Dalton
www.rsc.org/dalton

σ-Organyl complexes of ruthenium and osmium supported by a mixed-donor ligand

James D. E. T. Wilton-Ely,*[a] Sanaz J. Honarkhah,[a] Ming Wang,[a] Derek A. Tocher[a] and Alexandra M. Z. Slawin[b]

[a] *Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ. E-mail: j.wilton-ely@ucl.ac.uk*

[b] *School of Chemistry, University of St. Andrews, St. Andrews, Fife, UK KY16 9ST*

Received 7th February 2005, Accepted 14th April 2005
First published as an Advance Article on the web 29th April 2005

A series of vinyl, aryl, acetylide and silyl complexes [Ru(R)(κ²-MI)(CO)(PPh_3)$_2$] (R = CH=CH_2, CH=CHPh, CH=$CHC_6H_4CH_3$-4, CH=CH^{t}Bu, CH=$CHCPh_2OH$, C(C≡CPh)=CHPh, C_6H_5, C≡CPh, $SiMe_2OEt$; MI = 1-methylimidazole-2-thiolate) were prepared from either [Ru(R)Cl(CO)(PPh_3)$_2$] or [Ru(R)Cl(CO)(BTD)(PPh_3)$_2$] (BTD = 2,1,3-benzothiadiazole) by reaction with the nitrogen–sulfur mixed-donor ligand, 1-methyl-2-mercaptoimidazole (HMI), in the presence of base. In the same manner, [Os(CH=CHPh)(κ²-MI)(CO)(PPh_3)$_2$] was prepared from [Os(CH=CHPh)(CO)Cl(BTD)(PPh_3)$_2$]. The *in situ* hydroruthenation of 1-ethynylcyclohexan-1-ol by [RuH(CO)Cl(BTD)(PPh_3)$_2$] and subsequent addition of the HMI ligand and excess sodium methoxide yielded the dehydrated 1,3-dienyl complex [Ru(CH=CHC_6H_9)(κ²-MI)(CO)(PPh_3)$_2$]. Dehydration of the complex [Ru(CH=CH-CPh_2OH)(κ²-MI)(CO)(PPh_3)$_2$] with HBF_4 yielded the vinyl carbene [Ru(=CHCH=CPh_2)(κ²-MI)(CO)(PPh_3)$_2$]BF_4. The hydride complexes [MH(κ²-MI)(CO)(PPh_3)$_2$] (M = Ru, Os) were obtained from the reaction of HMI and KOH with [RuHCl(CO)(PPh_3)$_3$] and [OsHCl(CO)(BTD)(PPh_3)$_2$], respectively. Reaction of [Ru(CH=$CHC_6H_4CH_3$-4)(κ²-MI)(CO)(PPh_3)$_2$] with excess HC≡CPh leads to isolation of the acetylide complex [Ru(C≡CPh)(κ²-MI)(CO)(PPh_3)$_2$], which is also accessible by direct reaction of [Ru(C≡CPh)Cl(CO)(BTD)(PPh_3)$_2$] with 1-methyl-2-mercaptoimidazole and NaOMe. The thiocarbonyl complex [Ru(CPh=CHPh)Cl(CS)(PPh_3)$_2$] reacted with HMI and NaOMe without migration to yield [Ru(CPh=CHPh)(κ²-MI)(CS)(PPh_3)$_2$], while treatment of [Ru(CH=CHPh)Cl(CO)$_2$(PPh_3)$_2$] with HMI yielded the monodentate acyl product [Ru{η¹-C(=O)CH=CHPh}(κ²-MI)(CO)(PPh_3)$_2$]. The single-crystal X-ray structures of five complexes bearing vinyl, aryl, acetylide and dienyl functionality are reported.

Introduction

The coordinatively-unsaturated vinyl complexes [Ru(CR=CHR)Cl(CO)(PR'_3)$_2$] (R = H, Ph *etc.*; R′ = ^{i}Pr,[1] Ph[2]) have been shown to be useful starting points for the exploration of the chemistry of the vinyl ligand[3–7] and this has been the focus of our previous work on the addition of mono- bi- and tridentate ligands.[8] This has been mirrored by recent work on the phosphavinyl analogues[9] which shows a wealth of reactivity at the unsaturated phosphorus ligand as well as at the metal centre. The addition of π-acid ligands such as carbon monoxide[10,11*b*] and isocyanide[11*a*,*c*] to [Ru(CR=CHR)Cl(CO)(PR'_3)$_2$] yields coordinatively saturated compounds[10,11*b*] and can even induce migration of the vinyl group to form acyl complexes.[11] In the last ten years, significant interest has been shown in their reactivity with polydentate donors such as pyrazolylborates[8*a*–*c*] and macrocyclic thioethers.[8*c*,*d*] However, typically these ligands have contained just one type of donor element (O, S or N). Bidentate examples include carboxylate,[12] xanthate[13] dithiocarbamate,[13,14] S_2CPCy_3,[15] alkenyldithiocarboxylate,[16] alkynyldithiocarboxylate,[17] dihydrobispyrazolylborate,[8*a*] amidine,[18] phenanthroline[19] and bipyridyl[19] ligands. Our current work explores the reactivity of vinyl complexes with mixed-donor bidentate ligands and the effect of these chelates on subsequent functional group transformations. Their potential hemilabile behaviour is highly desirable in many situations (*e.g.*, catalysis) where a vacant site needs to be generated for reaction to occur.

There has been significant biological interest in 1-methyl-2-mercaptoimidazole (also referred to as 1-methylimidazole-2-thiol, methimazole) as a thioureylene antithyroid agent that inhibits the formation of thyroid hormones.[20] Despite its high profile as a biorelevant molecule and the presence of both sulfur and nitrogen donors, there has been very little exploration of the coordination chemistry of such mercaptoimidazoles as ligands for metal complexes.[21] Apart from one study[21*c*] in which mercaptoimidazole was used to bridge two platinum(II) centres (through N and S donors), in all reports the molecule was used in the neutral form as a monodentate ligand. No ruthenium or osmium complexes have been reported. 1-Methyl-2-mercaptoimidazole is readily deprotonated by potassium hydroxide or sodium methoxide to give 1-methylimidazole-2-thiolate (MI) which can act as a bidentate, three-electron S,N-donor. This forms a strained, four-membered chelate which suggest its potential for hemilabile behaviour. A series of complexes were prepared to examine the ability of this ligand to support a wide range of organic ligands bound to divalent ruthenium.

Results and discussion

Vinyl and acyl complexes

An excess of potassium hydroxide was added to a suspension of 1-methyl-2-mercaptoimidazole and the ruthenium hydride complex [RuHCl(CO)(PPh_3)$_3$]. Due to the strong *trans* effect of the hydride ligand in the starting material, the loss of the PPh_3 ligand occurs readily, creating a vacant site for coordination of the MI ligand, and the reaction is complete within 10 min (^{31}P NMR). A pale green product was isolated in which the retention of both hydride and carbonyl ligands was indicated by absorptions in the solid state IR spectrum at 1978 and 1919 cm^{-1}, respectively. The presence of the hydride was confirmed by a triplet resonance at −13.05 ppm in the ^{1}H NMR spectrum showing coupling of 19.4 Hz to the phosphorus nuclei of the phosphine ligands. The coupling of the hydride peak and the singlet resonance at 49.9 ppm in the ^{31}P NMR spectrum indicated a mutually *trans*-disposition for the phosphine ligands. Three additional resonances were seen in the ^{1}H NMR spectrum at 2.61 (s, NCH_3), 5.58 (d, J_{HH} = 1.4 Hz) and 5.67 (d, J_{HH} = 1.4 Hz) ppm in addition to those for the PPh_3 ligands. Heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond coherence

DOI: 10.1039/b501906k

(HMBC) NMR experiments permitted the latter resonances to be assigned to the H^4 and H^5 protons (Chart 1) of the imidazole ring, respectively. These features, common to all the complexes discussed here, provided diagnostic evidence for the presence of the MI ligand.

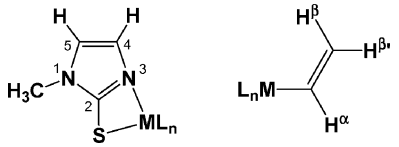
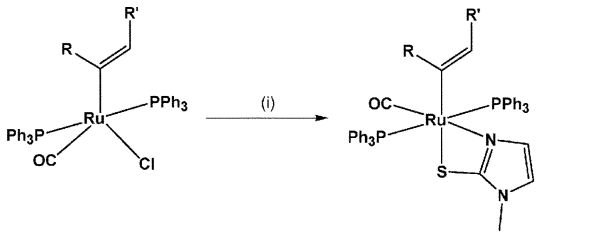


Chart 1 Numbering scheme for the 1-methylimidazole-2-thiolate (MI) and ethenyl ligands.

