2(\text{Hbpt})]^{2+}$, where $\text{L}_2 = \text{diolefin}$, $(\text{CO})_2$ or $(\text{CO})(\text{PPh}_3)$, have also been prepared. Ion-pair complexes of formulae $[\text{Rh}(\text{L}_2)(\text{Hbpt})][\text{RhCl}_2\text{L}_2]$ were obtained by adding Hbpt to dichloromethane solutions of $[\text{RhClL}_2]$.

Introduction

There is considerable interest in the chemical and physical properties of new anisotropic materials [1]. Some mononuclear rhodium(I) complexes form linear stacks [2] and recently it has been reported that binuclear and trinuclear rhodium(I) complexes with azolate ligands present stackings arrangements of square-planar rhodium units along one axis, forming nearly linear chains of metal atoms [3, 4].

Due to the possibility of unusual solid state properties for related compounds and following our interest in rhodium azolate complexes [4–6] we have focussed our attention on the triazole ligand 3,5-bis(pyridin-2-yl)-1,2,4-triazole; this undemanding and planar ligand has also the appropriate features to behave as bi- or tetradentate chelating anionic or neutral group, and so it has been used to prepare mono- and dinuclear compounds of copper [7], ruthenium [8] or osmium [9]. Furthermore as a multidentate aromatic nitrogen heterocycle it should favour, when acting as a bridging ligand, communication between the metal centres via the π system of the ligand.

In this paper we describe the synthesis of mono- and dinuclear rhodium(I) complexes with the ligand in its neutral (Hbpt) or deprotonated (bpt^-) forms.

Results and discussion

Mononuclear complexes

Addition of dichloromethane solutions of $[\text{Rh}_2\text{Cl}_2(\text{diolefin})_2]$ to solutions of the ligand 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt) and potassium hydroxide, gives neutral complexes of the type $[\text{Rh}(\text{diolefin})(\text{bpt})]$ (diolefin = tetrafluorobenzobicyclo[2.2.2]octadiene (tfb) and 1,5-cyclooctadiene (cod) (compounds I and II). An alternative route used for the synthesis of these complexes is based on the ability of ligands containing N–H bonds to abstract the methoxy group from $[\text{Rh}(\mu\text{-MeO})(\text{L}_2)]_2$ complexes [6–10].

A related compound of formula $[\text{Rh}(\text{CO})(\text{PPh}_3)(\text{bpt})]$ (III) ($\nu(\text{CO})$: 1975 cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$, CDCl_3 : 46.07 d ppm, $J(\text{Rh-P}) = 163.6$ Hz) has been prepared by treatment of *trans*- $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{PPh}_3)_2]$ with the Hbpt ligand and potassium hydroxide.

After working-up the compounds are isolated as air-stable yellow microcrystalline solids in good yield. They are non-electrolyte in acetone and the molecular weights of I and II are in agreement with the mononuclear neutral formulation proposed (Table 1).

Cationic species of the type $[\text{Rh}(\text{L}_2)(\text{Hbpt})]^+$ ($\text{L}_2 = \text{tfb}$, cod, bicyclo[2.2.1]heptadiene (nbd), $(\text{CO})(\text{PPh}_3)$ or $(\text{CO})_2$) (complexes IV–VIII) can be prepared using a general route that involves the reaction of the solvates $[\text{Rh}(\text{L}_2)(\text{Me}_2\text{CO})_x]\text{ClO}_4$ intermediate with Hbpt ligand in the stoichiometric ratio 1:1. Compounds IV–VII were also obtained by treating the appropriate neutral complex $[\text{Rh}(\text{L}_2)(\text{bpt})]$ in acetone with perchloric acid and compound VIII by bubbling

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TABLE 1. Colour, analytical results, conductance, yield and spectroscopic data for the new complexes

