Journal of Organometallic Chemistry, 471 (1994) 221–228

Coordination of primary amine ligands to an allyl ruthenium(IV) centre

Jonathan W. Steed and Derek A. Tocher

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ (UK)

(Received September 9, 1993)

Abstract

The bis(allyl)ruthenium(IV) chloro-bridged dimer $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (**1**) reacts with aromatic amines in methanol to give the simple equatorial adducts $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(NH_2R)]$ (R = Ph, **2**; *p*-$C_6H_4NH_2$, **3**; *o*-$C_6H_4NH_2$, **5**). In contrast, in dichloromethane the analogous reaction in the case of *o*- and *p*-phenylenediamine gives the binuclear compounds $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2\{\mu\text{-}(NH_2)_2C_6H_4\}]$ **4** and **6**. In the presence of atmospheric oxygen reaction of **1** with *o*-$(NH_2)_2C_6H_4$ in methanol gives the chelate compound $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{o\text{-}(NH_2)_2C_6H_4\}]X$ (X = Cl, **7**; PF_6, **8**). The analogous reaction with 2,2′-diaminodiphenyl also gives an ionic chelate complex. $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(o\text{-}NH_2C_6H_4\cdot C_6H_4NH_2)]X$ (X = Cl, **9**; BF_4, **10**), which contains a seven-membered heterocyclic ring.

Key words: Ruthenium; Allyl; Amine; Fluxionality

1. Introduction

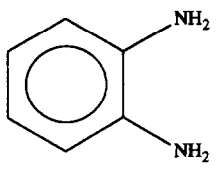
Nitrogen donor ligands such as amines, amides, imides and polypyridines are known in conjunction with a number of high oxidation state transition metal centres. Recently, reported examples include Os^{VI} amine/pyridyl complexes $[OsO_2(L)(L')]$ (L = bis(2-hydroxy-2,2-diphenylethyl)pyridinato, L′ = $NH_2{}^tBu$, py, 4-^{t}Bupy) [1], and the Ru^{IV} bis(imido) compound *trans*-$[Ru(2,6\text{-}{}^iPr_2C_6H_3N)_2(PMe_3)_2]$, formed by air oxidation of an unidentified Ru^{II} amido species [2]. Exposure of the Ru^{II} tetraphenylphorphorinato (TPP) amide complex $[Ru(TPP)(NH_2{}^tBu)_2]$ to O_2 also results in oxidation to the analogous ruthenium(VI) bis(imido) compound $[Ru(TPP)(N^tBu)_2]$ [2]. Amine donor ligands are also frequently observed in conjunction with ruthenium(II) centres: *e.g.* $[Ru(\eta^5\text{-}Cp)(NH_2R)(PR'_3)]^+$ (R = H,Me) [3], and the Ru^{II}/Ru^{III} Creutz–Taube ion $[(NH_3)_5Ru(\mu\text{-}pyz)Ru(NH_3)_5]^{n+}$ (n = 4, 5, 6) [4].

A great deal of activity including a considerable amount of very recent work [5–10], has been directed towards study of potentially bridging or chelating bifunctional amine ligands such as 1,2-diaminobenzene [*o*-phenylenediamine,*o*-pda, 1,2-$(NH_2)_2C_6H_4$]. Compounds containing neutral *o*-pda are uncommon and are often of limited stability, although anionic complexes $[MCl_4(o\text{-pda})]^-$ (M = Cr,V) have recently been reported, along with related Cr^{IV} oxidation products such as $[Cr(O_3SCF_3)_4(o\text{-pda})]$ [10]. The off-white complexes $[Fe(o\text{-pda})_3]X_2$ (X = ClO_4,I) have been known for some years [11], and in the presence of atmospheric oxygen are oxidised to the deep blue-black diiminobenzene [*o*-dib, 1,2-$(NH)_2C_6H_4$] complex $[Fe(o\text{-dib})_3]X_2$. Oxidation of coordinated *o*-pda in the presence of oxygen and a catalytic amount of base (often additional free amine) is a well known reaction, and a number of compounds are known with *o*-dib coordinated in either chelating or bridging modes (*e.g.* $[Ru(PPh_3)_3(o\text{-dib})]$ [7] and $[\{Ru(CO)_2(PPh_3)\}_2(\mu\text{-}o\text{-dib})]$ [8,9] in which the ligand is present as the dianion). A series of complex ions of general formula $[M(o\text{-dib})_2]^n$ (M = Ni,Co,Pt,Pd; n = −2 to +2) have been studied. In these, the *o*-dib ligands may exist as neutral, anionic or dianionic chelates [12]. The dianion is also known to bridge metals in such diverse oxidation states as Ru^I and W^V [5,6].

In view of this obvious versatility and stability in the presence of metals in high oxidation states, we have examined the reactions of a range of amine ligands with the ruthenium(IV) chloro-bridged dimer $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (**1**). Compound **1** is related

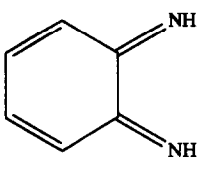
Correspondence to: Dr. D.A. Tocher.

0022-328X/94/$7.00
SSDI 0022-328X(93)24239-2



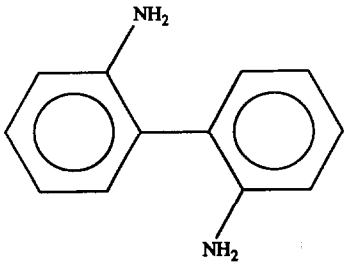
o-diaminobenzene

(*o*-pda)



o-diiminobenzene

(*o*-dib)



2,2'-diaminodiphenyl

to the intensively studied Ru^{II} compounds $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6 *etc.*) [13] and its unusual properties (high oxidation state organometallic, aqueous stability, and chirality) have made it the object of considerable recent study [14–22]. In this contribution, emphasis has been placed on the reactions of **1** with bifunctional amines related to *o*-pda. Reactions with polypyridyl ligands have been reported elsewhere [23].

