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Inorganica Chimica Acta 358 (2005) 3218–3226
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Ruthenium hydride and vinyl complexes supported by nitrogen–oxygen mixed-donor ligands

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Received 16 February 2005; accepted 26 April 2005

Dedicated to Prof. Dr. Hubert Schmidbaur in recognition of his vast contribution to so many areas of inorganic chemistry

Abstract

The Schiff base, 2-chlorophenylsalicylaldimine (HL_1), is formed readily from salicylaldehyde and 2-chloroaniline. After deprotonation, this ligand is found to react as a bidentate mixed-donor chelate with the complexes $[RuRCl(CO)(BTD)(PPh_3)_2]$ (R = H, CH=CHC_6H_5, CH=CHC_6H_4Me-4, CH=CH^{t}Bu, CC≡CPh=CHPh; BTD = 2,1,3-benzothiadiazole) to form the compounds $[RuR(L_1)(CO)(PPh_3)_2]$ through displacement of the chloride and BTD ligands. An analogous reaction occurs with the osmium complex $[OsHCl(CO)(BTD)(PPh_3)_2]$ to provide $[OsH(L_1)(CO)(PPh_3)_2]$. The compound $[Ru(CH{=}CHC_6H_4Me\text{-}4)(L_2)(CO)(PPh_3)_2]$ is formed through reaction of salicylaldehyde (HL_2) with $[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ in the presence of base. Two further ligands were investigated to extend the study to encompass 5- and 4-membered chelates; 8-hydroxyquinoline (HL_3) and 2-hydroxy-4-methylquinoline (HL_4) react with $[Ru(CH{=}CHPh)Cl(CO)(BTD)(PPh_3)_2]$ and $[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ in the presence of base to yield the complexes $[Ru(CH{=}CHPh)(L_3)(CO)(PPh_3)_2]$ and $[Ru(CH{=}CHC_6H_4Me\text{-}4)(L_4)(CO)(PPh_3)_2]$, respectively. The crystal structure of $[Ru(CH{=}CHC_6H_4Me\text{-}4)(L_1)(CO)(PPh_3)_2]$ is reported.

Keywords: Ruthenium; Schiff base; Hydride; Vinyl; Mixed-donor

1. Introduction

The vinyl ligand is an important member of the sigma-organyl ligand family and has attracted significant interest over the last 40 years. Vinyl complexes are known for many metals but examples of this ligand are most commonly found with metals of group 8. This is largely due to well-established synthetic routes such as hydrometallation and the reaction of coordinated alkynes with electrophiles or nucleophiles [1].

Since the discovery of hydrometallation of alkynes by the complexes $[RuHCl(CO)L_{2/3}]$ (L = P^{i}Pr$_3$, [2] PPh_3 [3]), the resulting vinyl complexes [4,5] have been the subject of much pioneering work by the groups of Werner and co-workers [6–11], Esteruelas and co-workers [12–24], Santos and co-workers [25–30], and Caulton, Eisenstein and co-workers [31–33] covering functional group transformation, ligand exchange and theoretical calculations. The hydride complexes themselves are known for their ability to catalyse hydrogenation reactions [34] and the formation of di-ynes [35,36]. A recent indication of the continuing importance of these starting materials is given by a recent report of their use in silylation catalysis [37].

Previous work from members of our own group has concentrated on vinyl complexes supported by bidentate and tridentate nitrogen and sulfur donor ligands and the reactions of these complexes [38]. This complemented

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doi:10.1016/j.ica.2005.04.036

work by other groups exploring the effect of polydentate donors on the structure and reactivity of vinyl complexes. The majority of this research has concentrated on the use of symmetrical, bidentate phosphorus [39,40], nitrogen [41,42] or chalcogen donors [43]. The work reported here is part of a programme [44,45] to synthesise vinyl complexes bearing mixed-donor bidentate ligands and to investigate their effect on migratory insertion reactions and hemilabile behaviour in these complexes.

Schiff bases have been used for many years to coordinate metal ions [46,47]. Interest has been rekindled recently with reports of their use in catalysts for olefin polymerisation [48]. Ruthenium Schiff base complexes have been known for 30 years [49] and have more recently found use in catalysis [49c,50] and biological applications [51]. Perhaps surprisingly, given the catalytic interest, no ruthenium Schiff base complexes bearing vinyl ligands have been reported. Here, we describe the use of a Schiff base ligand and two other N/O-donor ligands to prepare group 8 hydride and vinyl complexes with 4, 5 and 6-membered mixed-donor chelates.

2. Experimental

2.1. Methods and instrumentation

All manipulations were carried out under aerobic conditions using commercially available solvents and reagents as received. Infrared spectroscopy was carried out using a Shimadzu FTIR 8700 spectrometer with KBr plates and nujol. NMR spectra were obtained at 25 °C (unless stated otherwise) using Bruker AMX-300 (^{1}H: 299.87 MHz, ^{31}P: 121.39 MHz, ^{13}C: 75.40 MHz) or Bruker DRX-500 (^{1}H: 500.13 MHz, ^{13}C: 125.77 MHz) spectrometers. Spectroscopic features due to the triphenylphosphine ligands have been omitted to aid clarity. The term s(br) is used to denote a broadened singlet resonance. FAB-MS spectra (nitrobenzyl alcohol matrices) were measured using a VG 70-SB magnetic sector mass spectrometer. Elemental microanalyses were performed at University College London. The amount of solvent of crystallisation was determined by integration of ^{1}H NMR spectra. The complexes [RuHCl(CO)(PPh_3)$_3$] [3], [RuHCl(CO)(BTD)(PPh_3)$_2$] [52], [Ru(CH=CHC$_6$H$_4$CH$_3$-4)Cl(CO)(BTD)(PPh_3)$_2$] [53], [Ru(CH=CH^{t}Bu)Cl(CO)(BTD)(PPh_3)$_2$] [53], [Ru{C(C≡CPh)=CHPh}Cl(CO)(BTD)(PPh_3)$_2$] [54], and [OsHCl(CO)(BTD)(PPh_3)$_2$] [38e] were prepared according to published procedures. See Chart 1 for the numbering scheme used for the Schiff base ligand (HL_1).

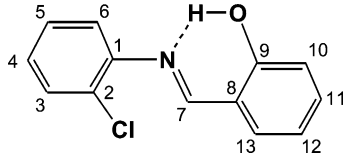


Chart 1. 2-chlorophenylsalicylaldimine (HL_1) with numbering scheme.