Typical features were observed for the carbonyl (t, 206.1 ppm, $J_{CP} = 15.0$ Hz) and triphenylphosphine ligands in the ^{13}C NMR spectrum alongside four resonances for the MI ligand with that at highest field assigned to the methyl carbon (30.2 ppm). HMQC and HMBC NMR experiments were used to assign the resonance at 155.6 ppm to the quaternary C^4 carbon and the 117.3 and 125.7 ppm resonances to the C^5 and C^4 carbons, respectively. The overall composition of the complex was confirmed by a molecular ion in the Fast Atom Bombardment (FAB) mass spectrum at m/z 767 and elemental analysis. On the basis of these data, the structure of the complex was formulated as [RuH(κ^2-MI)(CO)(PPh_3)$_2$] (**1**).

The 16-electron ruthenium vinyl species [Ru(CR=CHR′)Cl(CO)(PPh_3)$_2$] are conveniently prepared by hydroruthenation of the appropriate alkyne by [RuHCl(CO)(PPh_3)$_3$].[2] Coordinatively-saturated variants are accessible from starting materials [RuHCl(CO)(L)(PPh_3)$_2$] bearing weakly coordinating ligands (L) such as BTD (2,1,3-benzothiadiazole),[10,22] acetonitrile,[23] pyridine[24a] and pyrazoles.[24b] Reaction of the pale orange complex, [RuCl(CH=CH_2)(CO)(PPh_3)$_2$], with 1-methyl-2-mercaptoimidazole in the presence of sodium methoxide led to the isolation of a pale yellow–green solid in good yield (Scheme 1).



R = H, R' = H	A = O	**2**
R = H, R' = Ph	A = O	**3**
R = H, R' = C_6H_4Me-4	A = O	**4**
R = H, R' = CMe_3	A = O	**5**
R = C≡CPh, R' = Ph	A = O	**6**
R = Ph, R' = Ph	A = S	**7**

Scheme 1 *Reagents*: (i) MI, KOH or NaOMe.

The ^1H NMR spectrum of the complex showed a doublet of doublets at 4.76 ppm ($^3J_{H\beta H\alpha} = 17.5$, $^2J_{H\beta H\beta'} = 1.3$ Hz) for the β-proton *trans* to Hα. Another doublet of doublets was observed at 5.25 ppm for the β′-proton ($^3J_{H\beta' H\alpha} = 9.9$, $J_{H\beta' H\beta} = 1.7$ Hz). The proton, attached to the carbon directly bonded to ruthenium (Hα), appears as a doublet of doublet of triplets at 7.38 ppm, coupling to both β-protons ($^3J_{H\alpha H\beta} = 17.5$, $J_{H\alpha H\beta'} = 10.0$ Hz) and to the two phosphorus nuclei ($J_{H\alpha P} = 3.2$ Hz). Similar spectroscopic data for the MI ligand were observed to those for complex **1**. The new product was formulated as [Ru(CH=CH_2)(κ^2-MI)(CO)(PPh_3)$_2$] (**2**). Under the same experimental conditions, the yellow complex, [Ru(CH=CHPh)(κ^2-MI)(CO)(PPh_3)$_2$] (**3**), was prepared from [Ru(CH=CHPh)Cl(CO)(PPh_3)$_2$]. The ^1H NMR spectrum of **3** showed well-defined resonances for the vinylic α- and β-protons at 7.92 (ddt, $^3J_{HH} = 16.2$ Hz, $^3J_{PH} = 3.6$ Hz) and 5.92 ppm ($^3J_{HH} = 16.2$ Hz). The tolyl version of this complex [Ru(CH=$CHC_6H_4CH_3$-4)(κ^2-MI)(CO)(PPh_3)$_2$] (**4**), was isolated in an analogous fashion as a microcrystalline solid. The ^{13}C NMR spectrum displayed resonances for the MI ligand similar to those for complex **1**. Two low field triplets at 154.2 (t, $J_{CP} = 11.0$ Hz) and 206.5 ppm (t, $J_{CP} = 16.1$ Hz) were assigned to the α-carbon of the vinyl and the carbonyl ligand, respectively. The β-carbon of the vinyl ligand could not be observed directly in the ^{13}C NMR spectrum but an HMQC experiment showed a cross peak with the Hα proton locating the Cβ carbon at 134.4 ppm, underneath the virtual triplet of the phosphine *ortho*/*meta*-resonance. Slow diffusion of ethanol into a dichloromethane solution of complex **4** yielded single crystals suitable for an X-ray diffraction study (Fig. 1).

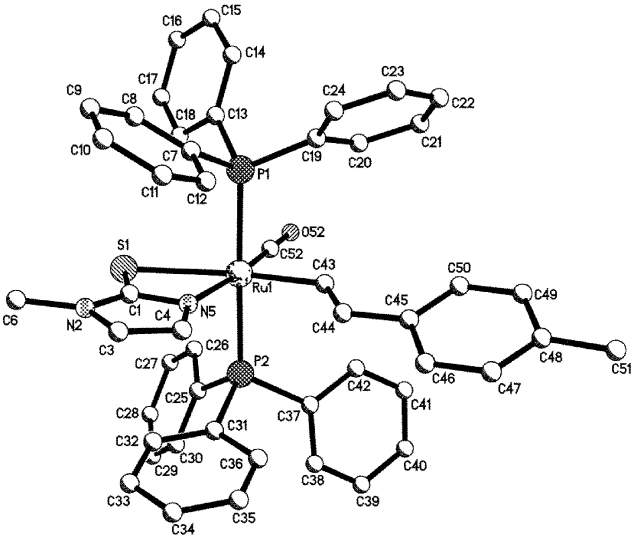


Fig. 1 Molecular structure of [Ru(CH=CHC_6H_4Me-4)(κ^2-MI)(CO)(PPh_3)$_2$] (**4**). Selected bond lengths (Å) and angles (°): Ru1–C52 1.808(6), Ru1–C43 2.058(6), Ru1–N5 2.159(4), Ru1–P2 2.3591(16), Ru1–P1 2.3796(16), Ru1–S1 2.5907(16), S1–C1 1.737(5), C1–N5 1.335(6), C43–C44 1.319(7); C52–Ru1–C43 91.9(2), C43–Ru1–N5 94.88(19), C52–Ru1–P2 92.31(18), C43–Ru1–P2 90.71(16), N5–Ru1–P2 88.23(11), C52–Ru1–P1 87.54(18), C43–Ru1–P1 88.03(16), N5–Ru1–P1 92.08(11), P2–Ru1–P1 178.72(6), C52–Ru1–S1 107.25(19), N5–Ru1–S1 66.00(12), P2–Ru1–S1 91.29(5), P1–Ru1–S1 89.97(5), N5–C1–S1 115.9(4), Ru1–C43–C44 128.7(5).

The complex [Ru(CH=CH^{t}Bu)(κ^2-MI)(CO)(PPh_3)$_2$] (**5**) was obtained from [Ru(CH=CH^{t}Bu)Cl(CO)(PPh_3)$_2$] by a similar route to that used for compound **4**. The reaction was sufficiently clean that complex **5** could also be isolated directly from [RuHCl(CO)(PPh_3)$_3$] by sequential treatment with 3,3-dimethylbut-1-yne, 1-methyl-2-mercaptoimidazole and NaOMe. Interestingly, reaction between the hydride complex, **1**, and excess terminal alkyne failed to generate vinyl complexes of the type discussed above. Although complex **1** is coordinatively saturated, creation of a suitable vacant site could be envisaged as resulting from dissociation of an arm of the MI chelate (or of a PPh_3 ligand). However, the requirement for hydrometallation of a vacant site *cis* to be the hydride may not be satisfied by hemilability of the MI ligand in this case.

A compound bearing a disubstituted vinyl ligand was prepared by the reaction of the enynyl complex [RuCl{C(C≡CPh)=CHPh}(CO)(PPh_3)$_2$][25] with 1-methyl-2-mercaptoimidazole in the presence of sodium methoxide. The presence of the vinyl ligand in the resulting yellow complex, [Ru{C(C≡CPh)=CHPh}(κ^2-MI)(CO)(PPh_3)$_2$] (**6**), was indicated by a ν(C≡C) absorption at 2150 cm^{-1} in the solid-state IR spectrum and a singlet in the ^1H NMR spectrum for the vinylic proton at 6.16 ppm.