2. Experimental details

2.1. Instrumental

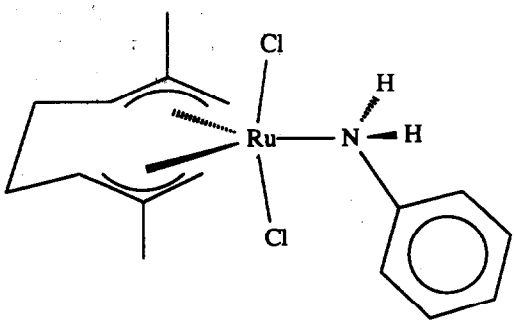
Infrared spectra were recorded on a PE983 grating spectrometer between 4000 and 180 cm^{-1} as either KBr disks or Nujol mulls on CsI plates. NMR spectra were recorded on a Varian VXR400 spectrometer. Microanalyses were carried out by the departmental service, and mass spectra were recorded by the University of London Intercolliegate Research Service at the School of Pharmacy. Cyclic voltammetric measurements were performed with a Metrohm E506 potentiostat interfaced with a Metrohm E612 VA scanner and a Hewlett Packard 7035B XY recorder. Electrolyte solutions were 0.2 M in tetra-n-butyl ammonium tetrafluoroborate. Deaeration of the solution was performed before the experiment and a stream of nitrogen passed throughout. The working electrode was a platinum wire (Metrohm EA285). A platinum wire was used as a pseudo-reference electrode and potentials were corrected relative to the ferrocene/ferrocinium couple (ferrocene was added at the end of each experiment). A massive platinum wire was used as the auxiliary electrode. All potentials are reported with respect to the Ag/AgCl couple against which ferrocene is oxidised at a potential of +0.60 V. Conductivity measurements were carried out at 20°C with a WPA CMD400 digital conductivity meter. Conductivity *vs.* concentration data were obtained over a range of concentrations (10^{-3}–10^{-4} mol dm^{-3}) and a plot of Λ_e (equivalent conductance) *vs.* $C_e^{1/2}$ (concentration in equivalents dm^{-3}) gave a straight line which, on extrapolation to $C_e^{1/2} = 0$ gave Λ_0. All manipulations were carried out under nitrogen with degassed solvents by conventional Schlenk line techniques except where otherwise stated. In general, isolated products were found to be air stable or to decompose only slowly in solution in the presence of atmospheric oxygen.

2.2. Materials

$[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ was prepared by published methods [15,18]. Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey plc. and was purified before use by repeated dissolution in water and subsequent boiling of the solution to dryness. All other reagents and materials were obtained from commercial sources.

2.3. Preparations

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(NH_2Ph)]$ (**2**). $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.07 g, 0.11 mmol) was stirred in methanol (5 cm^3) with aniline (0.1 cm^3, excess) for 3 h. The resulting orange-yellow precipitate was filtered off and washed sparingly with diethyl ether. A second crop of the product was obtained by evaporation of the yellow filtrate to *ca.* 2 cm^3. Combined yield 0.06 g, 0.15 mmol, 68%. Anal. Found: C, 48.20; H, 5.60; N, 3.65. $C_{16}H_{23}NCl_2Ru$ calc.: C, 47.90; H, 5.80; N, 3.50%.



2

TABLE 1. ^{1}H NMR data for new compounds [a]