2.2. Syntheses

2.2.1. Preparation of 2-chlorophenylsalicylaldimine (HL_1)

Salicylaldehyde (1.00 g, 8.19 mmol) and 2-chloroaniline (1.05 g, 8.23 mmol) were placed in a Schlenk flask and degassed ethanol (50 mL) added. The reaction was stirred and heated for 30 min until a bright yellow solution had developed. The solvent volume was reduced causing precipitation of an intense yellow product. This was filtered and washed with cold ethanol (5 × 3 mL). Yield: 1.64 g (86%). IR (KBr/nujol): 1620, 1566, 1273, 1188, 1145, 1057, 1030, 980, 945, 910 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500.1 MHz): 6.92 [td, H^{12}(L_1), 1H, J(H^{12}H$^{11/13}$) = 7.5 Hz, J(H^{12}H^{10}) = 1.2 Hz], 7.03 [dd, H^{10}(L_1), 1H, J(H^{10}H^{11}) = 8.7 Hz, J(H^{10}H^{12}) = 1.2 Hz], 7.18 [ddd, H^4(L_1), 1H, J(H^{4}H^3) = 8.0 Hz, J(H^{4}H^5) = 7.3 Hz, J(H^{4}H^6) = 1.6 Hz], 7.20 [dd, H^6(L_1), 1H, J(H^{6}H^5) = 8.0 Hz, J(H^{6}H^4) = 1.6 Hz], 7.29 [ddd, H^5(L_1), 1H, J(H^{5}H^6) = 8.0 Hz, J(H^{5}H^4) = 7.3 Hz, J(H^{5}H^3) = 1.4 Hz], 7.37 [dd, H^{13}(L_1), 1H, J(H^{13}H^{12}) = 7.7 Hz, J(H^{13}H^{11}) = 1.7 Hz], 7.38 [td, H^{11}(L_1), 1H, J(H^{11}H$^{10/12}$) = 7.5 Hz, J(H^{11}H^{13}) = 1.7 Hz] 7.45 [dd, H^3(L_1), 1H, J(H^{3}H^4) = 7.9 Hz, J(H^{3}H^5) = 1.3 Hz], 8.56 [s, H^7(L_1), 1H], 13.24 [s, OH, 1H] ppm. ^{13}C NMR ($CDCl_3$, 500.1 MHz): 117.3 (C^{10}), 118.9 (C^8), 119.0 (C^6 + C^{12}), 127.6 (C^4), 127.7 (C^5), 129.4 (C^2), 130.0 (C^3), 132.4 (C^{13}), 133.5 (C^{11}), 145.1 (C^1), 161.2 (C^9), 163.1 (C^7) ppm. FAB-MS *m/z* (abundance) = 231 (100) [M]$^+$, 196 (50) [M − Cl]$^+$. *Anal.* Calc. for $C_{13}H_{10}ClNO$: C, 67.4; H, 4.4; N, 6.1. Found: C, 67.3; H, 4.4; N, 5.9%.

2.2.2. Preparation of [RuH(L_1)(CO)(PPh_3)$_2$] (1)

[RuHCl(CO)(BTD)(PPh_3)$_2$] (100 mg, 0.121 mmol) and 2-chlorophenylsalicylaldimine (HL_1) (30 mg, 0.129 mmol) were suspended in dichloromethane (20 mL) and treated with sodium methoxide (13 mg, 0.241 mmol) in ethanol (10 mL). A colour change was observed from dark orange to yellow. The reaction was stirred for 1 h and the solvent volume reduced to ca. 10 mL. The flask was kept at −20 °C for 4 h and the resulting yellow precipitate filtered, washed with cold ethanol (5 mL) and hexane (10 mL). Yield: 57 mg (53%). IR (KBr/nujol): 1975 [ν(RuH)], 1906 [ν(CO)], 1604, 1195, 1142, 972 cm^{-1}. ^{31}P NMR (C_6D_6): 58.5 [s(br), PPh_3] ppm. ^{1}H NMR (C_6D_6): −10.77 [td, RuH, 1H, J_{HP} = 21.4 Hz, J_{HH7} = 2.9 Hz], 6.15 [t, (H^{12})L_1, 1H, J_{HH} = 7.3 Hz], 6.30 [d, (H^{10})L_1, 1H, J_{HH} = 8.4 Hz], 6.44 [dd, (H^6)L_1, 1H, J_{HH} = 7.9 Hz, J_{HH} = 1.8 Hz], 6.58

[dt, ($H^{4/5}$)L_1, 1H, J_{HH} = 7.8 Hz, J_{HH} = 1.5 Hz], 6.83 [m, (H^{11} + H^{13})L_1, 1H + 1H], 6.9 [dd, (H^3)L_1, 1H, J_{HH} = 8.00 Hz, J_{HH} = 1.4 Hz], 6.96–7.80 [m, C_6H_5 + ($H^{4/5}$)L_1, 30H + 1H], 7.54 [d, H^7(L_1), 1H, J_{H7H} = 2.9 Hz] ppm. FAB-MS *m/z* (abundance) = 884 (0.3) $[M]^+$, 653 (0.7) $[M - L_1]^+$. *Anal.* Calc. for $C_{50}H_{40}ClNO_2P_2Ru$: C, 67.8; H, 4.6; N, 1.6. Found: C, 67.7; H, 4.7; N, 1.3%.

2.2.3. Preparation of [OsH(L_1)(CO)(PPh_3)$_2$] (2)

[OsHCl(CO)(BTD)(PPh_3)$_2$] (50 mg, 0.055 mmol) and HL_1 (14 mg, 0.060 mmol) were suspended in dichloromethane (20 mL) and treated with sodium methoxide (6 mg, 0.111 mmol) in ethanol (10 mL). The colour of the solution lightened during stirring for 30 min. The solvent was reduced until precipitation of an orange product had started. The flask was kept at −20 °C for 4 h and the resulting precipitate filtered, washed with cold ethanol (5 mL) and hexane (10 mL). Yield: 37 mg (69%). IR (KBr/nujol): 2073 [*ν*(OsH)], 1888 [*ν*(CO)], 1607, 1580, 1531, 1360, 1185, 1146, 928 cm^{-1}. ^{31}P NMR (C_6D_6, 25°C): 18.0, 27.3 [AB, PPh_3, J_{AB} = 320 Hz] ppm. ^{31}P NMR (C_6D_6, 60 °C): 21.8 [s(br), PPh_3] ppm. ^1H NMR ($CDCl_3$): −11.68 [td, OsH, 1H, J_{HP} = 19.5 Hz, J_{HH7} = 2.4 Hz], 6.14 [t, (H^{12})L_1, 1H, J_{HH} = 7.1 Hz], 6.21 [d, (H^{10})L_1, 1H, J_{HH} = 8.6 Hz], 6.46 [dd, (H^6)L_1, 1H, J_{HH} = 7.8 Hz, J_{HH} = 1.7 Hz], 6.56 [td, ($H^{4/5}$)L_1, 1H, J_{HH} = 7.6 Hz, J_{HH} = 1.3 Hz], 6.79 [dd, (H^3)L_1, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.3 Hz], 6.86 [m, (H^{11})L_1 + ($H^{4/5}$)L_1, 1H + 1H], 6.95–7.82 [m, C_6H_5, 30H], 7.30 [dd, (H^{13})L_1, 1H, J_{HH} = 8.1 Hz, J_{HH} = 1.4 Hz], 7.57 [d, H^7(L_1), 1H, J_{H7H} = 2.4 Hz] ppm. FAB-MS *m/z* (abundance) = 975 (18) $[M]^+$, 743 (4) $[M - L_1]^+$, 713 (15) $[M - PPh_3]^+$, 685 (5) $[M - COPPh_3]^+$. *Anal.* Calc. for $C_{50}H_{40}ClNO_2OsP_2 \cdot 0.75CH_2Cl_2$: C, 58.7; H, 4.0; N, 1.4. Found: C, 58.9; H, 3.9; N, 1.4%.