Our previous work has explored the involvement of thiocarbonyl ligands in migratory insertion reactions with organic groups.[8c,e] In order to explore the effect of incorporating a thiocarbonyl ligand into the system, the orange 16-electron thiocarbonyl complex [Ru(CPh=CHPh)Cl(CS)(PPh_3)$_2$] was treated

with 1-methyl-2-mercaptoimidazole and sodium methoxide. A bright yellow solid, formulated as [Ru(CPh=CHPh)(κ²-MI)(CS)(PPh_3)$_2$] (**7**), was obtained from this reaction. The IR spectra showed an intense *ν*(CS) absorption at 1260 cm^{-1}, confirming the continuing presence of the thiocarbonyl ligand and thus ruling out the possibility of a migratory insertion process to yield [Ru(η²-SCCPh=CHPh)(κ²-MI)(PPh_3)$_2$]. There is precedent for the addition of sulfur donors such as [9]aneS_3 (1,4,7-trithiacyclononane) to induce migration in the same precursor to yield [Ru(η²-SCCPh=CHPh)([9]aneS_3)(CO)(PPh_3)]$^+$.[8f] Single crystals were grown of this complex from a dichloromethane–ethanol mixture and a structural study undertaken. The resulting X-ray structure is shown in Fig. 2.

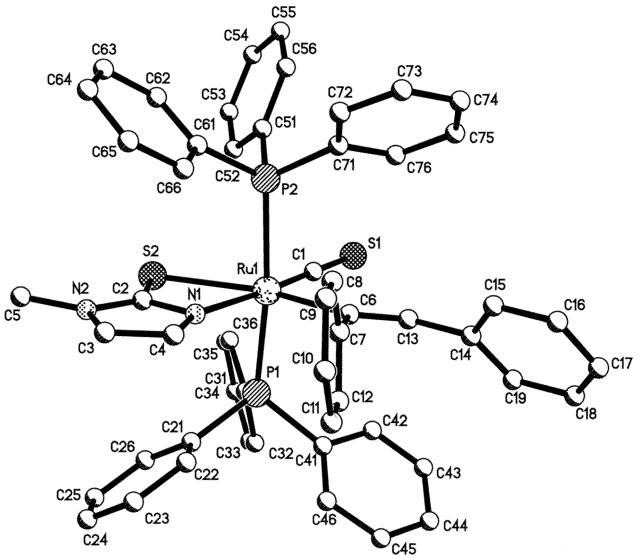
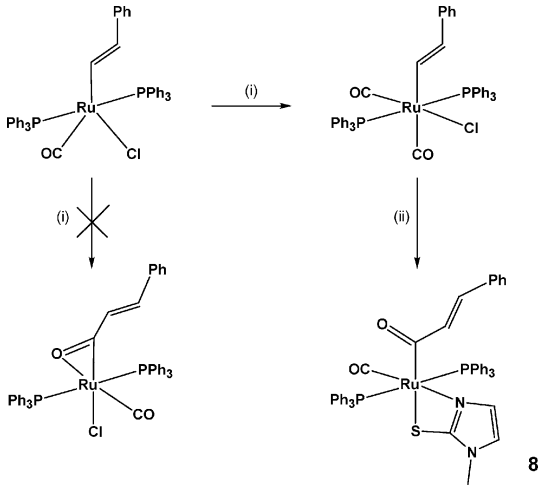


Fig. 2 Molecular structure of [Ru(CPh=CHPh)(κ²-MI)(CS)(PPh_3)$_2$] (**7**). Selected bond lengths (Å) and angles (°): Ru1–C1 1.789(2), Ru1–C6 2.102(2), Ru1–N1 2.2195(19), Ru1–P1 2.3845(6), Ru1–P2 2.4037(6), Ru1–S2 2.5807(6), S2–C2 1.715(2), N1–C2 1.326(3), C6–C13 1.337(3); C1–Ru1–C6 90.45(9), C6–Ru1–N1 95.57(8), C1–Ru1–P1 88.34(7), C6–Ru1–P1 94.09(6), N1–Ru1–P1 91.12(5), C1–Ru1–P2 87.84(7), C6–Ru1–P2 95.93(6), N1–Ru1–P2 91.63(5), P1–Ru1–P2 169.30(2), C1–Ru1–S2 108.29(7), N1–Ru1–S2 65.69(5), P1–Ru1–S2 85.601(19), P2–Ru1–S2 86.116(19), N1–C2–S2 118.54(17), C13–C6–Ru1 126.64(17).

Treatment of the coordinatively-saturated, colourless complex [RuCl(CH=CHPh)(CO)$_2$(PPh_3)$_2$][11b] with 1-methyl-2-mercaptoimidazole and sodium methoxide led to isolation of an intense yellow product that displayed not only a strong *ν*(CO) absorption at 1906 cm^{-1}, but also a peak of medium intensity to lower frequency at 1716 cm^{-1} in the IR spectrum. The ^{1}H NMR spectrum of the complex showed two mutually coupled doublets at 5.70 ppm ($^3J_{HH}$ = 15.3 Hz) and 6.46 ppm, ($^3J_{HH}$ = 15.3 Hz) with no sign of coupling to the phosphorus nuclei. The resonances were attributed to the protons of a migrated vinyl ligand (an acyl). Their chemical shift values are consistent with those found for the thioacyl complex [Ru(η²-SCCH=CHPh)Cl(CO)(PPh_3)$_2$].[8e] Typical resonances were also seen for the MI ligand. On the basis of these observations, a molecular ion at *m*/*z* 899 in the FAB mass spectrum and microanalytical data, the product was formulated as the monodentate acyl complex [Ru{η¹-C(=O)CH=CHPh}(κ²-MI)(CO)(PPh_3)$_2$] (**8**) (Scheme 2). Although migration has been shown to occur on treatment of [Ru(CR=CHR′)Cl(CO)(PPh_3)$_2$] (R = R′ = Me, Et, Ph) with CO, when R = H and R′ = Ph, the dicarbonyl complex used here is obtained as the sole product.[11b]

A number of examples have been reported of vinyl migration induced by addition of π-acid ligands such as carbon monoxide or isocyanide.[11a–d] It is rare for such a transformation to be observed on addition of a polydentate ligand. An example is the treatment of [Ru(CH_3)I(CO)$_2$(PMe_3)$_2$] with dihydrobis(pyrazol-1-yl)borate to yield the acetyl complex [Ru{η¹-C(=O)CH_3}(CO){κ²-H_2B(pz)$_2$}(PMe_3)$_2$].[11e] It has been noted, based on empirical observation, that the propensity for migration is greater for alkyl than aryl or vinyl ligands.[3] An elegant study by Esteruelas and co-workers compared these propensities in a single complex by treating [Ru(CH_3)(CH=CHPh)(CO)$_2$(P^iPr_3)$_2$] with carbon monoxide. The product was found to be an equilibrium mixture of the starting material and the acetyl species [Ru{η¹-C(=O)CH_3}(CH=CHPh)(CO)(P^iPr_3)$_2$].[11f]

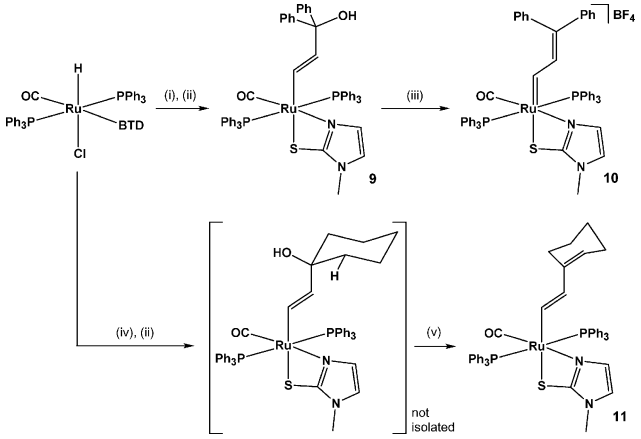


Scheme 2 *Reagents*: (i) CO; (ii) MI, NaOMe.