Compound	Colour	Yield (%)	Found (Calc.)			Λ_M^a	M_w	$\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ (cm^{-1})
			N	C	H			
I [Rh(tfb)(bpt)]	yellow	85	12.4 (12.7)	51.6 (52.2)	2.5 (2.6)	603	1613, 1591, 1568w, 1527w	
II [Rh(cod)(bpt)]	yellow	89	15.9 (16.1)	54.2 (55.4)	4.6 (4.6)	480	1609, 1589, 1564, 1530	
III [Rh(CO)(PPh ₃)(bpt)]	yellow	71	10.7 (11.3)	59.9 (43.0)	3.7 (3.7)		1611, 1590, 1566, 1527 $\nu(\text{CO})=1990^e$	
IV [Rh(tfb)(Hbpt)]ClO ₄ ·H ₂ O	yellow	66	10.1 (10.4)	43.0 (43.0)	2.5 (2.5)	102	1630, 1610, 1545w	
V [Rh(cod)(Hbpt)]ClO ₄ ·H ₂ O	yellow	84	12.6 (12.6)	42.7 (43.5)	3.7 (4.1)	108	1630, 1610, 1545w	
VI [Rh(nbd)(Hbpt)]ClO ₄ ·H ₂ O	orange	87	13.4 (13.5)	43.8 (44.0)	3.1 (3.2)	110	1620, 1605	
VII [Rh(CO)(PPh ₃)(Hbpt)]ClO ₄	yellow	67	9.9 (9.7)	51.9 (51.8)	3.7 (3.4)	98	1624, 1605, 1530 $\nu(\text{CO})=1995$	
VIII [Rh(CO) ₂ (Hbpt)]ClO ₄ ·H ₂ O	dark blue	79	14.4 (14.0)	33.2 (33.6)	1.9 (2.0)	115	1633, 1615, 1533 $\nu(\text{CO})=2098, 2032^e$	
IX [[Rh(tfb)] ₂ (bpt)]ClO ₄ ·H ₂ O	yellow	72	7.0 (7.0)	42.9 (43.3)	2.0 (2.2)	106	1610	
X [[Rh(CO)(PPh ₃)] ₂ (bpt)]ClO ₄ ·H ₂ O	dark green	57	6.3 (6.2)	53.8 (53.3)	3.9 (3.9)	102	1612 $\nu(\text{CO})=1980$	
XI [[Rh(cod)] ₂ (Hbpt)](ClO ₄) ₂	yellow	90	8.5 (8.3)	39.7 (39.8)	3.8 (3.9)	151	1612	
XII [[Rh(CO)(PPh ₃)] ₂ (Hbpt)](ClO ₄) ₂	yellow	41	6.0 (5.8)	50.4 (49.7)	3.6 (3.2)	145	1615 $\nu(\text{CO})=2000$	
XIII [RhCl ₂ (tfb)][Rh(tfb)(Hbpt)]	orange	72	7.7 (7.4)	44.4 (45.4)	1.9 (2.2)	20 ^b	1610	
XIV [RhCl ₂ (CO) ₂][Rh(CO) ₂ (Hbpt)]	dark green	82	12.0 (11.5)	30.1 (31.4)	1.3 (1.4)		1615, 1520w $\nu(\text{CO})=2095, 2075m, 2034, 1995m^e$	

^aAcetone solvent (in $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$).

^bNitromethane solvent.

^cIn dichloromethane solutions.

carbon monoxide through a dichloromethane solution of any of the [Rh(diolefin)(Hbpt)]ClO₄ complexes.

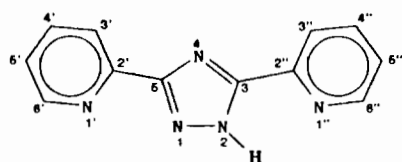
Compounds IV–VIII are 1:1 electrolytes in acetone and their IR spectra show bands due to the uncoordinated perchlorate anion at *c.* 1100s and 620 cm^{-1} ; complex VII shows, in dichloromethane, a strong $\nu(\text{CO})$ band at 1995 cm^{-1} ; complex VIII shows two $\nu(\text{CO})$ bands at 2098 and 2032 cm^{-1} , in dichloromethane solution, typical of *cis*-dicarbonyl derivatives.

Most probably, all of these mononuclear compounds (I–VIII) are square planar with the Hbpt (or bpt) ligand acting as chelate; so the rhodium atom should be coordinated to a N atom of the pyridine ring and a N atom of the triazole ring; however the coordination to the triazole ring can occur either through the N₁ or the N₄ atom; the coordination mode will have an effect on the electronic properties of the ligand [11]. The IR spectra of the complexes, in the region of 1650–1520 cm^{-1} , show a pattern very similar to that of the free ligand and the ¹H NMR spectra (Table 2) reveal dynamic behaviour in solution at room temperature and at –50 °C, showing the same absorptions at both temperatures. However, X-ray crystal structures

of mononuclear compounds of Ru [12] and Cu [7] or spectroscopies properties of mono- and dinuclear Os compounds [9], with the Hbpt (or related) ligand show that coordination to the triazole ring is through the N₁ atom. Only very recently Reedijk and coworkers [13] have found, and have separated by HPLC, two isomers of the 3-(pyridin-2-yl)-1H-1,2,4-triazole complex of ruthenium(II) bis(2,2'-bipyridyl); in one of the isomers the central atom is bound to the N₁ and in the other to the N₄ of the triazole ring.