2.2.4. Preparation of [Ru(CH=CHPh)(L_1)(CO)(PPh_3)$_2$] (3)

[Ru(CH=CHPh)Cl(CO)(PPh_3)$_2$] (100 mg, 0.126 mmol) and HL_1 (32 mg, 0.138 mmol) were suspended in dichloromethane (20 mL) and treated with sodium methoxide (13 mg, 0.241 mmol) in ethanol (10 mL). A colour change was observed from deep red to orange. The mixture was stirred for 1 h to yield an orange solution. The solvent was reduced until precipitation of the yellow product was complete. This was washed with water (5 mL), cold ethanol (5 mL) and hexane (10 mL). Yield: 71 mg (57%). IR (KBr/nujol): 1909 [*ν*(CO)], 1609, 1578, 1549, 1530, 1332, 1188, 1180, 1148, 925, 840, 810 cm^{-1}. ^{31}P NMR ($CDCl_3$): 29.8 [s(br), PPh_3] ppm. ^1H NMR ($CDCl_3$): 5.79 [d, Hβ, 1H, J_{HH} = 16.9 Hz], 6.09 [t, (H^{12})L_1, 1H, J_{HH} = 6.9 Hz], 6.38 [dd, (H^6)L_1, 1H, J_{HH} = 7.87 Hz, J_{HH} = 1.7 Hz], 6.44 [d, (H^{10})L_1, 1H, J_{HH} = 8.6 Hz], 6.50 [d, *ortho*-C_6H_5, 2H, J_{AB} = 7.3 Hz], 6.82 [t, *para*-C_6H_5, 1H, J_{HH} = 7.2 Hz], 6.97 [t, *meta*-C_6H_5, 2H, J_{HH} = 7.5 Hz], 7.00–7.45 [m, PC_6H_5 + ($H^{3,4,5,7,11,13}$)L_1, 30H + 6H], 8.25 [dt, Hα, 1H, J_{HH} = 16.9 Hz, J_{HP} = 3.1 Hz] ppm. FAB-MS *m/z* (abundance) = 988 (5) $[M]^+$, 884 (6) $[M - vinyl]^+$, 725 (40) $[M - PPh_3]^+$, 697 (6) $[M - CO - PPh_3]^+$, 623 (15) $[M - vinyl - PPh_3]^+$, 594 (20) $[M - CO - vinyl - PPh_3]^+$. *Anal.* Calc. for $C_{58}H_{46}ClNO_2P_2Ru$: C, 66.1; H, 4.5; N, 1.3. Found: C, 65.5; H, 4.4; N, 1.6%.

2.2.5. Preparation of [Ru(CH=CHC_6H_4Me-4)(L_1)(CO)(PPh_3)$_2$] (4)

[Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)$_2$] (100 mg, 0.106 mmol) and HL_1 (27 mg, 0.117 mmol) were suspended in dichloromethane (20 mL) and treated with sodium methoxide (11 mg, 0.204 mmol) in ethanol (10 mL). The mixture was stirred for 1 h and then all solvent was removed. The residue was taken up in a minimum quantity of dichloromethane and filtered through diatomaceous earth. The solvent was reduced to ca. 5 mL and diethyl ether (40 mL) added gradually to precipitate the orange product. This was washed with diethyl ether (10 mL) and hexane (10 mL). Yield: 68 mg (64%). IR (KBr/nujol): 1911 [*ν*(CO)], 1607, 1578, 1530, 1324, 1174, 1147, 972, 924, 828 cm^{-1}. ^{31}P NMR ($CDCl_3$): 31.0 [s(br), PPh_3] ppm. ^1H NMR ($CDCl_3$): 2.21 [s, CH_3, 3H], 5.74 [d, Hβ, 1H, J_{HH} = 16.8 Hz], 6.10 [t, (H^{12})L_1, 1H, J_{HH} = 7.1 Hz], 6.38 [m, (H^6)L_1 + (H^{10})L_1, 1H + 1H], 6.40, 6.95 [AB, C_6H_4, 4H, J_{AB} = 7.5 Hz], 6.65 [t, (H^4)L_1, 1H, J_{HH} = 7.2 Hz], 6.79 [d, (H^3)L_1, 1H, J_{HH} = 7.8 Hz], 6.89 [m, (H^{11})L_1, 1H], 7.05–7.42 [m, C_6H_5 + ($H^{5,7,13}$)L_1, 30H + 3H], 8.13 [dt, Hα, 1H, J_{HH} = 16.8 Hz, J_{HH} = 3.3 Hz] ppm. FAB-MS *m/z* (abundance) = 1001 (0.1) $[M]^+$, 855 (2) $[M - vinyl]^+$, 739 (15) $[M - PPh_3]^+$, 594 (5) $[M - CO - vinyl - PPh_3]^+$. *Anal.* Calc. for $C_{59}H_{48}ClNO_2P_2Ru \cdot 2CH_2Cl_2$: C, 62.5; H, 4.4; N, 1.2. Found: C, 62.5; H, 4.2; N, 1.1%.

2.2.6. Preparation of [Ru(CH=CH^{t}Bu)(L_1)(CO)(PPh_3)$_2$] (5)

[Ru(CH=CH^{t}Bu)Cl(CO)(BTD)(PPh_3)$_2$] (100 mg, 0.110 mmol) and HL_1 (28 mg, 0.121 mmol) were suspended in dichloromethane (20 mL) and treated with sodium methoxide (12 mg, 0.222 mmol) in ethanol (10 mL). The mixture was stirred for 1 h and then all solvent was removed. The residue was taken up in a minimum quantity of dichloromethane and filtered through diatomaceous earth. The solvent was reduced to ca. 5 mL and diethyl ether (40 mL) added gradually to precipitate the brown product. This was washed with diethyl ether (10 mL) and hexane (10 mL). Yield: 68 mg (64%). IR (KBr/nujol): 1902 [*ν*(CO)], 1607, 1574, 1335, 1254, 1173, 1146, 976, 924, 854 cm^{-1}. ^{31}P NMR ($CDCl_3$): 26.6 [s(br), PPh_3] ppm. ^1H NMR ($CDCl_3$): 0.37 [s, CH_3, 9H], 4.96 [dt, Hβ, 1H, J_{HH} = 16.8 Hz, J_{HH} = 2.0 Hz], 6.10 [td, (H^{12})L_1, 1H, J_{HH} = 7.3 Hz,

J_{HH} = 1.0 Hz], 6.54 [m, $(H^6)L_1 + (H^{10})L_1$, 1H + 1H], 6.77 [dd, $(H^3)L_1$, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.5 Hz], 6.85–7.05 [m, $C_6H_5 + (H^{4,5,7,11,13})L_1 + H\alpha$, 30H + 5H + 1H], 8.13 [dt, Hα, 1H, J_{HH} = 16.8 Hz, J_{HH} = 3.3 Hz] ppm. FAB-MS *m/z* (abundance) = 737 (1) $[M - L_1]^+$, 705 (33) $[M - PPh_3]^+$, 677 (10) $[M - CO - PPh_3]^+$, 653 (3) $[M - vinyl - L_1]^+$, 625 (7) $[M - vinyl - CO - L_1]^+$, 594 (10) $[M - vinyl - CO - PPh_3]^+$. *Anal*. Calc. for $C_{56}H_{50}ClNO_2P_2Ru \cdot 0.5CH_2Cl_2$: C, 67.2; H, 5.1; N, 1.4. Found: C, 67.0; H, 5.0; N, 1.1%.