Dehydration reactions

A fascinating extension of the use of conventional alkynes in hydrometallation reactions is the use of propargylic alcohols. Hydroruthenation of 1,1-diphenylprop-2-yn-1-ol with [RuHCl(CO)(BTD)(PPh_3)$_2$] has been shown to yield [Ru(CH=CHCPh_2OH)Cl(CO)(BTD)(PPh_3)$_2$].[10] The BTD and chloride ligands in this complex were readily replaced by the MI ligand to yield [Ru(CH=CHCPh_2OH)(κ²-MI)(CO)(PPh_3)$_2$] (**9**). This complex gave rise to a molecular ion at *m*/*z* 977 in the FAB-MS spectrum along with a fragmentation for [M − OH]$^+$. This can be effected on a preparative level by treatment of a diethyl ether suspension of complex **9** with HBF_4·OEt_2, which resulted in a dramatic colour change to yield an intense green precipitate. The solution IR spectrum of this material displayed a *ν*(CO) absorption at 1969 cm^{-1}, a shift of 46 cm^{-1} to higher frequency with respect to the precursor. In the ^{1}H NMR spectrum, no resonance due to a hydroxy group was observed. Instead, new doublet resonances at 8.13 and 14.81 ppm were noted, both showing couplings of 13.4 Hz. These data compare well to those reported (8.70, 17.94 ppm, J_{HH} = 10.2 Hz) for the Grubbs vinyl carbene complex [RuCl$_2$(=CHCH=CPh_2)(PPh_3)$_2$],[26] which indicated that protonation and subsequent dehydration had occurred to yield the cation, [Ru(=CHCH=CPh_2)(κ²-MI)(CO)(PPh_3)$_2$]BF_4 (**10**) (Scheme 3). The vinyl carbene ligand is a strong chromophore and also gives rise to a distinctive band at 1605 cm^{-1} in the solid-state IR spectrum. A noteworthy observation is that treatment of **9** in deuterochloroform with HBF_4·Et_2O resulted initially in the expected green coloration which then gave way to a red solution consisting of a number of species (^{31}P NMR). A possible explanation for this is that after the initial reaction, the presence of excess acid results in protonation at the nitrogen centre(s) of the MI ligand.

The complex [Ru{CH=CH(HO)C_6H_{10}}Cl(CO)(BTD)(PPh_3)$_2$] has been shown to result from hydroruthenation of 1-ethynylcyclohexanol by [RuHCl(CO)(BTD)(PPh_3)$_2$].[27] Treatment of this vinyl compound with HMI in the presence of an excess of sodium methoxide led to a new complex that exhibited a singlet at 42.5 ppm in the ^{31}P NMR spectrum. A carefully dried sample was analysed by ^{1}H NMR spectroscopy. The region



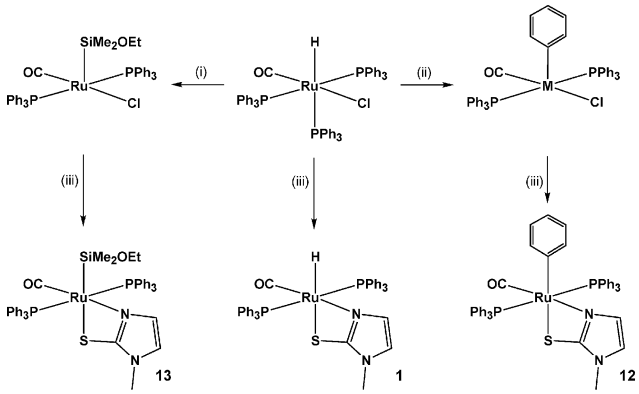
Scheme 3 *Reagents*: (i) $HC{\equiv}CCPh_2OH$; (ii) MI, NaOMe; (iii) $HBF_4{\cdot}OEt_2$; (iv), $HC{\equiv}CC(OH)C_6H_{10}$; (v) NaOMe.

between 1.4 and 2.0 ppm showed three multiplets at 1.41, 1.48 and 1.94 ppm, integrating for a sum of eight protons. These were assigned to the CH_2 protons of the vinyl substituent. No resonance attributable to a hydroxy proton was observed. In addition to characteristic resonances for the MI ligand and the vinylic α- and β-protons, a broadened triplet resonance, integrating for one proton, was noted at 4.79 ppm showing coupling of 3.5 Hz. This feature was assigned to an olefinic proton on a cyclohexenyl substituent formed by dehydration of the γ-hydroxyvinyl moiety under basic conditions. ^{1}H NMR data reported for *E*-(2-cyclohex-1-enyl)styrene[28] supports this assignment with a triplet at 5.90 ppm ($J_{HH} = 4.0$ Hz) reported for the analagous feature in the organic product. On the basis of these data, the complex was formulated as [Ru(CH=CHC_6H_9)(κ^2-MI)(CO)(PPh_3)$_2$] (**11**) (Scheme 3). Single crystals were grown by slow diffusion of ethanol into a dichloromethane solution of the complex and the structure determined (Fig. 3).

The isolation of the γ-hydroxyvinyl intermediate proved difficult due to rapid dehydration even with a single equivalent of base.

Complexes bearing σ-organyl and σ-silyl ligands

The study was broadened to include other species bearing sigma-bonded ligands. Roper described how mercury reagents could be used to prepare coordinatively-unsaturated σ-aryl complexes such as [Ru(C_6H_5)Cl(CO)(PPh_3)$_2$].[29] This red complex undergoes rapid reaction with the deprotonated MI ligand to yield [Ru(C_6H_5)(κ^2-MI)(CO)(PPh_3)$_2$] (**12**) as shown in Scheme 4.



Scheme 4 *Reagents*: (i) $HgPh_2$, $HSiMe_2Cl$, EtOH; (ii) $HgPh_2$; (iii) MI, NaOMe.

The aryl ligand was identified in the ^{1}H NMR spectrum from an overlapping multiplet at 6.41 ppm for the *meta*- and *para*-protons and a doublet at 6.99 ppm ($J_{HH} = 6.7$ Hz) attributed to the *ortho*-protons. Single crystals of this complex were also obtained and a structural study undertaken (Fig. 4):

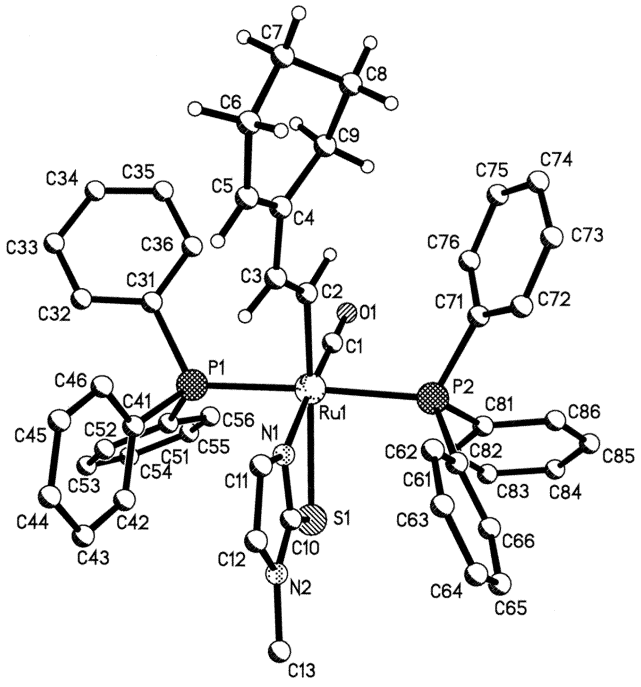


Fig. 3 Molecular structure of [Ru(CH=CHC_6H_9)(κ^2-MI)(CO)(PPh_3)$_2$] (**11**). Selected bond lengths (Å) and angles (°): Ru1–C1 1.821(3), Ru1–C2 2.085(3), Ru1–N1 2.151(2), Ru1–P1 2.3516(8), Ru1–P2 2.3749(9), Ru1–S1 2.5940(9), O1–C1 1.148(3), C2–C3 1.307(4), C4–C5 1.335(4); C1–Ru1–C2 89.82(12), C2–Ru1–N1 94.27(9), C1–Ru1–P1 92.70(9), C2–Ru1–P1 92.90(7), N1–Ru1–P1 87.83(6), C1–Ru1–P2 87.31(9), C2–Ru1–P2 90.10(7), N1–Ru1–P2 91.94(6), P1–Ru1–P2 176.99(3), C1–Ru1–S1 109.92(9), N1–Ru1–S1 65.95(6), P1–Ru1–S1 89.75(2), P2–Ru1–S1 87.42(2), C3–C2–Ru1 128.1(2), N1–C10–S1 117.4(2).