Compound	δ				
	Terminal allyl	Internal allyl	Ethylenic	Me	Ligand
$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(NH_2Ph)]$ (2)	4.15 (s, 2H) 3.76 (s, 2H)	4.48 (m, 2H)	2.57 (m, 4H)	2.29 (s, 6H)	7.33 (d, 2H, ^3J = 7.4, *o*-C_6H_5); 2.27 (t, 2H, ^3J = 7.5, *m*-C_6H_5); 7.16 (t, 1H, ^3J = 7.3, *p*-C_6H_5); 6.13 (s, br, N*H*); 5.67 (s, br, N*H*)
$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(NH_2C_6H_4NH_2)]$ (3)	4.15 (s, 2H) 3.75 (s, 2H)	4.45 (m, 2H)	2.58 (m, 4H)	2.29 (s, 6H)	7.15 (d, 2H, ^3J = 6.5, C_6H_4); 6.57 (d, 2H, ^3J = 6.5, C_6H_4); 6.01 (d, br, ^2J = 6.1, N*H*); 5.55 (d, br, ^2J = 6.1, N*H*); 3.58 (s, br, 2H, N*H*)
$[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2\{\mu\text{-}1,4\text{-}(NY_2)_2C_6H_4\}]$ (4)	4.17 (s, 8H) 3.74 (s, 8H)	4.46 (m, 8H)	2.58 (m, 16H)	2.30 (s, 12H) 2.29 (s, 12H)	7.27 (s, 4H, C_6H_4); 7.26 (s, 4H, C_6H_4); 6.12 (d, br, 4H, ^2J = 7.9); 5.67 (d, br, 4H, ^2J = 7.9)
$\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(1,2\text{-}NH_2C_6H_4NH_2)\}$ (5)	4.33 (s, 2H) 4.03 (s, 2H)	4.64 (t, 2H, ^3J = 5.3)	2.68 (m, 2H) 2.51 (m, 2H)	2.32 (s, 6H)	7.26 (dd, 1H, ^3J = 7.7, ^4J = 1.4, C_6H_4); 6.95 (dt, 1H, ^3J = 7.7, ^4J = 1.4, C_6H_4); 6.72 (dd, 1H, ^3J = 7.7, ^4J = 1.4, C_6H_4); 6.68 (dt, 1H, ^3J = 7.7, ^4J = 1.4, C_6H_4); 5.87 (d, br, 1H, ^2J = 8.8, N*H*); 5.53 (d, br, 1H, ^2J = 8.8, N*H*); 3.40 (s, br, 2H, N*H*)
$\{[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2\{\mu\text{-}1,2\text{-}(NH_2)_2C_6H_4\}]$ (6) [b] Major diastereoisomer	4.60, 4.48, 4.21 [c] 4.18, 4.11, 3.99	4.62 (m, 4H)	2.69 (m, 4H) 2.46 (m, 4H)	2.26 (s, 12H)	8.26 (m, 2H, C_6H_4); 7.49 (d, 1H, ^2J = 7.0, N*H*); 7.21 (d, 1H, ^2J = 7.0, N*H*); 5.74 (d, 1H, ^2J = 9.5, N*H*); 5.33 (d, 1H, ^2J = 9.5, N*H*)
$[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2\{\mu\text{-}1,2\text{-}(NH_2)_2C_6H_4\}]$ (6) [b] Minor diastereoisomer		4.62 (m, 4H)	2.69 (m, 4H) 2.46 (m, 4H)	2.31 (s, 6H) 2.24 (s, 6H)	8.36 (m, 2H, C_6H_4); 7.42 (s, 1H, N*H*); 7.25 (s, 1H, N*H*); 5.62 (s, 1H, N*H*); 5.22 (s, 1H, N*H*)
$[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{1,2\text{-}(NH_2)_2C_6H_4\}]Cl$ (7) [b]	4.14 (s, 1H) 3.88 (s, 1H) 3.74 (s, 1H) 3.38 (s, 1H)	4.44 (m, 1H) 4.37 (m, 1H)	2.90–2.54 (m, 4H)	2.25 (s, 6H)	8.45 (s, br, 1H, N*H*); 7.61 (d,1H, ^3J = 7.8, C_6H_4); 7.34 (d, 1H, ^3J = 7.1, C_6H_4); 7.28 (t, 1H, ^3J = 7.3, C_6H_4); 7.11 (t, 1H, ^3J = 7.3, C_6H_4); 6.93 (s, br, 1H, N*H*); 6.42 (s, br, 1H, N*H*); 4.79 (s, br, 1H, N*H*)
$[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{1,2\text{-}(NH_2)_2C_6H_4\}][PF_6]$ (8) [d]	4.48 (s, 1H) 4.25 (s, 1H) 3.60 (s, 1H) 3.03 (s, 1H)	4.48 (m, 1H) 3.60 (m, 1H)	2.88–2.66 (m, 4H)	2.39 (s, 3H) 2.30 (s, 3H)	7.51 (d, 1H, ^3J = 7.9, C_6H_4); 7.35 (t, 1H, ^3J = 7.5, C_6H_4); 7.29 (t, 1H, ^3J = 7.9, C_6H_4); 7.21 (d, 1H, ^3J = 7.9, C_6H_4); 6.96 (d, br, 1H, ^2J = 12.5, N*H*); 6.64 (d, br, 1H, ^2J = 12.5, N*H*); 4.29 (s, br, 2H, N*H*)
$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NH_2C_6H_4C_6H_4NH_2)]Cl$ (9) [b]	4.36 (s, 1H) 4.10 (s, 1H) 3.59 (s, 1H) 3.05	4.73 (m, 2H)	2.80–2.50 (m, 4H)	2.44 (s, br, 3H) 2.35 (s, 3H)	7.48 (m, br, 3H, C_6H_4); 7.28 (m, 3H, C_6H_4); 7.19 (d, 1H, ^3J = 7.6, C_6H_4); 7.12 (d, 1H, ^3J = 7.5, C_6H_4); 6.10 (d, 1H, ^2J = 9.0, N*H*), 5.47 (d, 1H, ^2J = 9.0, N*H*); 3.61 (s, br, 2H, N*H*)
$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NH_2C_6H_4C_6H_4NH_2)][BF_4]$ (10)	4.41 (s, 1H) 4.13 (s, 1H) 3.60 (s, 1H) 3.04 (s, 1H)	4.79 (dd, 1H, ^3J = 8.1 and 3.9) 4.18 (d, 1H, ^3J = 7.5)	3.38 (m, 1H) 2.85 (m, 1H) 2.76 (m, 1H) 2.60 (m, 1H)	2.42 (s, 3H) 2.29 (s, 3H)	7.62 (m, 2H, C_6H_4); 7.36 (m, 3H, C_6H_4); 7.26 (d, 1H, ^3J = 6.2); 7.21 (dd, 1H, ^3J = 7.4, ^4J = 1.7, C_6H_4); 7.10 (d, 1H, ^3J = 7.8, C_6H_4); 6.08 (d, 1H, ^2J = 9.3, N*H*); 5.57 (d, 1H, ^2J = 9.3, N*H*); 5.09 (d, 1H, ^2J = 8.3, N*H*); 3.81 (d, 1H, ^2J = 8.3, N*H*)

[a] δ in ppm, *J*(H–H) in Hz, 400 MHz, 20°C, solvent $CDCl_3$, unless otherwise stated, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, se = septet, m = multiplet, br = broad. [b] Signals broad due to fluxionality. [c] Overlap and broadness of spectrum makes assignment of resonances to their respective isomers impossible. All resonances are broad singlets of varying intensity, total integral 12H for each diastereoisomer. [d] Solvent MeCN-d_3.