2.2.7. Preparation of [Ru{C(C≡CPh)=CHPh}(L1)(CO)(PPh3)2] (6)

[Ru{C(C≡CPh)=CHPh}Cl(CO)(BTD)$(PPh_3)_2$] (100 mg, 0.097 mmol) and HL_1 (25 mg, 0.108 mmol) were suspended in dichloromethane (20 mL) and treated with sodium methoxide (11 mg, 0.204 mmol) in ethanol (10 mL). This gave rise to a colour change from an orange solution to yellow. The mixture was stirred for 30 min to yield a yellow solution. All solvent was removed and the residue taken up in a minimum volume of dichloromethane. This solution was filtered through diatomaceous earth and again all solvent was removed. Diethylether (20 mL) was added and the flask triturated in an ultrasound bath to yield a yellow product which was filtered and washed with diethylether (10 mL) and hexane (10 mL). Yield: 68 mg (65%). IR (KBr/nujol): 2154 [ν(C≡C)], 1921 [ν(CO)], 1614, 1593, 1313, 1185, 1146, 975, 845 cm^{-1}. ^{31}P NMR ($CDCl_3$): 31.7 [s(br), PPh_3] ppm. ^1H NMR ($CDCl_3$): 5.96 [t, $(H^{12})L_1$, 1H, J_{HH} = 7.1 Hz], 6.23 [dd, $(H^6)L$, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.74 Hz], 6.4 [t, $(H^{10})L_1$, 1H, J_{HH} = 8.7 Hz], 6.68 [s(br), Hβ, 1H], 6.95–7.55 [m, $PC_6H_5 + C_6H_5 + (H^{3,4,5,7,11,13})L_1$, 30H + 5H + 6H] ppm. FAB-MS *m/z* (abundance) = 1087 (0.1) $[M]^+$, 856 (0.7) $[M - L_1]^+$. *Anal*. Calc. for $C_{66}H_{50}ClNO_2P_2Ru \cdot 1.25CH_2Cl_2$: C, 67.7; H, 4.4; N, 1.2. Found: C, 67.4; H, 4.6; N, 0.9%.

2.2.8. Preparation of [Ru(CH=CHC6H4Me-4)(L2)(CO)(PPh3)2] (7)

[Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)$(PPh_3)_2$] (100 mg, 0.106 mmol) and salicylaldehyde (HL_2) (14 mg, 0.115 mmol) were dissolved in dichloromethane (20 mL) and treated with sodium methoxide (11 mg, 0.204 mmol) in ethanol (10 mL). A colour change was observed from deep red to yellow. The mixture was stirred for 1 h and the solvent volume reduced until precipitation of the product had started. The flask was kept at −20 °C for 3 h and the resulting bright yellow precipitate filtered, washed with water (5 mL), cold ethanol (5 mL) and hexane (10 mL). Yield: 63 mg (67%). IR (KBr/nujol): 1913 [ν(CO)], 1615, 1575, 1341, 1316, 1278, 1179, 1145, 966, 903, 833 cm^{-1}. ^{31}P NMR ($CDCl_3$): 30.9 [s, PPh_3] ppm. ^1H NMR ($CDCl_3$): 2.17 [s, CH_3, 3 H], 5.97 [m, $H\beta + H^{2/6}(L_2)$, 1H + 1H], 6.30 [t, $H^{4/5}(L_2)$, 1H, J_{HH} = 8.3 Hz], 6.52, 6.85 [AB, C_6H_4, 4H, J_{AB} = 8.0 Hz], 6.91 [m, $H^{4/5}(L_2)$, 1H], 7.19–7.49 [m, $C_6H_5 + H^{2/6}(L_2)$, 30H + 1H], 8.10 [dt, Hα, 1H, J_{HH} = 16.2 Hz, J_{HP} = 2.8 Hz], 8.12 [s, CHO, 1H] ppm. FAB-MS *m/z* (abundance) = 891 (12) $[M]^+$, 774 (4) $[M - vinyl]^+$, 629 (37) $[M - PPh_3]^+$, 601 (5) $[M - CO - PPh_3]^+$. *Anal*. Calc. for $C_{66}H_{50}ClNO_2P_2Ru \cdot 1.25CH_2Cl_2$: C, 67.7; H, 4.4; N, 1.2. Found: C, 67.4; H, 4.6; N, 0.9%.

2.2.9. Preparation of [Ru(CH=CHPh)(L3)(CO)(PPh3)2] (8)

[Ru(CH=CHPh)Cl(CO)(BTD)$(PPh_3)_2$] (100 mg, 0.108 mmol) and 8-hydroxyquinoline (HL_3) (17 mg, 0.117 mmol) were dissolved in dichloromethane (20 mL) and treated with sodium methoxide (11 mg, 0.204 mmol) in ethanol (10 mL). A colour change was observed from deep red to yellow. The mixture was stirred for 1 h and then all solvent removed under reduced pressure. The residue was taken up in a minimum volume of dichloromethane and filtered through diatomaceous earth to remove NaCl and excess NaOMe. The solvent volume was reduced to ca. 5 mL and diethyl ether (10 mL) was added and the flask cooled at −20 °C for 3 h. The resulting yellow precipitate was filtered, washed with cold diethylether (5 mL) and hexane (10 mL). Yield: 65 mg (67%). IR (KBr/nujol): 1908 [ν(CO)], 1568, 1323, 1261 cm^{-1}. ^{31}P NMR (C_6D_6): 30.8 [s, PPh_3] ppm. ^1H NMR (C_6D_6): 6.17 [dd, L_3, 1H, J_{HH} = 8.3 Hz, J_{HH} = 4.7 Hz], 6.32 [dd, L_3, 1H, J_{HH} = 7.1 Hz, J_{HH} = 1.91 Hz], 6.75 [dt, Hβ, 1H, J_{HH} = 16.8 Hz, J_{HP} = 2.1 Hz], 6.89, 7.14, 7.66 [m × 3, $C_6H_5 + L_3$, 30H + 3H], 7.88 [d, L_3, 1H, J_{HH} unresolved], 8.94 [dt, Hα, 1H, J_{HH} = 16.8 Hz, J_{HP} = 3.4 Hz] ppm. FAB-MS *m/z* (abundance) = 915 (5) $[M]^+$, 798 (3) $[M - vinyl]^+$, 653 (12) $[M - PPh_3]^+$, 625 (4) $[M - CO - PPh_3]^+$, 508 (4) $[M - L_3 - PPh_3]^+$. *Anal*. Calc. for $C_{55}H_{45}NO_2P_2Ru$: C, 72.2; H, 5.0; N, 1.5. Found: C, 71.8; H, 5.0; N, 1.6%.

2.2.10. Preparation of [Ru(CH=CHC6H4Me-4)(L4)(CO)(PPh3)2] (9)

[Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)$(PPh_3)_2$] (100 mg, 0.106 mmol) and 2-hydroxy-4-methylquinoline (HL_4) (18 mg, 0.113 mmol) were dissolved in dichloromethane (20 mL) and ethanol (10 mL). Potassium hydroxide (12 mg, 0.214 mmol) was added and the mixture was stirred for 30 min. The solvent volume was reduced until precipitation of a colourless microcrystalline product was complete. This was washed with water (5 mL), ethanol (5 mL) and hexane (10 mL). Yield: 75 mg (76%). IR (KBr/nujol): 1908, 1894 [ν(CO)], 1634, 1549, 1312, 1263, 1198, 972, 849 cm^{-1}. ^{31}P NMR (C_6D_6): 36.3 [s, PPh_3] ppm. ^1H NMR (C_6D_6): 1.88 [s, $CH_3(L_4)$, 3H], 2.09 [s, CH_3(vinyl), 3H], 4.48 [d, L_4, 1H, J_{HH} unresolved], 5.65 [s, $H^3(L_4)$, 1H], 6.41 [d, Hβ, 1H,

J_{HH} = 16.2 Hz], 6.58, 6.80 [AB, C_6H_4, 4H, J_{AB} = 7.7 Hz], 6.91, 7.55 [m × 2, C_6H_5, 30 H], 7.22 [m, L_4, 3H], 8.18 [dt, Hα, 1H, J_{HH} = 16.2 Hz, J_{HP} = 2.5 Hz] ppm. FAB-MS *m/z* (abundance) = 929 (4) $[M]^+$, 812 (3) $[M - vinyl]^+$, 667 (6) $[M - PPh_3]^+$, 639 (3) $[M - CO - PPh_3]^+$. *Anal.* Calc. for $C_{56}H_{47}NO_2P_2Ru \cdot 1.25CH_2Cl_2$: C, 66.4; H, 4.8; N, 1.4. Found: C, 66.8; H, 4.9; N, 1.3%.