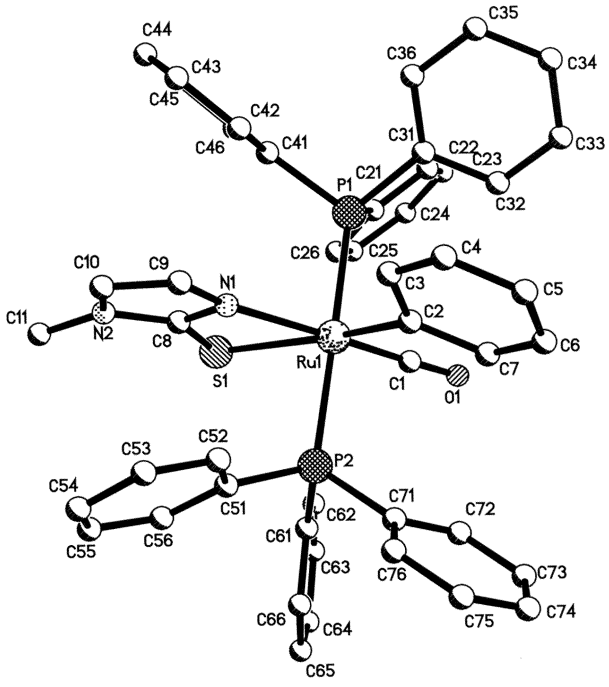
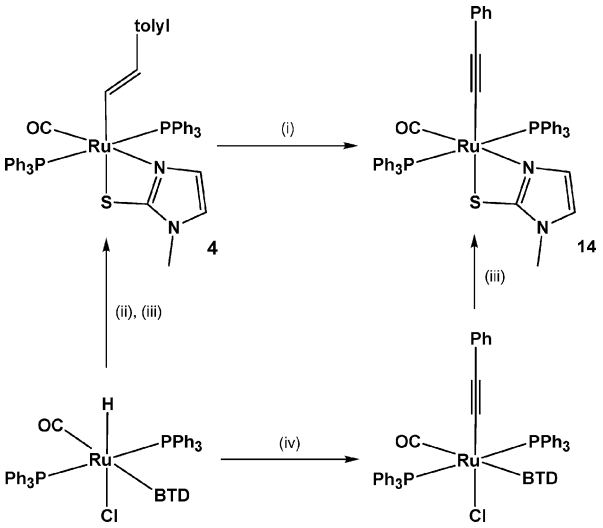


Fig. 4 Molecular structure of [Ru(C_6H_5)(κ^2-MI)(CO)(PPh_3)$_2$] (**12**). Selected bond lengths (Å) and angles (°): Ru1–C1 1.821(2), Ru1–C2 2.077(2), Ru1–N1 2.189(2), Ru1–P2 2.3663(6), Ru1–P1 2.3802(6), Ru1–S1 2.5954(6); C1–Ru1–C2 90.99(11), C1–Ru1–N1 171.96(9), C2–Ru1–N1 96.95(9), C1–Ru1–P2 90.43(8), C2–Ru1–P2 91.45(6), N1–Ru1–P2 90.70(5), C1–Ru1–P1 88.20(8), C2–Ru1–P1 91.66(6), N1–Ru1–P1 90.23(5), P2–Ru1–P1 176.62(2), C1–Ru1–S1 106.28(8), C2–Ru1–S1 162.34(7), N1–Ru1–S1 65.90(5), P2–Ru1–S1 84.90(2), P1–Ru1–S1 92.52(2), N1–C8–S1 118.48(18).

The compound $[Ru(C_6H_5)Cl(CO)(PPh_3)_2]$ is also a versatile starting material for complexes with other σ-bonded ligands such as $[Ru(SiMe_2OEt)Cl(CO)(PPh_3)_2]$,[30] which was found to react with the MI ligand in an analogous fashion to the vinyl and aryl species discussed above to give $[Ru(SiMe_2OEt)(\kappa^2\text{-MI})(CO)(PPh_3)_2]$ (**13**). Resonances for the methyl (0.07 ppm) and ethoxy (1.24, 3.69 ppm) groups were observed at typical chemical shift values in the ^{1}H NMR spectrum.

Acetylide complexes of ruthenium(II) are readily accessible by a variety of routes.[3] For example, the complex $[Ru(C{\equiv}CPh)Cl(CO)(BTD)(PPh_3)_2]$ can be conveniently prepared from $[RuHCl(CO)(BTD)(PPh_3)_2]$ and $Hg(C{\equiv}CPh)_2$,[31] however, it is worth noting that $[RuHCl(CO)(PPh_3)_3]$ reacts with mercury bis(acetylides) to yield the but-3-en-1-yn-3-yl complexes, $[Ru\{C(C{\equiv}CR){=}CHR\}Cl(CO)(PPh_3)_2]$, rather than products bearing an acetylide ligand.[25,32] Treatment of $[Ru(C{\equiv}CPh)Cl(CO)(BTD)(PPh_3)_2]$ with 1-methyl-2-mercaptoimidazole and base yields $[Ru(C{\equiv}CPh)(\kappa^2\text{-MI})(CO)(PPh_3)_2]$ (**14**) in moderate yield as shown in Scheme 5:



Scheme 5 *Reagents and conditions*: (i) excess HC≡CPh, heat; (ii) $HC{\equiv}CC_6H_4Me$-4; (iii) MI, NaOMe, (iv) $Hg(C{\equiv}CPh)_2$, heat.

The retention of the acetylide functionality was indicated by a $\nu(C{\equiv}C)$ absorption of medium intensity at 2095 cm^{-1} in the solid-state IR spectrum as well as resonances attributable to the protons of the phenyl substituent in the ^{1}H NMR spectrum. A crystal structure of this complex was obtained from a single crystal grown by the slow diffusion method (Fig. 5)

Our previous work[8c] and that of others[18,19] has shown an acetylide ligand can be generated by heating vinyl species with excess alkyne. Thus, heating $[Ru(CH{=}CHC_6H_4Me\text{-}4)(\kappa^2\text{-MI})(CO)(PPh_3)_2]$ (**4**) with excess phenylacetylene in 1,2-dichloroethane yielded the acetylide complex $[Ru(C{\equiv}CPh)(\kappa^2\text{-MI})(CO)(PPh_3)_2]$ (**14**) by a second route. The mechanism of this reaction is unclear but a plausible suggestion[18,19] is the formation of a Ru(IV) intermediate from oxidative addition of the H–C bond of the alkyne followed by reductive elimination of $H_2C{=}C(H)C_6H_4Me$-4 (detected by ^{1}H NMR). For this pathway to occur, a vacant site at the metal centre needs to be created either by dissociation of a ligand (*e.g.*, PPh_3) or by opening of the MI chelate. No free triphenylphosphine was detected in samples of the reaction mixture analysed by ^{31}P NMR spectroscopy. Hemilabile behaviour is potentially an important facet of mixed-donor ligands. We plan to investigate this behaviour in future work using high-pressure NMR and IR techniques.

Osmium complexes

This investigation of the coordination properties of the MI ligand was extended to include osmium complexes. The compound

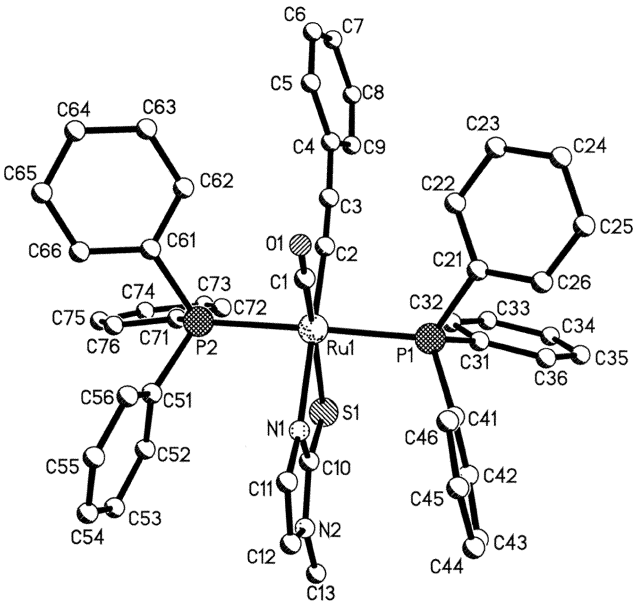
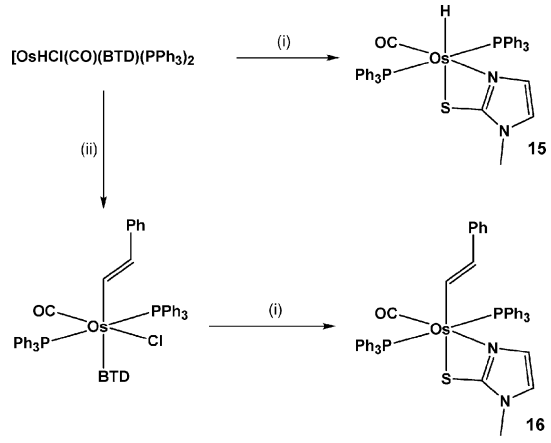