Dinuclear complexes

The mononuclear complexes, neutral or cationic, have the capability of acting as N-donor ligands; so, homobinuclear rhodium compounds of formula $[\{\text{Rh}(\text{L}_2)\}_2(\mu\text{-bpt})]\text{ClO}_4$ (IX–X) can be prepared by reacting $[\text{Rh}(\text{L}_2)(\text{Me}_2\text{CO})_x]\text{ClO}_4$ with the neutral $[\text{Rh}(\text{L}_2)(\text{bpt})]$ compounds (1:1) or by treating the cationic $[\text{Rh}(\text{L}_2)(\text{Hbpt})]^+$ species with the dimers $[\text{Rh}(\mu\text{-OMe})(\text{L}_2)]_2$ in the ratio 2:1. These products are 1:1 electrolytes in acetone. Complexes of the type $[\{\text{Rh}(\text{L}_2)\}_2(\mu\text{-Hbpt})](\text{ClO}_4)_2$ (XI–XII) are obtained by adding the ligand Hbpt to the solvated species

TABLE 2. ¹H NMR data ^a for the free ligand and some selected complexes

Compound	Solvent	T (°C)	H ₃ , ^b H _{3'}	H ₄ , H _{4'}	H ₅ , H _{5'}	H ₆ , H _{6'}	H ₂	Others
Hbpt	CDCl ₃	20	8.38d(2)	7.88td(2)	7.40ddd(2)	8.81d(2)	2.1(1)	
	d ₆ -acetone	20	8.26d(2)	7.98td(2)	7.48ddd(2)	8.70ddd(2)	2.9(1)	
II	CDCl ₃	20	8.14d	7.84t(1), 7.68td(1)	7.20m	7.36d(1), 8.69d(1)		4.04(4), 1.45(8)
III	CDCl ₃	20	8.28d	7.92t	7.07t	8.59d		7.75, 7.66, 7.40
IV	CDCl ₃	20	8.07m	7.48m	7.26m	8.34m	2.05s	5.74(2), 4.33(2), 4.14(2)
V	d ₆ -acetone	20	8.2m ^{*c}	7.7m ^{**}	7.7m ^{**}	8.2m [*]	3.53s	4.74(4), 2.54, 2.16(8)
VI	d ₆ -acetone	20	8.45m [*]	8.45m [*]	7.89m	8.78m	3.56s	4.6(4), 4.1(2), 1.66(2)
VII	CDCl ₃	20	8.38t	8.06d	7.20m	8.75t	2.17s	7.71(6), 7.44(9)
IX	CDCl ₃	20	7.54d	7.57d	7.24m	8.02td		5.75(2), 4.12(4)
X	CDCl ₃	20	8.46	8.00	6.80	8.64		

^aSpectra were measured at 200 MHz. Chemical shifts are given in δ (ppm) relative to TMS. ^bAccepting that the pyridine group of the ligand coordinated to the Rh atom is that called ('). ^cPeaks with the same number of (*) are together (for the same compound). Apparency: s, singlet; d, doublet; t, triplet; m, multiplet; td, triplet of doublets; ddd, double doublet of doublets.

[Rh(L₂)(Me₂CO)₂]⁺ in the ratio 1:2; they are 1:2 electrolytes in acetone.

The coordinated ligand in these homobinuclear compounds (**IX–XII**) presents, in the IR spectrum, differences from their monometallic precursors; in the 1650–1500 region, they show only a strong band at *c.* 1610 cm⁻¹ while the mononuclear complexes show four bands in the same region. This behavior is similar to that found for mononuclear and binuclear compounds of related ligands such as 2,2'-bipyrimidine or 1,10-phenanthroline [14]. In these dinuclear complexes the coordination of 'RhL₂' units probably takes place at two different coordination sites; in addition to the pyridine ring the central triazole ring binds one metal centre through N₁ and the other through N₄ [9].