2.3. X-ray crystallography

Crystals of complex **3** were grown by slow diffusion of a dichloromethane solution of the complex into ethanol. A single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 ± 2 K. Data reduction and integration was carried out with SAINT+ and absorption corrections applied using the programme SADABS. The structure was solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). Structure solution and refinement used the SHELXTL PLUS V6.10 program package [55]. See Table 1 for selected crystal data.

Table 1
Crystal data for compound **3**

3 · $2CH_2Cl_2$	
Chemical formula	$C_{59}H_{48}Cl_3NO_2P_2Ru$
Formula weight	1072.34
Crystal system	triclinic
Crystal colour	yellow
Crystal size (mm)	0.44 × 0.38 × 0.12
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.7683(8)
b (Å)	13.2497(9)
c (Å)	17.5273(12)
α (°)	82.1570(10)
β (°)	77.6070(10)
γ (°)	71.3950(10)
V (Å^3)	2523.0(3)
Z	2
Calculated density (g/cm^3)	1.412
T (K)	150(2)
μ(Mo Kα) (mm^{-1})	0.578
$F_{(000)}$	1100
Reflections collected	22473
Unique reflections (R_{int})	11633 (0.0183)
R_1 ($I > 2\sigma(I)$)	0.0343
wR'_2 (all data)	0.0887
Residual e Å^{-3} (max, min)	1.057, −0.827

3. Results and discussion

3.1. Preparation and characterisation of L_1

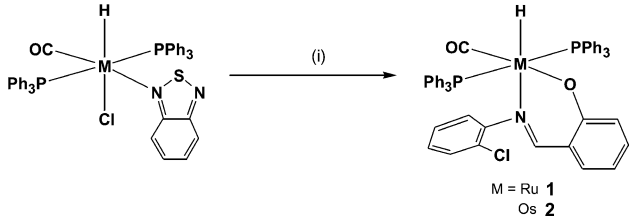
The Schiff base ligand, 2-chlorophenylsalicylaldimine (L_1), shown in Chart 1, was readily prepared from the reaction of 2-choroaniline and salicylaldehyde in ethanol in high yield.

The ligand was characterised by one- and two-dimensional ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. All protons and carbon nuclei were assigned using heteronuclear multiple quantum correlation (HMQC), heteronuclear multiple bond correlation (HMBC) and nuclear overhauser enhancement (NOE) experiments. The imine proton resonates in the characteristic region for such features at 8.56 ppm while the hydroxy proton appears as a singlet at 13.24 ppm. The chemical shift and independence of concentration of this resonance indicates that intermolecular hydrogen bonding does not occur in solution. Instead, an intramolecular 6-membered interaction is more likely, as has been reported in recent structural [56] and spectroscopic [57] studies of Schiff bases.

3.2. Preparation of hydride complexes of L_1

An alternative to the coordinatively unsaturated starting complexes $[RuRCl(CO)(PPh_3)_3]$ (R = hydride, vinyl) is provided by the use of the 2,1,3-benzoselenadiazole (BSD) complexes $[RuRCl(CO)(BSD)(PPh_3)_2]$ [52,53] These avoid contamination by free triphenylphosphine and generate microcrystalline starting complexes of excellent purity which can be easily (re)crystallised from dichloromethane–ethanol mixtures. BSD is no longer commercially available, however, we have found that the sulfur analogue, 2,1,3-benzothiadiazole (BTD), can be used without compromising the advantages mentioned above. Dropwise addition of an ethanolic solution of sodium methoxide to a dichloromethane solution of HL_1 and the dark green hydride complex $[RuHCl(CO)(BTD)(PPh_3)_3]$ in dichloromethane led to a gradual colour change to yellow. After stirring for 1 h, ethanol was added and the solvent volume reduced to provide a yellow product (Scheme 1).

A clean reaction to give a single product containing *trans* phosphines was indicated by a new broad singlet



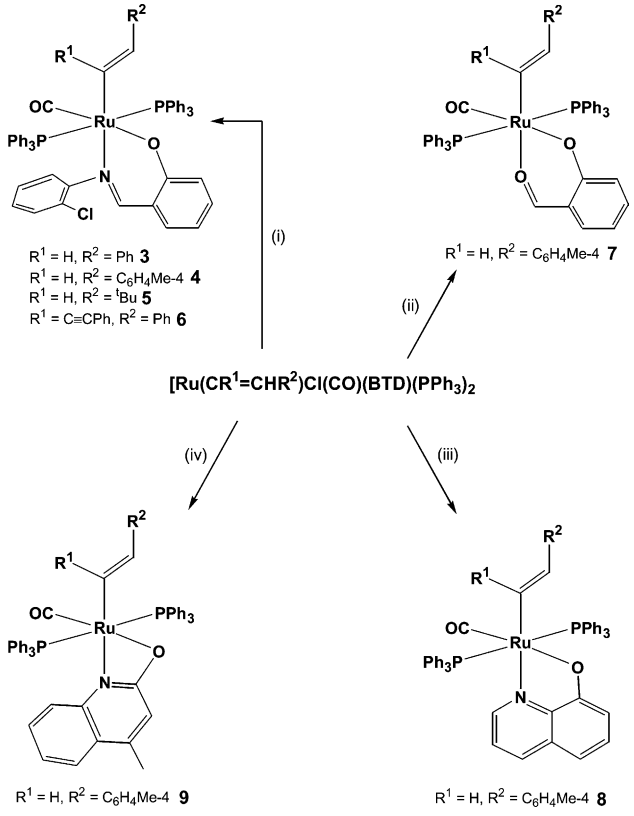
Scheme 1. (i) $C_{13}H_{10}ClNO$ (HL_1), NaOMe.

resonance in the ^{31}P NMR spectrum at 58.5 ppm. Infrared spectroscopic analysis showed an intense ν(CO) absorption at 1906 cm^{-1} due to the carbonyl ligand and a band of weaker intensity which was attributed to the hydride ligand at 1975 cm^{-1}. Confirmation of the retention of the hydride ligand was provided by the ^1H NMR spectrum of the complex which displayed a high field hydride triplet resonance at δ −10.77 ppm showing coupling to the two phosphorus nuclei of 21.4 Hz. The fine structure of this triplet of doublets revealed a 2.90 Hz coupling through the ruthenium centre to the imine proton (H^7) of the Schiff base ligand (see Chart 1). This coupling was also observed for the H^7 resonance at 7.54 ppm. The eight other resonances associated with the ligand were observed at chemical shift values shifted downfield with respect to the corresponding features in the free ligand. The fast atom bombardment mass spectrum provided clear evidence for the overall composition with a molecular ion at m/z = 884 and fragmentation due to $[M - L_1]^+$ at m/z = 653. Along with elemental analysis data, this confirmed that the chloride and BTD ligands had been replaced by L_1 to yield $[RuH(L_1)(CO)(PPh_3)_2]$ (**1**). In the initial stages of this work, the complex $[RuH(L)(CO)(PPh_3)_2]$, formed from phenylsalicylaldimine (HL) was reported [58]. However, no spectroscopic data were given. The osmium analogue [59] of the versatile ruthenium complex $[RuHCl(CO)(PPh_3)_3]$ [3] is far less reactive. This stems from the reluctance of the complex to lose a phosphine ligand in solution, in contrast to the ruthenium species. This drawback is circumvented by the use of the osmium compound $[OsHCl(CO)(BTD)(PPh_3)_2]$, which provides a convenient entrypoint into osmium(II) hydride and vinyl chemistry [38e, 45] Thus, treatment of $[OsHCl(CO)(BTD)(PPh_3)_2]$ with HL_1 and sodium methoxide resulted in an orange compound which was formulated as the osmium analogue of complex **1**. The ^{31}P NMR spectrum of the product $[OsH(L_1)(CO)(PPh_3)_2]$ (**2**) revealed an AB system at 18.0 and 27.3 with a coupling between the phosphorus nuclei of 320 Hz. This suggested that the Schiff base ligand must render the phosphines inequivalent. This can be explained by hindrance to the rotation of the 2-chlorophenyl substituent of L_1. Heating the sample (in C_6D_6) to 60 °C resulted in a singlet resonance being obtained at 21.8 ppm. The ^{31}P NMR spectra of all the complexes discussed here bearing the L_1 ligand displayed broadened singlet resonances at 25 °C indicating that the coalescence temperature for the osmium complex (**2**) is significantly higher than for the ruthenium species.