Fig. 5 Molecular structure of $[Ru(C{\equiv}CPh)(\kappa^2\text{-MI})(CO)(PPh_3)_2]$ (**14**). Selected bond lengths (Å) and angles (°): Ru1–C1 1.845(2), Ru1–C2 2.019(2), Ru1–N1 2.1441(18), Ru1–P1 2.3617(8), Ru1–P2 2.3638(8), Ru1–S1 2.5618(7), C2–C3 1.204(3); C1–Ru1–C2 90.58(9), C1–Ru1–N1 101.96(8), C1–Ru1–P1 90.55(7), C2–Ru1–P1 91.35(6), N1–Ru1–P1 90.04(5), C1–Ru1–P2 91.68(7), C2–Ru1–P2 88.84(6), N1–Ru1–P2 89.29(5), P1–Ru1–P2 177.759(18), C2–Ru1–S1 101.08(6), N1–Ru1–S1 66.43(5), P1–Ru1–S1 87.696(19), P2–Ru1–S1 90.076(19), C3–C2–Ru1 176.63(19), N1–C10–S1 116.47(15).

$[OsHCl(CO)(BTD)(PPh_3)_2]$[8c] has been prepared recently and provides a useful entry point into osmium(II) chemistry through the lability of the 2,1,3-benzothiadiazole (BTD) ligand. This is important as a combination of steric crowding and the *trans* effect of the hydride in $[OsHCl(CO)(PPh_3)_3]$[33] is not sufficient to labilise a phosphine and generate a vacant coordination site, in contrast to the ruthenium analogue.

Reaction of $[OsHCl(CO)(BTD)(PPh_3)_2]$ with the HMI ligand in the presence of potassium hydroxide led to isolation of $[OsH(\kappa^2\text{-MI})(CO)(PPh_3)_2]$ (**15**) in good yield (Scheme 6). A high field triplet resonance was observed at −15.31 ppm (J_{PH} = 16.4 Hz) in the ^{1}H NMR spectrum for the hydride. Hydroosmation of phenylacetylene by $[OsHCl(CO)(BTD)(PPh_3)_2]$ provides the purple complex $[Os(CH{=}CHPh)Cl(CO)(BTD)(PPh_3)_2]$.[8c] This species reacts with 1-methyl-2-mercaptoimidazole in the presence of KOH to give $[Os(CH{=}CHPh)(\kappa^2\text{-MI})(CO)(PPh_3)_2]$ (**16**). This complex could also be prepared directly from $[OsHCl(CO)(BTD)(PPh_3)_2]$ by sequential reaction with phenylacetylene and 1-methyl-2-mercaptoimidazole with base (Scheme 6).



Scheme 6 *Reagents*: (i) MI, NaOMe, (ii) HC≡CPh.

Structural discussion

All compounds investigated by X-ray diffraction in this study have distorted octahedral geometries with *cis*-interligand angles in the range 65.54–110.19°. The smallest of these angles in each case corresponds to the N–Ru–S bite angle of the methylimidazolethiolate (MI) chelate, which range from 65.69(5)° in [Ru(CPh=CHPh)(κ^2-MI)(CS)(PPh_3)$_2$] (**7**) to 66.43(5)° in [Ru(C≡CPh)(κ^2-MI)(CO)(PPh_3)$_2$] (**14**). The MI ligand is planar indicating that the lone pair of the methyl-substituted nitrogen atom is also involved in the bonding in the imidazole ring. The only exception to this is the structure of [Ru(C_6H_5)(κ^2-MI)(CO)(PPh_3)$_2$] (**12**) in which this methyl substituent deviates from the plane of the imidazole ring by around 5°. No previous structural study has been carried out for a complex bearing the MI ligand bonded in a bidentate fashion. A number of structures exist with the MI ligand coordinated in monodentate mode, in the two-electron donating thione form. The structure of the complex [CuI(MI)(PPh_3)$_2$] has recently been reported[21a] in which the C–S length [1.692(4) Å] has significant double bond character and the distance between this carbon and each nitrogen to which it is bonded is closer to a single bond [1.339(5) and 1.341(5) Å]. These will be compared to the corresponding distances found in the MI ligand coordinated in a bidentate manner in the complexes reported here. For [Ru(CH=CH$C_6H_4CH_3$-4)(κ^2-MI)(CO)(PPh_3)$_2$] (**4**), the C1–S1 length is longer at 1.737(5) Å while the C1–N2 [1.349(6) Å] and C1–N5 [1.335(6) Å] lengths do not differ from those in the copper complex. The bond distances within the MI ligand do not vary significantly in the complexes **4**, **7**, **11**, **12** and **14**. The C1–S1 bond length in complex **4** is slightly shorter than the C–S bond of 1.781(8) Å in the thiolate complex [Ru(η^5-C_5H_5)(SPh)(dippe)]BPh_4[34] and considerably longer than the C–S bond length of 1.615(9) Å in the thioaldehyde complex [Ru(η^5-C_5H_5){S=CH(C_6H_4Cl-4)}(dppm)]PF_6.[35] The Ru1–S1 distance of 2.5907(16) Å is longer than the Ru–S bond lengths in both the thioaldehyde [2.252(2) Å] and thiolate [2.272(2) Å] literature complexes mentioned above. Of all the complexes discussed here, in which the σ-organyl ligand is *trans* to the sulfur of the MI ligand, the Ru–S1 length, 2.5807(6) Å, in [Ru(CPh=CHPh)(κ^2-MI)(CS)(PPh_3)$_2$] (**7**) stands out as being significantly shorter than the others.

The bond distances and angles of the vinyl ligands in the complexes **4**, **7** and **11** are similar and compare well to coordinatively-saturated literature complexes such as [Ru(CH=CHC_3H_7)Cl(CO)(Me_2Hpz)(PPh_3)$_2$] (Me_2Hpz = 3,5-dimethylpyrazole).[24b] However, the Ru1–C43–C44 angle, 128.7(5)°, is considerably smaller than that found in the literature complex of 134(1)°. The structure of complex **7**, the only example discussed here with a disubstituted vinyl ligand, revealed that the phenyl substituent of the vinyl α-carbon adopts a torsion angle of 81.58° for the Ru1–C6–C7–C8 linkage.

The crystal of the dienyl complex [Ru(CH=CHC_6H_9)(κ^2-MI)(CO)(PPh_3)$_2$] (**11**) chosen for structural analysis contained two independent molecules in the asymmetric unit, one of which showed moderate levels of disorder. The ordered molecule was found to have similar bond distances and angles to those associated with the vinyl ligand in complexes **4** and **7**. The dienyl unit and its cyclohexenyl substituent were found to be essentially coplanar with only slight deviation from the plane around the C7, C8 and C9 atoms. The C4–C5 distance in the cyclohexenyl ring is clearly a double bond at 1.335(4) Å while the remaining lengths are all typical for C–C single bonds (1.496–1.544 Å). The vinyl C2–C3 distance is 1.307(4) Å and the single bond between the vinyl and cyclohexenyl double bonds (C3–C4) falls between single and double bond in length [1.470(4) Å].

The bond length for Ru–S1 [2.5954(6) Å] in the phenyl complex [Ru(C_6H_5)(κ^2-MI)(CO)(PPh_3)$_2$] (**12**) shows that the *trans* influence of the aryl group is comparable to that of the vinyl ligand [Ru1–S1 2.5907(16) Å in **4**]. Otherwise the structure is unremarkable.