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(p-$NH_2C_6H_4NH_2$)] (**3**). [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (0.05 g, 0.08 mmol) was stirred in methanol (5 cm^3) with *p*-$(NH_2)_2C_6H_4$ (0.02 g, 0.18 mmol). Work-up and isolation were as described for **2**. Yield 0.06 g, 0.14 mmol, 88%. Anal. Found: C, 46.15; H, 5.90; N, 6.55; Cl, 17.00. $C_{16}H_{24}N_2Cl_2Ru$ calc.: C, 46.15; H, 5.80; N, 6.75; Cl, 17.05%.

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2${μ-p-$(NH_2)_2C_6H_4$}] (**4**). [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (0.10 g, 0.16 mmol) was stirred in CH_2Cl_2 (5 cm^3) with *p*-$(NH_2)_2C_6H_4$ (0.02 g, 0.17 mmol) for 1 h, giving a bright yellow precipitate which was filtered off. A second crop of precipitate was obtained by concentrating the filtrate to *ca.* 2 cm^3. Combined yield 0.10 g, 0.14 mmol, 86%. Anal. Found: C, 42.35; H, 5.50; N, 3.65. $C_{26}H_{40}N_2Cl_4Ru_2$ calc.: C, 43.10; H, 5.55; N, 3.85%.

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(o-$NH_2C_6H_4NH_2$)] (**5**). [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (0.07 g, 0.11 mmol) was stirred in methanol (5 cm^3) with *o*-$(NH_2)_2C_6H_4$ (0.03 g, 0.24 mmol) for 4 h to give an orange solution. The solvent was removed *in vacuo* and the product dissolved in the minimum amount of CH_2Cl_2. Trituration with diethyl ether resulted in the formation of a red precipitate, which was filtered off and washed with diethyl ether. Yield 0.04 g, 0.10 mmol, 45%. Anal. Found: C, 46.20; H, 6.20; N, 6.45. $C_{16}H_{24}N_2Cl_2Ru$ calc.: C, 46.15; H, 5.80; N, 6.75%.

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2${μ-o-$(NH_2)_2C_6H_4$}] (**6**). [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (0.08 g, 0.13 mmol) was stirred in CH_2Cl_2 (5 cm^3) with *o*-$(NH_2)_2C_6H_4$ (0.015 g, 0.14 mmol) for 2 h to give a bright orange solution. The solvent was removed *in vacuo* and the resulting orange oil triturated with diethyl ether to give a bright orange precipitate which was filtered off and dried *in vacuo*. Yield 0.08 g, 0.11 mmol, 85%. Anal. Found: C, 43.75; H, 5.90; N, 3.75. $C_{26}H_{40}N_2Cl_4Ru_2$ calc.: C, 43.10; H, 5.55; N, 3.85%.

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl{o-$(NH_2)_2C_6H_4$}]Cl (**7**). [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (0.07 g, 0.11 mmol) was stirred in oxygenated methanol (5 cm^3) with *o*-$(NH_2)_2C_6H_4$ (0.03 g, 0.24 mmol) for 2 h to give of a ruby red solution. The solvent was removed *in vacuo* and the residual deep red oil was triturated with diethyl ether. The red solid was filtered off and washed with diethyl ether. Yield 0.08 g, 0.10 mmol, 91%. Anal. Found: C, 45.70; H, 6.15; N, 6.50; Cl, 15.45. $C_{16}H_{24}N_2Cl_2Ru$ calc.: C, 46.15; H, 5.80; N, 6.75; Cl, 15.45%.

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl{o-$(NH_2)_2C_6H_4$}][PF_6] (**8**). [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (0.09 g, 0.15 mmol) was stirred in oxygenated methanol (5 cm^3) with *o*-$(NH_2)_2C_6H_4$ (0.036 g, 0.33 mmol). After 1 h a red colouration was observed and all the starting material had gone into solution. A methanolic solution of [NH_4][PF_6] (0.057 g, 0.35 mmol) was added and the mixture stirred for a further hour. The volume of the solvent was reduced to *ca.* 1 cm^3, resulting in the deposition of the product as an orange-red solid, which was filtered off and washed with diethyl ether. Yield 0.12 g, 0.23 mmol, 77%. Anal. Found: C, 36.55; H, 4.55; N, 5.45. $C_{16}H_{24}ClF_6PRu$ calc.: C, 36.55; H, 4.60; N, 5.35%.

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl(o-$NH_2C_6H_4$·$C_6H_4NH_2$)]Cl (**9**). [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (0.10 g, 0.16 mmol) was stirred in oxygenated methanol (5 cm^3) with 2,2′-diaminodiphenyl (0.06 g, 0.32 mmol) for 3 h. The resulting yellow solution was filtered and the solvent removed *in vacuo* to leave a bright yellow solid. This was filtered off and washed with diethyl ether. Yield 0.15 g, 0.30 mmol, 94%. Anal. Found: C, 52.40; H, 5.80; N, 5.60; Cl, 14.55. $C_{22}H_{28}N_2Cl_2Ru$ calc.: C, 53.65; H, 5.75; N, 5.70; Cl, 14.40%.

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl(o-$NH_2C_6H_4$·$C_6H_4NH_2$)][BF_4] (**10**). [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (0.09 g, 0.14 mmol) was stirred in acetone (5 cm^3) with Ag[BF_4] (0.06 g, 0.31 mmol) for 30 min. The resulting orange solution was filtered through Celite to remove the precipitate of AgCl, and 2,2′-diaminodiphenyl (0.05 g,0.27 mmol) was then added causing an immediate colour change to greenish-yellow. The mixture was stirred for a further 30 min and the solvent removed *in vacuo* to give a greenish oil. Trituration with diethyl ether gave the product as a yellow-brown precipitate. Yield 0.13 g, 0.24 mmol, 86%. Anal. Found: C, 47.55; H, 5.30; N, 4.85; Cl, 5.75. $C_{22}H_{28}N_2ClF_4Ru$ calc.: C, 48.60; H, 5.20; N, 5.15; Cl, 6.50%.