3.3. Preparation of vinyl complexes of L_1

Hydrometallation of phenylacetylene by $[RuHCl(CO)(BTD)(PPh_3)_2]$ yields the vinyl complex $[Ru(CH{=}CHPh)Cl(CO)(BTD)(PPh_3)_2]$ [53]. This compound reacts readily with HL_1 under the same conditions as described above to give the complex $[Ru(CH{=}CHPh)(L_1)(CO)(PPh_3)_2]$ (**3**), as shown in Scheme 2. The vinyl ligand was identified by the characteristic resonances for the α- and β-protons at 8.25 and 5.79 ppm, respectively. In addition to $^3J_{HH}$ coupling (16.9 Hz), Hα showed coupling to the mutually *trans* phosphorus nuclei (3.1 Hz) to appear as a doublet of triplets. In contrast to the spectra for the hydride complexes **1** and **2**, the spectroscopic features associated with the L_1 ligand are largely obscured by those of the vinyl and phosphine substituents. Slow diffusion of ethanol into a dichloromethane solution of complex **3** yielded single crystals suitable for an X-ray study. The structure is shown in Fig. 1.

This reveals the Schiff base ligand to coordinate in a bidentate fashion with the 6-membered chelate coplanar with the carbon ligand and C2 and C3 of the vinyl ligand. The 2-chlorophenyl substituent of L_1, however, is twisted by approximately 45° out of this plane. This orientation is likely to be the cause of the inequivalence of the phosphorus nuclei which is manifested as an AB system in the ^{31}P NMR spectrum. The overall structure is essentially octahedral around Ru1. The *cis*-interligand angles are in the range 84.35(6)–101.21(7)° with the O2–Ru1–N1 bite angle of the bidentate chelate measuring



Scheme 2. (i) $C_{13}H_{10}ClNO$ (HL_1), NaOMe; (ii) $C_7H_6O_2$ (HL_2), NaOMe; (iii) C_9H_7NO (HL_3), NaOMe; (iv) $C_{10}H_9NO$ (HL_4), NaOMe.

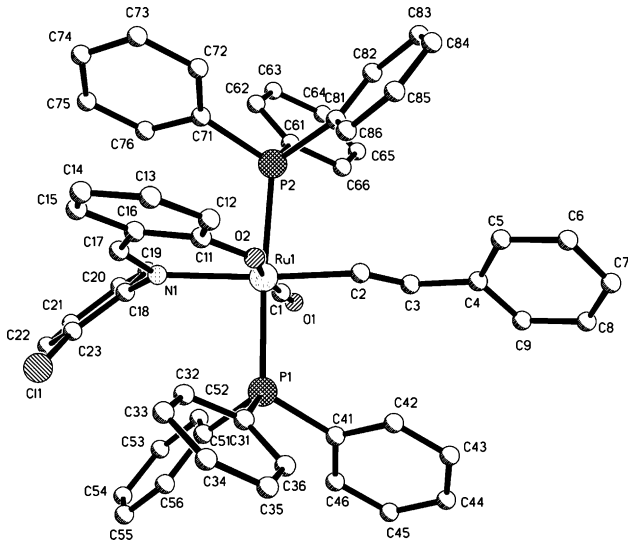


Fig. 1. Structure of [Ru(CH=CHPh)(L_1)(CO)(PPh_3)$_2$] (**3**). Selected bond lengths (Å) and angles (°): Ru1–C1 = 1.8134(18), Ru1–C2 = 2.0380(18), Ru1–O2 = 2.0998(13), Ru1–N1 = 2.2217(15), Ru1–P1 = 2.4078(5), Ru1–P2 = 2.4198(5), N1–C17 = 1.304(2), O2–C11 = 1.303 (2), C2–C3 = 1.338(3), C11–C16 = 1.423(3), C16–C17 = 1.432(3), C1–Ru1–C2 = 88.37(7), C2–Ru1–O2 = 84.35(6), C1–Ru1–N1 = 101.21(7), O2–Ru1–N1 = 86.08(5), C1–Ru1–P1 = 89.31(6), C2–Ru1–P1 = 91.05 (5), O2–Ru1–P1 = 90.20(4), N1–Ru1–P1 = 91.00(4), C1–Ru1–P2 = 93.00(6), C2–Ru1–P2 = 84.42(5), O2–Ru1–P2 = 86.92(4), N1–Ru1–P2 = 93.07(4), P1–Ru1–P2 = 174.847(16), C3–C2–Ru1 = 134.89(14).

86.08(5)°, which is the second smallest angle in the 6-membered ring after that for C2–Ru1–O2 [84.35(6)°]. No significant deviation from the plane formed by Ru1–N1–C17–C16–C11–O2 is observed. The C17–N1 distance of 1.304(2) Å is comparable to that of 1.295 Å found in the literature complex [Ru(κ^2-*p*-OC_6H_4-CH=NC_6H_4OMe-4)Cl(η^6-*p*-cymene)] reported by Beck and co-workers [60]. Both the Ru1–O2 bond length of 2.0998(13) Å and the Ru1–N1 distance of 2.2217(15) Å in **3** are significantly longer than the corresponding features in the *para*-cymene complex of 2.045(2) and 2.133(3) Å, respectively. The bite angle of the chelate in the literature complex is significantly smaller [79.00(10)°]. The difference in Ru1–O2 and Ru–N1 distances reflects the differing *trans* influence of the CO and vinyl ligands in **3** compared to *para*-cymene in the literature complex. The Ru1–C2 [2.0380(18) Å] and C2–C3 [1.338(3) Å] distances are similar to those reported for the styrenyl ligand in the formate complex [Ru(CH=CHPh)(κ^2-O_2CH)(CO)L_2] of 2.036(8) and 1.35(1) Å, respectively [43a]. The other structural features associated with the vinyl ligand are unremarkable.