Ionic-pair complexes

Reaction of [RhClL₂] with Hbpt (Rh:Hbpt=2:1) in dichloromethane results in the formation of the ionic pair [Rh(L₂)(Hbpt)][RhCl₂L₂] (L₂=tfb (**XIII**) or (CO)₂ (**XIV**)). Analytical results revealed the presence of only one molecule of Hbpt for two rhodium atoms; the IR spectra of these compounds show, in the solid state, characteristic absorptions of the ν (Rh–Cl) (**XIII**: 290 and 280 cm⁻¹; **XIV**: 310 and 280 cm⁻¹) band present in square planar rhodium complexes [15]; the 1650–1500 cm⁻¹ region shows a pattern very similar to that of the mononuclear complexes **I–VIII**; the 2000 cm⁻¹ region in compound **XIV** presents four bands: two of them, at 2095 and 2034 cm⁻¹, in a similar position to that found for complex **VIII**, and the other two, at 2075 and 1995 cm⁻¹, in a similar position to that described for [RhCl₂(CO)₂]⁻ [16]. Compounds **XIII**

and **XIV** are not soluble enough to run their ¹H NMR; the conductivity of **XIII** is relatively low for a 1:1 electrolyte, but a similar behaviour has been observed for the structurally characterized [Rh(cod)(tpzm)][RhCl₂(cod)] complex (tpzm = tris(pyrazol-1-yl)methane [17]). The above-mentioned formation of ion-pair species is analogous to that found with a chelating bidentate nitrogen donor ligand [18] and supports the tendency of 3,5-bis(pyridin-2-yl)-1,2,4-triazole to act as a chelate due to the stability conferred by the formation of a five-membered ring instead of the hypothetical formation of neutral dinuclear complexes of formulae [RhClL₂]₂(Hbpt).

Remarks on dicarbonyl complexes

Of the complexes described in this paper, the diolefin complexes are yellow in the solid state and in solution, while the dicarbonyl complexes **VIII** and **XIV**, are yellow in solution but have a different colour in the solid state, dark blue or green. This change of colour is paralleled by a marked change in the pattern of carbonyl stretching frequencies that became more complex, suggesting the presence of rhodium–rhodium interactions in the solid state, as previously observed for related complexes [16–19]. Such interactions are possible because of the flatness of the ligands surrounding the rhodium centre.

Experimental

Starting materials

The ligand Hbpt was prepared according to described methods [20]; its purity was checked by

NMR. The complexes $[\text{RhCl}(\text{cod})]_2$ [21], $[\text{RhCl}(\text{nbd})]_2$ [22], $[\text{RhCl}(\text{tfb})]_2$ [23], $[\text{RhCl}(\text{CO})_2]_2$ [24] and $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$ [25] were prepared by literature methods.

Equipment and techniques

All reactions were carried out in air except when $\text{L}_2 = (\text{CO})(\text{PPh}_3)$ or $(\text{CO})_2$. Proton and ^{31}P NMR spectra were recorded on a Varian XL 200 spectrometer. IR spectra ($4000\text{--}200\text{ cm}^{-1}$) were recorded on a Perkin-Elmer 788 spectrometer.

Conductivity measurements were performed using a Phillips PW-9509/01 conductivity bridge, they were measured at $20\text{ }^\circ\text{C}$ in $c. 5 \times 10^{-4}\text{ M}$ acetone, nitromethane, chloroform or methanol solutions. C, H and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer.

Preparation of complexes I–III

Method A

$[\text{RhCl}(\text{L}_2)]_2$ ($\text{L}_2 = \text{tfb, cod or } (\text{CO})(\text{PPh}_3)$) (0.15 mmol) in dichloromethane (3 ml) solution of 'Kbpt' (prepared by treating Hbpt (0.3 mmol, 66.9 mg) with KOH in methanol (0.1 N)) was stirred for 3 h at room temperature. The crystalline compounds were precipitated by addition of diethyl ether, filtered off, vacuum dried and washed with diethyl ether.

The solids were purified by dissolving them in dichloromethane, filtering the solution and removing the solvent under vacuum. When $\text{L}_2 = (\text{CO})(\text{PPh}_3)$ the solid was precipitated with hexane because it is quite soluble in diethyl ether.

Method B

$[\text{Rh}(\mu\text{-MeO})(\text{L}_2)]_2$ ($\text{L}_2 = \text{tfb, cod}$) (0.15 mmol) was suspended in dichloromethane (12 ml). Hbpt was added to the suspension and orange solutions were formed. After 2 h the products were precipitated by addition of diethyl ether, filtered, washed with diethyl ether and then dried *in vacuo*.