3. Results and discussion

Even in a highly polar solvent such as methanol, interaction of **1** with aniline does not result in deprotonation, the adduct [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(NH_2Ph)] (**2**) being formed instead as a bright yellow precipitate during *ca.* 1 h at room temperature. The complex exhibits a ^{1}H NMR spectrum characteristic of a simple equatorial adduct [18] (the two axial sites of the approximately trigonal bipyramidal ruthenium ion are equivalent and occupied by terminal chloride ligands) with only two singlet resonances for the terminal allyl protons (δ 4.15 and 3.76 ppm) and one methyl signal, δ 2.29 ppm (Table 1). Because of the chirality of the "Ru(η^3:η^3-$C_{10}H_{16}$)" fragment, the two NH protons of the prochiral NH_2R nitrogen atom are diastereotopic and consequently two broad N*H* resonances (δ 6.13 and 5.67 ppm, $^2J_{(H-H)}$ unresolved) are observed. The effect is analogous to that observed for the fluorophosphine compound [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(PF_2Me_2N)]

[24], in which two distinct ^{19}F NMR resonances are observed for the diastereotopic fluorine atoms attached to phosphorus. (At the time the inequivalence of the two fluorine atoms was thought to be due to a restricted rotation about the M–P bond [24]. The observation has since been re-interpreted by Cox and Roulet, however [18], and has been noted in related compounds [21].) Compound **2** also exhibits two $\nu(NH_2)$ bands in its infrared spectrum (3304 and 3230 cm^{-1}) and a characteristic $\delta(NH_2)$ mode at 1598 cm^{-1}.

The possibility of formation of cationic bis(aniline) compounds or deprotonation of the aniline to give amido/imido species was investigated by reaction of **1** with an excess of aniline in methanol over a period of 5 days. This resulted in the isolation of a yellow precipitate of **2** as before. The solution had, however, become a deep blue-black and removal of the solvent *in vacuo* gave a deep blue product soluble in common organic solvents, in which it gradually decomposed on exposure to atmospheric oxygen, giving a purple colouration. However, the ^1H NMR spectrum of this material, even over a very wide frequency range showed no signals other than those attributable to **2**, while analytical data were also consistent with the formulation **2**. It was concluded that the unusual colour of this material was caused by small amounts of a highly coloured, and possibly paramagnetic, second product, and that the bulk of the material was identical to that isolated after short reaction times.

The analogous reaction of **1** in methanol with 1,4-diaminobenzene (*p*-pda) also gave a yellow precipitate, analysing closely for the adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(p\text{-}NH_2C_6H_4NH_2)]$ (**3**). As with **2** the diastereotopic N*H* protons of the complexed amine donor appear as an AB pattern at δ 6.01 and 5.55 ($^2J(H\text{–}H) = 6.1$ Hz) ppm, whilst the protons of the uncomplexed amine function give rise to a broad singlet at δ 3.58 ppm. The infrared spectrum of **3** displays a total of four $\nu(NH_2)$ bands 3429, 3334, 3303 and 3236 cm^{-1}. The facile formation and isolation of **3** contrast markedly with that of the monodentate pyrazine adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(N_2C_4H_4)]$ [14,23,26], which is unstable with respect to disproportionation into the binuclear compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-}N_2C_4H_4)]$ and free pyrazine, and is only observed in the presence of a large excess of that ligand [14,23]. Interestingly, if a solution of **3** in chloroform is kept for *ca.* 10 min, disproportionation occurs, to give a mixture of **3**, free 1,4-diaminobenzene and a new compound displaying a further two terminal allyl resonances (δ 4.17 and 3.74 ppm). Two more signals in the methyl region are also observed (δ 2.30 and 2.29 ppm). No new signals for uncoordinated N*H* are observed but two broad coordinated N*H* resonances appear at δ 6.12 and 5.67 ppm (AB, $^2J(H\text{–}H) = 7.9$ Hz). The diaminobenzene aromatic protons appear as two singlets at very similar chemical shifts (δ 7.27 and 7.26 ppm). That these latter signals are singlets implies that both amine functionalities of the diamine ligand are complexed and are equivalent, and hence this new material is formulated as the 1,4-diaminobenzene bridged binuclear compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2\{\mu\text{-}p\text{-}(NH_2)_2C_6H_4\}]$ (**4**). The binuclear nature of the complex was confirmed by a FAB mass spectrum [*m/z* 724 (M^+ based on ^{102}Ru and ^{35}Cl, isotope distribution characteristic of two ruthenium and four chlorine atoms), 689 ($M^+ - Cl$)]. The slight splitting of the methyl and C_6H_4 resonances is explained by the fact that **4** exists as two diastereoisomers in the same way as does the parent compound **1**. Unlike **1**, in which the metal centres of the two chiral "$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})$" fragments are 3.98 Å [25] apart, the much larger bridging ligand in **4** probably results in a distance between the ruthenium ions in excess of 8 Å, and hence the magnetic environment of the protons of one "$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})$" fragment is very little affected by the handedness of the other bis(allyl)ruthenium moiety. Also, the ^1H NMR spectrum of **4** is slightly broad at room temperature, probably due to interconversion of the two diastereomeric forms *via* Ru–N bond fission and exchange of mononuclear "$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2$" units. Lowering the temperature in the NMR probe to -60°C resulted in a sharpening of the broad resonances but no further diastereomeric splittings were resolved.