The complex [Ru(CH=CHC_6H_4Me-4)(L_1)(CO)-(PPh_3)$_2$] (**4**) was prepared in an analogous fashion to **3** but in slightly improved yield. The spectroscopic data for this complex were found to be similar to those for **3** apart from those associated with the tolyl substituent, which gave rise to an AB system at 6.40 and 6.95 ppm (J_{AB} = 7.5 Hz) and a singlet resonance at 2.21 ppm. Hydrometallation of 3,3-dimethylbut-1-yne with [RuHCl(CO)(BTD)(PPh_3)$_2$] provided the complex [Ru(CH=CH^{t}Bu)Cl(CO)(BTD)(PPh_3)$_2$] in good yield. Subsequent addition (without isolation, if desired) of HL_1 and NaOMe in dichloromethane and ethanol affords [Ru(CH=CH^{t}Bu)(L_1)(CO)(PPh_3)$_2$] (**5**). A large singlet resonance at 0.37 ppm was assigned to the tertiarybutyl substituent of the vinyl ligand, while $^3J_{HH}$ (16.8 Hz) and $^4J_{HP}$ (2.0 Hz) couplings lead to an unusually well-defined doublet of triplets for the vinylic β-proton. A significantly larger coupling of 3.3 Hz was observed between the phosphorus nuclei and the α-proton at 8.13 ppm indicating their closer mutual proximity. A disubstituted analogue [Ru{C(C≡CPh)=CHPh}(L_1)(CO)(PPh_3)$_2$] (**6**) was also prepared from the enynyl complex [Ru{C(C≡CPh)-=CHPh}Cl(CO)(BTD) (PPh_3)$_2$] in good yield.

3.4. Preparation of vinyl complexes of L_2–L_4

The precursor to the Schiff base ligand HL_1 is salicylaldehyde (HL_2) which can be deprotonated to act as an asymmetrical 3-electron O/O-donor. This ligand was found to react cleanly with [Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)- (PPh_3)$_2$] by displacement of chloride and BTD ligands to provide [Ru(CH=CHC_6H_4Me-4)(L_2)(CO)(PPh_3)$_2$] (**7**) as shown in Scheme 2. The most distinctive spectral feature of the 6-membered metallacycle formed by coordination of L_2 was the CHO proton resonance at 8.12 ppm, which overlapped with the doublet of triplets for Hα at 8.10 ppm (J_{HH} = 16.2 Hz, J_{HP} = 2.8 Hz).

In order to extend these investigations to smaller chelate sizes, 8-hydroxyquinoline (HL_3) was employed as a mixed-donor N/O-ligand. Deprotonation of HL_3 in the presence of [Ru(CH=CHC_6H_4Me-4)Cl(BTD)(CO)-(PPh_3)$_2$] led to the isolation of a microcrystalline complex which gave rise to new spectroscopic features in the ^{1}H NMR spectrum at 6.17, 6.32 and 7.88 ppm in addition to the resonances for the vinyl ligand, which were essentially unchanged from the precursor. These were assigned as resulting from three of the six protons of the coordinated L_3 ligand, with the remainder obscured by the resonances arising from the triphenylphosphine ligands. Elemental analysis and fast atom bombardment (FAB) mass spectrometry led to the complex being formulated as [Ru(CH=CHC_6H_4Me-4)(L_3)(CO)(PPh_3)$_2$] (**8**) with the L_3 ligand forming a 5-membered chelate with the ruthenium centre. In a similar fashion, 2-hydroxy-4-methylquinoline (HL_4) was allowed to react with the same precursor to yield [Ru(CH=CHC_6H_4Me-4)(L_4)(CO)(PPh_3)$_2$] (**9**). The presence of the mixed-donor ligand was indicated by four new resonances, of which, that corresponding to the methyl substituent at 1.88 ppm was most diagnostic.

The overall composition of complex **9** was provided by elemental analysis and mass spectrometry. The singlets obtained in the ^{31}P NMR spectra for products **7**–**9** were sharp and betrayed no fluxional behaviour, suggesting that the ligands L_1–L_3 adopt the expected planar geometry.

4. Conclusions

A Schiff base ligand has been prepared and fully characterised by two-dimensional NMR techniques. Along with three other ligands, the Schiff base was used to prepare a new family of hydride and vinyl complexes bearing 4-, 5- and 6-membered mixed-donor chelates, all of which are bonded through oxygen and nitrogen donors. The structure of the first example of a ruthenium vinyl complex supported by a Schiff base ligand is reported and used to explain the fluxional behaviour observed in the ^{31}P NMR spectra obtained. The potential for hemilability in these complexes will now be investigated in our laboratory.

5. Supplementary material

Crystallographic data for the structure of complex **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 260974. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: int. code +44 1223 336 033, e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

Acknowledgements

J.D.E.T.W.-E. gratefully acknowledges the Ramsay Memorial Trust for provision of a Fellowship. We thank the Department of Chemistry and the University of London Central Research Fund for funding for consumables and Johnson Matthey Ltd. for a generous loan of ruthenium salts. We thank Dr. A. Aliev for discussions of NMR data.

References

[1] For an overview of hydride and vinyl chemistry of ruthenium(II), see A.F. Hill, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 7, Pergamon, Oxford, 1995.
[2] M.A. Esteruelas, H. Werner, J. Organomet. Chem. 303 (1986) 221.
[3] K.R. Laing, W.R. Roper, J. Chem. Soc. A (1970) 2149.
[4] H. Werner, M.A. Esteruelas, H. Otto, Organometallics 5 (1986) 2295.
[5] M.R. Torres, A. Vegas, A. Santos, J. Ros, J. Organomet. Chem. 309 (1986) 169.
[6] S. Jung, K. Ilg, C.D. Brandt, J. Wolf, H. Werner, Eur. J. Inorg. Chem. (2004) 469.
[7] S. Jung, C.D. Brandt, J. Wolf, H. Werner, J. Chem. Soc., Dalton Trans. (2004) 375.
[8] H. Werner, S. Jung, P. González-Herrero, K. Ilg, J. Wolf, Eur. J. Inorg. Chem. (2001) 1957.
[9] S. Jung, K. Ilg, J. Wolf, H. Werner, Organometallics 20 (2001) 2121.
[10] H. Werner, W. Stüer, S. Jung, B. Weberndörfer, J. Wolf, Eur. J. Inorg. Chem. (2002) 1076.
[11] H. Werner, A. Stark, P. Steinert, C. Grunwald, J. Wolf, Chem. Ber. 128 (1995) 49.
[12] R. Castarlenas, M.A. Esteruelas, E. Oñate, Organometallics 20 (2001) 2294.
[13] M.A. Esteruelas, C. García-Yebra, M. Oliván, E. Oñate, M. Tajada, Organometallics 19 (2000) 5098.
[14] R. Castarlenas, M.A. Esteruelas, E. Oñate, Organometallics 19 (2000) 5454.
[15] M.L. Buil, M.A. Esteruelas, C. García- Yebra, E. Gutiérrez-Puebla, M. Oliván, Organometallics 19 (2000) 2184.
[16] C. Bohanna, M.L. Buil, M.A. Esteruelas, E. Oñate, C. Valero, Organometallics 18 (1999) 5176.
[17] C. Bohanna, B. Callejas, A.J. Edwards, M.A. Esteruelas, F.J. Lahoz, L.A. Oro, N. Ruiz, C. Valero, Organometallics 17 (1998) 373.
[18] M.A. Esteruelas, A.V. Gómez, A.M. López, E. Oñate, Organometallics 17 (1998) 3567.
[19] M.A. Esteruelas, F. Liu, E. Oñate, E. Sola, B. Zeier, Organometallics 16 (1997) 2919.
[20] M.L. Buil, S. Elipe, M.A. Esteruelas, E. Oñate, E. Peinado, N. Ruiz, Organometallics 16 (1997) 5748.
[21] M.A. Esteruelas, F.J. Lahoz, E. Oñate, L.A. Oro, E. Sola, J. Am. Chem. Soc. 118 (1996) 89.
[22] C. Bohanna, M.A. Esteruelas, J. Herrero, A.M. López, L.A. Oro, J. Organomet. Chem. 498 (1995) 199.
[23] C. Bohanna, M.A. Esteruelas, F.J. Lahoz, E. Oñate, L.A. Oro, E. Sola, Organometallics 14 (1995) 4825.
[24] C. Bohanna, M.A. Esteruelas, F.J. Lahoz, E. Oñate, L.A. Oro, Organometallics 14 (1995) 4685.
[25] B. Gómez-Lor, A. Santos, M. Ruiz, A.M. Echavarren, Eur. J. Inorg. Chem. (2001) 2305.
[26] A.M. Castaño, A.M. Echavarren, J. López, A. Santos, J. Organomet. Chem. 379 (1989) 171.
[27] J. Montoya, A. Santos, A.M. Echavarren, J. Ros, J. Organomet. Chem. 390 (1990) C57.
[28] H. Loumrhari, J. Ros, M.R. Torres, A. Santos, A.M. Echavarren, J. Organomet. Chem. 411 (1991) 255.
[29] J. Montoya, A. Santos, J. López, A.M. Echavarren, J. Ros, A. Romero, J. Organomet. Chem. 426 (1992) 383.
[30] J. López, A. Romero, A. Santos, A. Vegas, A.M. Echavarren, P. Noheda, J. Organomet. Chem. 373 (1989) 249.
[31] A. Pedersen, M. Tilset, K. Folting, K.G. Caulton, Organometallics 14 (1995) 875.
[32] A.V. Marchenko, H. Gérard, O. Eisenstein, K.G. Caulton, New. J. Chem. 25 (2001) 1244.
[33] A.V. Marchenko, H. Gérard, O. Eisenstein, K.G. Caulton, New. J. Chem. 25 (2001) 1382.
[34] R.A. Sanchez-Delgado, A. Andriollo, O.L. De Ochoa, T. Suarez, N. Valencia, J. Organomet. Chem. 209 (1981) 77.
[35] A.M. Echavarren, J. López, A. Santos, J. Montoya, J. Organomet. Chem. 414 (1991) 393.
[36] R.B. Bedford, A.F. Hill, A.R. Thompsett, A.J.P. White, D.J. Williams, Chem. Commun. (1996) 1059.
[37] H. Katayma, M. Nagao, R. Moriguchi, F. Ozawa, J. Organomet. Chem. 676 (2003) 49.