Preparation of complexes IV–VIII

Method A

To a suspension of Hbpt (0.3 mmol, 66.9 mg) in acetone (5 ml) was added an acetone solution of $[\text{Rh}(\text{L}_2)(\text{Me}_2\text{CO})_x]^+$ ($\text{L}_2 = \text{tfb, cod, nbd, } (\text{CO})(\text{PPh}_3)$ or $(\text{CO})_2$) (0.15 mmol) (obtained by reaction of $[\text{RhCl}(\text{L}_2)]_2$ (0.15 mmol) with AgClO_4 (0.3 mmol) in acetone and filtering off the AgCl formed). Evaporation of this solution to $c. 1\text{ ml}$, followed by addition of diethyl ether gave solids, complexes IV–VIII, which were filtered off, washed with diethyl ether and dried *in vacuo*.

Method B

Complexes IV–VII were prepared by treating the appropriate $[\text{Rh}(\text{L}_2)(\text{bpt})]$ ($\text{L}_2 = \text{tfb, cod, or } (\text{CO})(\text{PPh}_3)$) (0.1 mmol) in acetone with acid HClO_4 (0.1 mmol). This solution was evaporated to $c. 1\text{ ml}$ and by addition of diethyl ether gave complexes IV–VII as microcrystalline solids.

Method C

An alternative route for preparation of complex VIII is the diolefin displacement by CO in complexes IV–VI $[\text{Rh}(\text{diolef})(\text{Hbpt})]\text{ClO}_4$ (diolef = tfb, cod or nbd). Dry CO was bubbled through a dichloromethane solution of complexes $[\text{Rh}(\text{diolef})(\text{Hbpt})]\text{ClO}_4$ for 15 min. A dark blue solid was precipitated by addition of diethyl ether.

Preparation of complexes IX and X

Method A

To a suspension of the complexes $[\text{Rh}(\text{L}_2)(\text{bpt})]$ ($\text{L}_2 = \text{tfb or } (\text{CO})(\text{PPh}_3)$) (I, III) (0.06 mmol) in acetone was added an acetone solution of $[\text{Rh}(\text{L}_2)(\text{Me}_2\text{CO})_x]^+$. The solutions were stirred for 1 h at room temperature. After concentration to $c. 1\text{ ml}$, the products were precipitated with diethyl ether, filtered off, washed with diethyl ether and then dried *in vacuo*.

The corresponding $\text{L}_2 = (\text{CO})(\text{PPh}_3)$ compound was prepared at room temperature under a nitrogen atmosphere.

Method B

Complex IX was also obtained by reacting the $[\text{Rh}(\text{tfb})(\text{Hbpt})]\text{ClO}_4$ complex with $[\text{Rh}(\mu\text{-MeO})(\text{tfb})]_2$ in stoichiometric amounts.

Preparation of complexes XI and XII

To a suspension of the ligand Hbpt (0.1 mmol) in dichloromethane were added solutions of $[\text{Rh}(\text{L}_2)(\text{Me}_2\text{CO})_x]\text{ClO}_4$ in acetone ($\text{L}_2 = \text{cod or } (\text{CO})(\text{PPh}_3)$). The solutions were then stirred for 2 h and concentrated to $c. 1\text{ ml}$. The products were precipitated with diethyl ether, filtered and dried *in vacuo*.

Preparation of complexes XIII and XIV

Method A

The complexes XIII and XIV were synthesized by dissolving the appropriate metal compound $[\text{RhCl}(\text{L}_2)]_2$ ($\text{L}_2 = \text{tfb or } (\text{CO})_2$) in dichloromethane and adding an equivalent amount of ligand Hbpt. The solutions were then stirred for 2 h to give yellow or orange solids. The microcrystalline solids were isolated and washed with diethyl ether.

Method B

[RhCl₂(tfb)][Rh(tfb)(Hbpt)] (0.2 mmol) was dissolved in dichloromethane (7 ml) and the carbonyl derivative was prepared by bubbling CO into the solutions for 15 min. The microcrystalline solid which was precipitated by addition of diethyl ether was filtered off and washed with diethyl ether.