Complex **4** was obtained free of **3** by reaction of **1** with one molar equivalent of *p*-pda in CH_2Cl_2. In this medium, both reactants and products are soluble and the reaction takes place almost instantaneously (colour change from pink to yellow-orange). The most likely mechanism for this reaction is bridge cleavage of **1** to generate the adduct **3**, which separates out of a methanol solution. In CH_2Cl_2, **3** remains in solution, where the pendant amine functionality reacts with a further molecule of **1** to give **4**.

The reaction of **1** with 1,2-diaminobenzene (*o*-pda) is rather more complicated. Addition of two equivalents of *o*-pda to **1** in methanol results in the formation of a bright orange solution during *ca.* 1 h. Work-up gives orange-red crystals analysing for a bridge-cleaved adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(o\text{-}NH_2C_6H_4NH_2)]$ (**5**) (analogous to **2** and **3**). This compound may also be obtained as one component of a mixture of products from the analogous reaction in CH_2Cl_2. The ^1H NMR spectrum of **5** is sharp at room temperature and closely resembles that of the 1,4-diaminobenzene adduct **3** (Table 1). Like **3**, compound **5** rapidly disproportionates in $CDCl_3$ solution, into free ligand and the binu-

clear compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2\{\mu\text{-}o\text{-}(NH_2)_2C_6H_4\}]$ (**6**), reaching an equilibrium at room temperature in which $K_{20} = [\mathbf{5}]/[\mathbf{6}] = ca.\ 1$. Addition of a small quantity of $H[BF_4]$ to an NMR sample containing **5** and **6** resulted in the immediate selective precipitation of **5** from the chloroform-*d* solvent, probably because of protonation of the uncomplexed amine function. Complex **6** was not precipitated and was found to be the sole ruthenium species present upon re-examination of the ^1H NMR spectrum. Complexation doubtless greatly reduces the basicity of the amine functions.

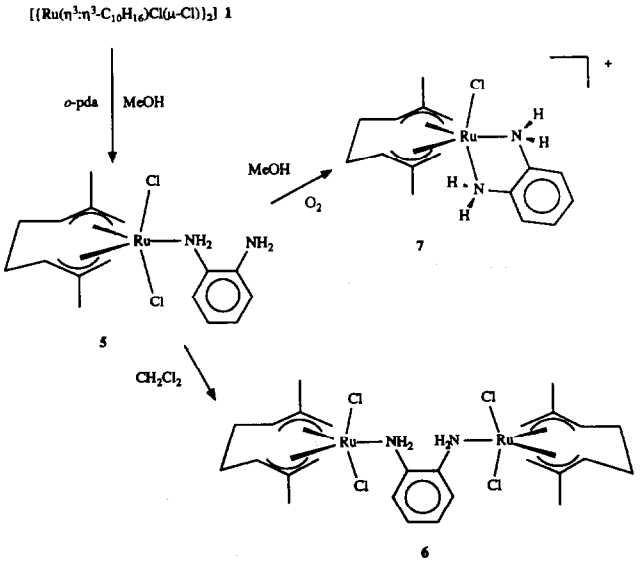
Compound **6** may be synthesised in pure form by reaction of **1** with one molar equivalent of *o*-pda in either MeOH or CH_2Cl_2 and is soluble in both solvents. The binuclear nature of **6** was confirmed by a FAB mass spectrum which showed a clear molecular ion peak *m/z* 724 with isotopic distribution characteristic of two ruthenium ions and four chloride ligands. Fragmentation peaks corresponding to sequential loss of all four chloride ligands were observed as well as a strong peak (*m/z* 381) corresponding to $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(o\text{-pda})]^+$. The ^1H NMR spectrum of **6** in acetone-d_6 solution at +50°C is consistent with the proposed formulation, and qualitatively resembles that of **4**. Like **4** and **1**, complex **6** exists as two diastereoisomers which may be distinguished by ^1H NMR spectroscopy. Integration of the ^1H NMR resonances for each isomer gives an equilibrium constant at this temperature, $K_{50} = 1.6$. The corresponding ratio for **1**, $K_{20} = [C_2]/[C_i]$ is 1.25 [18]. In the absence of an X-ray crystal structure determination, it is not possible to assign the resonances for **6** to one particular diastereoisomer, but there is clearly a significant preference for one form over the other.

At room temperature in either acetone-d_6 or $CDCl_3$ the resonances for one of the two diastereoisomers of **6** split further, apparently dividing into two sets of resonances of unequal intensities. At −80°C in acetone-d_6 solution, the spectrum contained a very complicated, although sharp, set of resonances. The precise nature of this dynamic behaviour, is unclear but examination of molecular models seems to indicate the possible existence of several rotational conformers, probably with significant barriers to their interconversion.

When compound **1** was stirred with two equivalents of *o*-pda in methanol, from which no attempt had been made to exclude atmospheric oxygen, a deep red colour was observed (*cf.* the bright orange solutions of **5** formed in the absence of O_2). The deep red product, which is isolated by addition of diethyl ether to this solution, analyses for a bridge-cleaved adduct of the same empirical formula as **5**. However, unlike **5**, the new material, **7**, is highly soluble in methanol and even water, but only sparingly so in chloroform and other less polar solvents, suggesting that one of the chloride ions is not associated with the metal centre. The ^1H NMR spectrum of this material displays peaks assignable to coordinated N*H* (δ 8.45, 6.93, 6.42 and 4.79 ppm). Four signals (δ 4.14, 3.88, 3.74 and 3.38 ppm) are observed for the terminal allyl protons of the bis(allyl) ligand. Each of the protons of the aromatic C_6H_4 moiety are also unique. These observations imply that **7** should be formulated as an ionic chelate $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(o\text{-}(NH_2)_2C_6H_4)]Cl$ in which the *o*-pda ligand occupies one equatorial and one axial coordination site. Consistent with the proposed formulation, the infrared spectrum of **7** exhibits two $\nu(NH_2)$ bands 3359 and 3157 cm^{-1} (complex **6** exhibits two bands at 3199 and 3102 cm^{-1}). The formulation of this product as an ionic material would account for the high solubility in polar solvents, and was confirmed by a measurement of its molar conductivity in methanol at 20°C, $\Lambda_0 = 160$ S cm^2 mol^{-1}.