[38] (a) A.F. Hill, A.J.P. White, D.J. Williams, J.D.E.T. Wilton-Ely, Organometallics 17 (1998) 4249;
(b) J.C. Cannadine, A.F. Hill, A.J.P. White, D.J. Williams, J.-D.E.T. Wilton-Ely, Organometallics 15 (1996) 5409;
(c) A.F. Hill, A.J.P. White, D.J. Williams, J.D.E.T. Wilton-Ely, unpublished results;
(d) A.F. Hill, C.T. Ho, J.D.E.T. Wilton-Ely, Chem. Commun. (1997) 2207;
(e) A.F. Hill, J.D.E.T. Wilton-Ely, J. Chem. Soc., Dalton Trans. (1998) 3501.
[39] A. Santos, J. López, A. Galán, J.J. González, P. Tinoco, M.A. Echavarren, Organometallics 16 (1997) 3482.
[40] A. Santos, J. López, J. Montoya, P. Noheda, A. Romero, A.M. Echavarren, Organometallics 13 (1994) 3605.
[41] A. Romero, A. Vegas, A. Santos, M. Martinez-Ripoll, J. Organomet. Chem. 319 (1987) 103.
[42] J. López, A. Santos, A. Romero, A.M. Echavarren, J. Organomet. Chem. 443 (1993) 221.
[43] (a) H. Loumrhari, L. Matas, J. Ros, M.R. Torres, A. Perales, J. Organomet. Chem. 403 (1991) 373;
(b) M.R. Torres, A. Perales, H. Loumrhari, J. Ros, J. Organomet. Chem. 384 (1990) C61;
(c) H. Loumrhari, J. Ros, R. Yáñez, M.R. Torres, J. Organomet. Chem. 408 (1991) 233;
(d) M.R. Torres, A. Perales, H. Loumrhari, J. Ros, J. Organomet. Chem. 385 (1990) 379;
(e) H. Loumrhari, J. Ros, M.R. Torres, Polyhedron 10 (1991) 421;
(f) A.L. Hector, A.F. Hill, J. Organomet. Chem. 447 (1993) C7;
(g) R.B. Bedford, C.S.J. Cazin, J. Organomet. Chem. 598 (2000) 20;
(h) H. Adams, P.E. McHugh, M.J. Morris, S.E. Spey, P.J. Wright, J. Organomet. Chem. 619 (2001) 209.
[44] P.J. Pogorzelec, D.H. Reid, D.A. Tocher, J.D.E.T. Wilton-Ely, Z. Naturforsch. 59b (2004) 1.
[45] J.D.E.T. Wilton-Ely, S.J. Honarkhah, M. Wang, D.A. Tocher, A.M.Z. Slawin, J. Chem. Soc., Dalton Trans. (2005) 1930.
[46] R. Hernández-Molina, A. Mederos, in: J. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol. 1, Elsevier, 2004.
[47] M. Calligaris, L. Randaccio, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 2, Pergamon, 1987.
[48] M. Brookhart, L.K. Johnson, S.D. Ittel, Chem. Rev. 100 (2000) 1169.
[49] (a) F. Calderazzo, C. Floriani, R. Henzi, F. L'Eplattenier, J. Chem. Soc. A (1969) 1378;
(b) K.S. Finney, G.W. Everett, Inorg. Chim. Acta 11 (1974) 183;
(c) G. Henrici-Olive, S. Olive, J. Mol. Cat. 1 (1976) 121;
(d) J.R. Thornback, G. Wilkinson, J. Chem. Soc., Dalton Trans. (1978) 110.
[50] (a) C.-M. Che, J.-S. Huang, Coord. Chem. Rev. 242 (2003) 97;
(b) J.A. Miller, W. Jin, S.T. Nguyen, Angew. Chem., Int. Ed. Engl. 41 (2002) 2953;
(c) B. De Clercq, F. Verpoort, Macromolecules 35 (2002) 8943;
(d) R. Schumacher, F. Dammast, H.-U. Reißig, Chem. Eur. J. 3 (1997) 614.
[51] M.J. Clarke, Coord. Chem. Rev. 232 (2002) 69.
[52] The complexes were prepared by substituting BTD for BSD in the experimental procedure reported in N.W. Alcock, A.F. Hill, M.S. Roe, J. Chem. Soc., Dalton Trans. (1990) 1737.
[53] Complexes obtained by substitution of BTD for BSD in the experimental procedure reported in M.C.J. Harris, A.F. Hill, Organometallics 10 (1991) 3903.
[54] A.F. Hill, M.C.J. Harris, R.P. Melling, Polyhedron 11 (1992) 781.
[55] SHELTXTL V 6.10 Bruker AXS 2000.
[56] S. Thamotharan, V. Parthasarathi, S.M. Anitha, A. Prasad, T.R. Rao, A. Linden, Acta Crystallogr., Sect. E 59 (2003) 1856.
[57] W. Schilf, B. Kamienski, A. Szady-Chelmieniecka, E. Grech, J. Mol. Struct. 700 (2004) 105.
[58] H. Sasabe, S. Nakanishi, T. Takata, Inorg. Chem. Commun. 6 (2003) 1140.
[59] L. Vaska, J. Am. Chem. Soc. 86 (1964) 1943.
[60] O. Briel, A. Fehn, K. Polborn, W. Beck, Polyhedron 18 (1998) 225.