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References

- 1 J. S. Miller (ed.), *Extended Linear Chain Compounds*, Vols. 1–3, Plenum, New York, 1982; A. E. Underhill and D. M. Watkins, *Chem. Soc. Rev.*, 9 (1980) 429; J. M. Williams, *Adv. Inorg. Chem. Radiochem.*, 26 (1983) 238.
- 2 N. A. Bailey, E. Coates, G. B. Robertson, F. Bonatti and R. Ugo, *J. Chem. Soc., Chem. Commun.*, (1967) 1041; M. J. Decker, D. O. Kimberley Fjeldsted, S. R. Stobart and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, (1983) 1525.
- 3 B. M. Louie, S. J. Retting, A. Storr and J. Trotter, *Can. J. Chem.*, 63 (1985) 688.
- 4 L. A. Oro, M. T. Pinillos, C. Tejel, C. Foces-Foces and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, (1986) 1087; L. A. Oro, M. T. Pinillos, C. Tejel, M. C. Apreada, C. Foces-Foces and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, (1988) 1927.
- 5 M. P. García, A. M. López, M. A. Esteruelas, F. J. Lahoz and L. A. Oro, *J. Chem. Soc., Dalton Trans.*, (1990) 3465; M. T. Pinillos, A. Elduque, J. A. López, F. J. Lahoz and L. A. Oro, *J. Chem. Soc., Dalton Trans.*, (1991) 1391; M. A. Esteruelas, M. P. García, A. M. López and L. A. Oro, *Organometallics*, 10 (1991) 129.
- 6 M. P. García, J. A. Manero, L. A. Oro, M. C. Apreada, F. H. Cano, C. Foces-Foces, J. G. Haasnoot, R. Prins and J. Reedijk, *Inorg. Chim. Acta*, 122 (1986) 235.
- 7 R. Prins, P. J. M. W. L. Birker, J. G. Haasnoot, G. C. Verschoor and J. Reedijk, *Inorg. Chem.*, 24 (1985) 4128.
- 8 R. Hage, A. H. J. Dijkhuis, J. G. Haasnoot, R. Prins, J. Reedijk, B. E. Buchanan and J. G. Vos, *Inorg. Chem.*, 27 (1988) 2185.
- 9 F. Barigelletti, L. De Cola, V. Balzani, R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, *Inorg. Chem.*, 30 (1991) 641.
- 10 L. A. Oro, M. J. Fernández, J. Modrego, C. Foces-Foces and F. H. Cano, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 913; L. A. Oro, M. J. Fernández, J. Modrego and J. M. López, *J. Organomet., Chem.*, 287 (1985) 409.
- 11 R. Hage, R. Prins, J. G. Haasnoot, J. Reedijk and J. G. Vos, *J. Chem. Soc., Dalton Trans.*, (1987) 1389.
- 12 R. Hage, J. P. Turkenburg, R. A. G. De Graaff, J. G. Haasnoot, J. Reedijk and J. G. Vos, *Acta Crystallogr., Sect. C*, 45 (1989) 381.
- 13 B. E. Buchanan, R. Wang, J. G. Vos, R. Hage, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 29 (1990) 3263.
- 14 V. F. Sutcliffe and G. B. Young, *Polyhedron*, 3 (1984) 87; M. P. García, J. L. Millan, M. A. Esteruelas and L. A. Oro, *Polyhedron*, 6 (1987) 1427.
- 15 M. A. Bennett, R. J. H. Clark and D. L. Milner, *Inorg. Chem.*, 6 (1967) 1647.
- 16 F. Pruchnik and W. Wajda, *J. Organomet. Chem.*, 164 (1979) 71; R. D. Gillard, K. Harrison and I. H. Mather, *J. Chem. Soc., Dalton Trans.*, (1975) 133.
- 17 M. A. Esteruelas, L. A. Oro, M. C. Apreada, C. Foces-Foces, F. H. Cano, R. M. Claramunt, C. López, J. Elguero and M. Begtrup, *J. Organomet. Chem.*, 344 (1988) 93.
- 18 M. A. Garralda and L. Ibarlucea, *J. Organomet. Chem.*, 311 (1986) 225.
- 19 P. W. DeHaven and V. L. Goedken, *Inorg. Chem.*, 18 (1979) 827.
- 20 J. F. Geldard and F. Lions, *J. Organomet. Chem.*, 30 (1965) 318.
- 21 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 19 (1979) 218.
- 22 E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, (1959) 3178.
- 23 D. M. Roe and A. G. Massey, *J. Organomet. Chem.*, 28 (1971) 273.
- 24 J. Powell and B. L. Shaw, *J. Chem. Soc. A*, (1968) 211.
- 25 D. F. Steele and T. A. Stephenson, *J. Chem. Soc. A*, (1972) 2161.