Of all the structures discussed here, the acetylide complex [Ru(C≡CPh)(κ^2-MI)(CO)(PPh_3)$_2$] (**14**) is unique by virtue of the σ-organyl ligand being *trans* to the nitrogen donor of the MI ligand in contrast to the other four structures, where the sulfur occupies this position. As a result, the Ru–S and Ru–N distances to the MI ligand are significantly different to those for the other complexes. Undoubtedly a factor in this is the well-documented strong *trans* influence of the acetylide ligand.[3] Recently the structure of the acetylide complex [Ru(C≡C^{t}Bu)Cl(κ^2-Me_2bipy)(PPh_3)$_2$] (Me_2bipy = dimethylbipyridyl) has been reported.[36] In this structure, the *trans* influence of the C≡C^{t}Bu ligand results in Ru–N bond lengths of 2.120(4) Å (*trans* to acetylide) and 2.051(3) Å (*trans* to chloride). This compares well with the Ru1–N1 distance of 2.1441(18) Å in complex **14**. The Ru1–C2 bond length of 2.019(2) Å in **14** is similar to the same feature in [Ru(C≡C^{t}Bu)Cl(κ^2-Me_2bipy)(PPh_3)$_2$] of 2.053(5) Å, while the C2–C3 triple bond is slightly longer [1.204(3) Å] in **14** than the distance found in [Ru(C≡C^{t}Bu)Cl(κ^2-Me_2bipy)(PPh_3)$_2$] of 1.174(6) Å. The acetylide ligand is essentially linear in both complexes.

Conclusion

This report has demonstrated the 1-methylimidazole-2-thiolate (MI) ligand to be an effective bidentate mixed-donor chelate for complexes of ruthenium(II) bearing a wide range of σ-organyl and σ-silyl groups. These are the first examples of ruthenium and osmium complexes bearing this ligand as bidentate donor. Functional group transformations in the presence of acid and base and at elevated temperatures (80 °C) have also revealed the MI ligand to be robust. This is the first report to investigate the complexation and structural properties of this ligand. Further work is currently underway to investigate the hemilabile properties of this ligand in catalytic processes.

Experimental

Apart from where stated, all manipulations were carried out under aerobic conditions using commercially available solvents and reagents as received. IR spectra were obtained using a Shimadzu FTIR 8700 spectrometer with KBr plates and Nujol mulls or in CH_2Cl_2 solution. Spectroscopic features due to the triphenylphosphine ligands have been omitted to aid clarity. The term 'sh' denotes a shoulder on a larger carbonyl-associated absorption in the IR spectrum, while 't^v' indicates a virtual triplet nuclear magnetic resonance. NMR spectroscopy was carried out at 25 °C 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: 501.13 MHz, ^{13}C: 125.77 MHz) spectrometers. FAB-MS spectra (nitrobenzyl alcohol matrices) were measured using a VG 70-SB magnetic sector mass spectrometer. All solid-state IR samples were measured with KBr plates unless stated otherwise. Elemental microanalyses were performed at University College London. Crystal solvates were confirmed by integration of the dichloromethane resonance in the ^{1}H NMR spectra of the complexes. The complexes [RuHCl(CO)(PPh_3)$_3$],[37] [RuHCl(CO)(BTD)(PPh_3)$_2$],[22] [Ru(CH=CH_2)Cl(CO)(PPh_3)$_2$],[8a] [Ru(CH=CH$C_6H_4CH_3$-4)Cl(CO)(BTD)(PPh_3)$_2$],[10] [Ru(CH=CHPh)Cl(CO)(PPh_3)$_2$],[2] [Ru(CH=CHPh)Cl(CO)$_2$(PPh_3)$_2$],[11b] [Ru(CH=CH^{t}Bu)Cl(CO)(PPh_3)$_2$],[38] [Ru(CH=CHCPh_2OH)Cl(CO)(BTD)(PPh_3)$_2$],[10] [Ru{CH=CHC(OH)C_6H_{10}}(BTD)(PPh_3)$_2$],[27] [Ru{C(C≡CPh)=CHPh}Cl(CO)(PPh_3)$_2$],[25] [Ru(CPh=CHPh)Cl(CS)(PPh_3)$_2$],[8g] [Ru(C_6H_5)Cl(CO)(PPh_3)$_2$][29] [Ru(C≡CPh)Cl(CO)(BTD)(PPh_3)$_2$],[31] [Ru($SiMe_2$OEt)Cl(CO)(PPh_3)$_2$],[30] [OsHCl(CO)(BTD)(PPh_3)$_2$],[8c] [Os(CH=CHPh)Cl(BTD)(CO)(PPh_3)$_2$],[8c] were prepared according to published procedures.

Preparation of [RuH(κ^2-MI)(CO)(PPh_3)$_2$] (1)

[RuHCl(CO)(PPh_3)$_3$] (200 mg, 0.210 mmol) and 1-methyl-2-mercaptoimidazole (26 mg, 0.228 mmol) were suspended in

dichloromethane (20 mL) and ethanol (10 mL) and treated with potassium hydroxide (18 mg, 0.321 mmol) in water (0.5 mL) and ethanol (5 mL). The reaction was stirred for 1 h to yield a pale green solution. The solvent volume was concentrated under reduced pressure until precipitation of a pale green product was complete. This was washed with water (5 mL), ethanol (10 mL) and hexane (10 mL). Yield: 130 mg (81%). IR (CsI/Nujol): 1978 [ν(RuH)], 1919 [ν(CO)], 1310, 1289, 971 cm^{-1}. IR (CH_2Cl_2): 1973 (sh) [ν(RuH)] 1919 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 49.9 ppm. ^1H NMR ($CDCl_3$): −13.05 [t, RuH, 1H, J_{PH} = 19.4 Hz], 2.61 [s, CH_3, 3H], 5.58 [d, NCH^4, 1H, J_{HH} = 1.4 Hz], 5.67 [d, NCH^5, 1H, J_{HH} = 1.4 Hz], 7.25, 7.62 [m × 2, C_6H_5, 30H] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 30.2 [s, CH_3], 117.3 [s, NC^5H], 125.7 [s, NC^4H], 127.9 [t^v, *o/m*-PC_6H_5, J_{CP} = 5.9 Hz], 129.7 [s, *p*-PC_6H_5], 134.6 [t^v, *o/m*-PC_6H_5, J_{CP} = 4.6 Hz], 135.4 [t^v, *ipso*-PC_6H_5, J_{CP} = 20.7 Hz], 155.6 [s, NCN], 206.1 [t, CO, J_{CP} = 15.0 Hz] ppm. FAB-MS *m/z* (abundance): 767 (0.8) [M]$^+$, 739 (0.2) [M − CO]$^+$, 652 (0.3) [M − MI]$^+$. Anal. Calc. for $C_{41}H_{36}N_2OP_2RuS$: C, 64.2; H, 4.7; N, 3.7%. Found: C, 63.8; H, 4.8; N, 3.6%.

Preparation of [Ru(CH=CH$_2$)(κ^2-MI)(CO)(PPh$_3$)$_2$] (2)

[Ru(CH=CH$_2$)Cl(CO)(PPh$_3$)$_2$] (100 mg, 0.140 mmol) and 1-methyl-2-mercaptoimidazole (18 mg, 0.158 mmol) were suspended in a mixture of dichloromethane (20 mL) and ethanol (10 mL). Sodium methoxide (9 mg, 0.167 mmol) was dissolved in ethanol (10 mL) and added to the mixture dropwise which resulted in a colour change to a yellow solution. The reaction was stirred for 1 h. The solvent volume was concentrated under reduced pressure until pale yellow–green crystals precipitated. The product was filtered, washed with water (5 mL), ethanol (10 mL) and hexane (10 mL) and dried. Yield: 75 mg (68%). IR (KBr/Nujol): 1900 [ν(CO)], 1542, 1308, 1277, 1257, 1140, 854 cm^{-1}. IR (CH_2Cl_2): 1913 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 43.6 ppm. ^1H NMR ($CDCl_3$): 2.44 [s, CH_3, 3H], 4.76 [dd, Hβ, 1H, $J_{H\beta H\alpha}$ = 17.5, $J_{H\beta H\beta'}$ = 1.3 Hz], 5.25 [dd, Hβ′, 1H, $J_{H\beta' H\alpha}$ = 9.9, $J_{H\beta' H\beta}$ = 1.7 Hz], 5.58 [d, NCH, 1H, J_{HH} = 1.6 Hz], 6.13 [d, NCH, 1H, J_{HH} = 1.6 Hz], 7.26, 7.53 [m × 2, C_6H_5, 30H], 7.38 [ddt, Hα, 1H, $J_{H\alpha H\beta}$ = 17.5, $J_{H\alpha H\beta'}$ = 10.0 Hz, $J_{H\alpha P}$ = 3.2 Hz] ppm. FAB-MS *m/z* (abundance): 794 (37) [M]$^+$, 767 (100) [M − CO]$^+$, 681 (4) [M − MI]$^+$, 654 (13) [M − vinyl − MI]$^+$, 625 (**7**) [Ru(PPh$_3$)$_2$]$^+$, 532 (57) [M − PPh$_3$]$^+$, 504 (53) [M − CO − PPh$_3$]$^+$, 477 (48) [M − vinyl − CO − PPh$_3$]$^+$. Anal. Calc. for $C_{43}H_{38}N_2OP_2RuS{\cdot}0.8CH_2Cl_2$: C, 61.0; H, 4.6; N 3.3%. Found: C, 60.8; H, 4.5; N, 3.2%.