At room temperature, the ^1H NMR spectrum of **7** is slightly broad. Lowering the temperature of the NMR probe resulted in significant broadening of all the resonances until, at −90°C (the lowest accessible temperature in CD_2Cl_2) the signals had apparently begun to resolve into two or more new sets of resonances. Interpretation of this spectrum was hampered by its extreme broadness, caused in part by extensive precipitation of the compound from solution. Owing to the poor solubility of the compound, lower temperature NMR experiments in Freon solvents were not attempted. It is possible that this apparent fluxionality results from hydrogen bonding interactions of the amine functionalities with the chloride counterion, and hence extensive ion-pairing, but the precise nature of the process remains unknown.

It is interesting to note that complex **7** was only formed in solutions which had not been deaerated. Use of methanol which had been deoxygenated resulted in the formation of orange solutions from which **5** and **6** could be isolated. Such solutions did not become red even when kept under N_2 for several days, but gradually decomposed to give a deep purple colouration. Reaction of metal *o*-pda complexes with O_2 frequently results in dehydrogenation/deprotonation of the ligand to give diiminobenzene derivatives which are often highly coloured [2,11]. In the case of **7**, however, all four NH protons are clearly evident in the ^1H NMR spectrum of the complex, and similarly two $\nu(NH)$ bands are observed in the infrared spectrum. Such an oxidation process may, however, occur during the course of the reaction, and may be instrumental in removing one of the axial chloride ligands (by enhancing the nucleophilicity of the uncomplexed amine func-



Scheme 1. Formation of the amine compounds $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(1,2\text{-}NH_2C_6H_4NH_2)]$ (**5**), $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\}_2\{\mu\text{-}(NH_2)_2C_6H_4\}]$ (**6**) and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(1,2\text{-}\{(NH_2)_2C_6H_4\})]Cl$ (**7**).

tionality in adducts such as **5**) to enable chelation to take place. The ligand may then be re-protonated to give **7**.

Addition of $[NH_4][PF_6]$ to the reaction mixture formed in the synthesis of **7**, and subsequent stirring for several hours, gave the hexafluorophosphate salt $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(o\text{-pda})][PF_6]$ (**8**) [$\Lambda_0(NO_2Me, 20°C) = 106$ S cm^2 mol^{-1}] as a red-orange precipitate on concentration the solution. The ^{1}H NMR spectrum of **8** (Table 1) was sharp at room temperature and exhibited a much smaller range of chemical shifts for the N*H* protons, consistent with the proposal that these protons are no longer involved in strong hydrogen bonding to the counter ion. In the infrared spectrum, **8** displayed a strong, broad band at 1168 cm^{-1}, confirming the presence of the hexafluorophosphate anion, as well as four bands assignable to ν(NH) 3319, 3288, 3265 (m,sharp) and 3125 (w,br) cm^{-1}, and a strong band at 1576 cm^{-1} assigned to $\delta(NH_2)$. A strong band assigned to ν(RuCl) was observed at 271 cm^{-1}. The reactions of **1** with *o*-pda are summarised in Scheme 1.

Attempted syntheses of amido compounds by reaction of **1** with *o*-pda in the presence of $Na_2[CO_3]$ resulted in the formation of an extremely air sensitive deep purple solution from which a brown-black solid was isolated. The ^{1}H NMR spectrum of this material indicated that the bis(allyl) ligand was no longer present, but no further attempts at characterisation were made because of the instability of the compound. The possibility of oxidation to amido/imido species was also investigated by examination of the cyclic voltammetry of **7**. Over a variety of scan speeds (200–600 mV s^{-1}) only irreversible waves were observed at *ca.* +1.57, −0.72 and −1.00 V (*vs.* Ag/AgCl). It seems likely that the electron transfer reactions are followed by rapid chemical decomposition of the complex, and irreversible loss of the bis(allyl) ligand. The cyclic voltammogram of the bridged complex **6** was also examined. Like **7**, it also displayed only irreversible waves although the observation of a pair of oxidations (+1.60 and +1.76 V) may well be associated with the diamine ligand.

The reaction of **1** with 2,2′-diaminodiphenyl ($o\text{-}NH_2C_6H_4 \cdot C_6H_4NH_2$) was also investigated. Analogously to the preparation of **7**, use of methanol as the solvent (in the presence or absence of air) resulted in the formation of an ionic compound $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(o\text{-}NH_2C_6H_4 \cdot C_6H_4NH_2)]Cl$ (**9**). The FAB mass spectrum of this material displayed a strong peak at *m/z* 475 corresponding to the expected molecular cation and, as expected for an ionic compound, **9** is soluble in methanol and water [$\Lambda_0(NO_2Me, 20°C) = 69.3$ S cm^2 mol^{-1}]. The ^{1}H NMR spectrum of **9** displays two doublet resonances assignable to one set of coordinated N*H* protons [δ 6.10 and 5.47 (^2J(H–H) = 9.0 Hz) ppm] and a broad singlet resonance [δ 3.61 (2H) ppm] for the second set. Four terminal allyl and two methyl resonances are observed (Table 1), as expected for a chelate complex with inequivalent axial sites However, one methyl and two terminal allyl signals are significantly broadened at room temperature, suggesting a fluxional process which is to some degree localised on one side of the complex cation. Lowering the temperature in the NMR probe results initially in a general broadening of the spectrum, but at −60°C a pattern of sharp resonances similar to the room temperature spectrum is again observed, the only noteworthy difference being the splitting of the broad N*H* resonance at δ 3.61 into two broad singlets at δ 3.69 and 3.52 ppm (probably an unresolved AB pattern). This fluxionality is consistent with that suggested for **7**, and may well take the form of exchange between two or more modes of hydrogen bonding interaction between the amino protons and the chloride counterion.

Strong evidence, both for the formulation of **9** and the nature of the fluxionality involved, comes from the synthesis of the tetrafluoroborate salt of the compound $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(o\text{-}NH_2C_6H_4 \cdot C_6H_4NH_2)][BF_4]$ (**10**) [$\Lambda_0(NO_2Me, 20°C) = 110$ S cm^2 mol^{-1}] by reaction of an acetone solution of **1** pre-treated with two molar equivalents of $Ag[BF_4]$, with 2,2′-diaminodiphenyl. The ^{1}H NMR spectrum of **10** bears a strong resemblance to that of **9** except that the coordinated

N*H* protons appear as four sharp, doublet resonances [δ 6.08 ($^2J = 9.3$) Hz), 5.57 ($^2J = 9.3$), 5.09 ($^2J = 8.3$) and 3.81 ($^2J = 8.3$) ppm] and the remainder of the spectrum is sharp at room temperature. This is consistent with the suggestion that the chloride counterion is involved in the fluxionality of **9**.

The formation of **9** and **10** is surprising in that both complexes possess seven-membered heterocyclic chelate rings which might be expected to exhibit a high degree of steric strain. Examination of molecular models shows unambiguously that the two aromatic rings in these complexes cannot both coordinate to the metal centre through their amino functionalities and retain a mutually co-planar arrangement as is generally observed in related complexes of 2,2′-bipyridyl. An unstrained seven-membered heterocyclic ring may be obtained, however, if the two rings are oriented at *ca.* 90° to one another, an arrangement achieved *via* rotation about the interannular carbon–carbon bond. This distortion is an extreme example of the geometry observed in the crystal structure of the analogous bipyridyl compound [$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(bipy)][BF_4]$, in which the small size of the Ru^{IV} centre results in the two pyridyl rings being inclined at an angle of 8.2° to one another [23].

Acknowledgement

We thank Johnson Matthey plc. for generous loans of ruthenium trichloride and the SERC for a studentship (to J.W.S.).

References

1 Z.-Y. Li, W.-Y. Yu, C.-M. Che, C.-K. Poon, R.-J. Wang and T.C.W. Mak, *J. Chem. Soc., Dalton Trans.*, (1992) 1657.
2 A.A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *Polyhedron*, *11* (1992) 2961.
3 F.L. Joslin, M.P. Johnson, J.T. Mague and D.M. Roundhill, *Organometallics*, *10* (1991) 2781.
4 U. Furholz, H.-B. Burgi, F.E. Wagner, A. Stebler, J.H. Ammeter, E. Krausz, R.J.H. Clark, M.J. Stead and A. Ludi, *J. Am. Chem. Soc.*, *106* (1984) 121.
5 A. Anillo, R. Obeso-Rosete, M.A. Pellinghelli and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, (1991) 2019.
6 C. Redshaw, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1992) 555.
7 A. Anillo, C. Barrio, S. Garcia-Granda and R. Obeso-Rosete, *J. Chem. Soc., Dalton Trans.*, (1993) 1125.
8 A. Anillo, J.A. Cabeza, R. Obeso-Rosete and V. Riera, *J. Organomet. Chem.*, *393* (1990) 423.
9 S. Garcia-Granda, R. Obeso-Rosete, J.M. Rubio and A. Anillo, *Acta Crystallogr., Sect. C*, *26* (1990) 2043.
10 C. Redshaw, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1992) 1803.
11 L.F. Warren, *Inorg. Chem.*, *16* (1977) 2814.
12 A.L. Balch and R.H. Holm, *J. Am. Chem. Soc.*, *88* (1966) 5201.
13 M.A. Bennett and A.K. Smith, *J. Chem. Soc., Dalton Trans.*, (1974) 233.
14 J.G. Toerien and P.H. van Rooyen, *J. Chem. Soc., Dalton Trans.*, (1991) 2693.
15 J.G. Toerien and P.H. van Rooyen, *J. Chem. Soc., Dalton Trans.*, (1991) 1563.
16 S.O. Sommerer and G.J. Palenik, *Organometallics*, *10* (1991) 1223.
17 D.N. Cox, R.W.H. Small and R. Roulet, *J. Chem. Soc., Dalton Trans.*, (1991) 2013.
18 D.N. Cox and R. Roulet, *Inorg. Chem.*, *29* (1990) 1360.
19 J.W. Steed and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1992) 459.
20 J.W. Steed and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1992) 2765.
21 B. Kavanagh, J.W. Steed and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1993) 327.
22 J.W. Steed and D.A. Tocher, *Polyhedron*, *11* (1992) 1849.
23 J.W. Steed and D.A. Tocher, *Polyhedron*, *11* (1992) 2729.
24 R.A. Head, J.F. Nixon, R. Swain and C.M. Woodard, *J. Organomet. Chem.*, *76* (1974) 393.
25 A. Colombo and G. Allegra, *Acta Crystallogr., Sect. B*, *27* (1971) 1658.
26 J.W. Steed and D.A. Tocher, *J. Organomet. Chem.*, *412* (1991) C34.