Preparation of [Ru(CH=CHPh)(κ^2-MI)(CO)(PPh$_3$)$_2$] (3)

Yellow product (143 mg, 65%) obtained by the same general procedure as for **2** from [Ru(CH=CHPh)Cl(CO)(PPh$_3$)$_2$] (200 mg, 0.252 mmol). IR (KBr/Nujol): 1938 [ν(CO)], 1593, 1310, 1283, 1246, 848 cm^{-1}. IR (CH_2Cl_2): 1915 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 42.9 ppm. ^1H NMR ($CDCl_3$): 2.50 [s, CH_3, 3H], 5.69 [d, NCH, 1H, J_{HH} = 1.6 Hz], 5.92 [d, Hβ, 1H, $J_{H\beta H\alpha}$ = 16.2 Hz], 6.21 [d, NCH, 1H, J_{HH} = 1.6 Hz], 6.48 [d, *ortho*-CC_6H_5, 2H, J_{HH} = 7.3 Hz], 6.88 [t, *para*-CC_6H_5, 1H, J_{HH} = 7.3 Hz], 7.02 [t, *meta*-CC_6H_5, 2H, J_{HH} = 7.3 Hz], 7.24, 7.48 [m × 2, PC_6H_5, 30H], 7.92 [dt, Hα, 1H, $J_{H\alpha H\beta}$ = 16.2, $J_{H\alpha P}$ = 3.6 Hz] ppm. FAB-MS *m/z* (abundance): 869 (1.5) [M]$^+$, 765 (0.25%) [M − vinyl]$^+$, 607 (2.4) [M − PPh$_3$]$^+$, 579 (1) [M − CO − PPh$_3$]$^+$. Anal. Calc. for $C_{49}H_{42}N_2OP_2RuS$: C, 67.7; H, 4.9; N, 3.2%. Found: C, 67.3; H, 4.9; N, 3.2%.

Preparation of [Ru(CH=CHC$_6$H$_4$CH$_3$-4)(κ^2-MI)(CO)(PPh$_3$)$_2$] (4)

Olive green product (65 mg, 59%) obtained by the same general procedure as for **2** from [Ru(CH=CHC$_6$H$_4$CH$_3$-4)Cl(CO)(PPh$_3$)$_2$] (100 mg, 0.124 mmol). IR (CsI/Nujol): 1909 [ν(CO)], 1309, 1291, 968, 890, 843, 829 cm^{-1}. IR (CH_2Cl_2): 1916 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 43.0 ppm. ^1H NMR ($CDCl_3$): 2.23 [s, NCH_3, 3H], 2.50 [s, CH_3, 3H] 5.67 [d, NCH, 1H, J_{HH} = 1.8 Hz], 5.86 [d, Hβ, 1H, $J_{H\beta H\alpha}$ = 16.2 Hz], 6.17 [d, NCH, 1H, J_{HH} = 1.8 Hz], 6.38, 6.83 [$(AB)_2$, C_6H_4, 4H, J_{AB} = 7.9 Hz], 7.21, 7.43 [m × 2, C_6H_5, 30H], 7.81 [dt, Hα, 1H, $J_{H\alpha H\beta}$ = 16.2 Hz, $J_{H\alpha P}$ = 3.8 Hz] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 21.1 [s, CCH_3], 30.4 [s, NCH_3], 115.8 [s, NC^5H], 122.2 [s, NC^4H], 124.3 [s, *o/m*-C_6H_4], 127.4 [t^v, *o/m*-PC_6H_5, J_{CP} = 4.5 Hz], 128.3 [*o/m*-C_6H_4], 129.1 [s, *p*-PC_6H_5], 132.6 [s, *p*-C_6H_4], 133.1 [t^v, *ipso*-PC_6H_5, J_{CP} = 21.2 Hz], 134.4 [t^v, *o/m*-PC_6H_5, J_{CP} = 5.4 Hz] 134.4 [Cβ, obscured], 139.2 [s, *ipso*-C_6H_4], 153.9 [s, NCN], 154.2 [t, Cα, J_{CP} = 11.0 Hz], 206.5 [t, CO, J_{CP} = 16.1 Hz] ppm. FAB-MS *m/z* (abundance): 883 (2) [M]$^+$, 766 (0.6) [M − vinyl]$^+$, 654 (0.4) [M − vinyl − MI]$^+$, 621 (3) [M − PPh$_3$]$^+$, 593 (1) [M − CO − PPh$_3$]$^+$. Anal. Calc. for $C_{50}H_{44}N_2OP_2RuS$: C, 67.9; H, 5.0; N, 3.2%. Found: C, 68.0; H, 5.0; N, 3.2%.

Preparation of [Ru(CH=CH^{t}Bu)(κ^2-MI)(CO)(PPh$_3$)$_2$] (5)

Pale yellow microcrystalline product (73 mg, 66%) obtained by the same general procedure as for **2** from [Ru(CH=CH^{t}Bu)Cl(CO)(PPh$_3$)$_2$] (100 mg, 0.130 mmol). IR (KBr/Nujol): 1909 [ν(CO)], 1572, 1320, 1288, 1258, 972 cm^{-1}. IR (CH_2Cl_2): 1908 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 43.6 ppm. ^1H NMR ($CDCl_3$): 0.42 [s, CMe_3, 9H], 2.49 [s, CH_3, 3H], 5.92 [d, Hβ, 1H, $J_{H\beta H\alpha}$ = 15.9 Hz], 5.51 [d, NCH, 1H, J_{HH} = 1.7 Hz], 6.05 [d, NCH, 1H, J_{HH} = 1.7 Hz], 6.44 [dt, Hα, 1H, $J_{H\alpha H\beta}$ = 15.9, $J_{H\alpha P}$ = 3.3 Hz], 7.23–7.96 [m, PC_6H_5, 30H] ppm. FAB-MS *m/z* (abundance): 850 (25) [M]$^+$, 767 (15%) [M − vinyl]$^+$, 654 (6) [M − vinyl − MI]$^+$, 625 (12) [M − vinyl − MI − CO]$^+$, 588 (100) [M − PPh$_3$]$^+$, 560 (57) [M − CO − PPh$_3$]$^+$, 505 (16) [M − vinyl − PPh$_3$]$^+$, 477 (52) [M − vinyl − CO − PPh$_3$]$^+$. Anal. Calc. for $C_{47}H_{46}N_2OP_2RuS{\cdot}0.5CH_2Cl_2$: C, 63.9; H, 5.3; N, 3.1%. Found: C, 64.0; H, 5.2; N, 3.1%.

Preparation of [Ru{C(C≡CPh)=CHPh}(κ^2-MI)(CO)(PPh$_3$)$_2$] (6)

Pale yellow product (69 mg, 64%) obtained by the same general procedure as for **2** from [Ru{C(C≡CPh)=CHPh}Cl(CO)(PPh$_3$)$_2$] (100 mg, 0.112 mmol). IR (KBr/Nujol): 2150 [ν(C≡C)], 1921 [ν(CO)], 1653, 1308, 1297, 905 cm^{-1}. IR (CH_2Cl_2): 2160 [ν(C≡C)], 1924 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 40.7 ppm; ^1H NMR ($CDCl_3$): 2.42 [s, CH_3, 3H], 5.72 [d, NCH, 1H, J_{HH} = 1.7 Hz], 6.16 [s, RuC=CH, 1H], 6.71 [d, NCH, 1H, J_{HH} = 1.7 Hz], 6.91 [d, *ortho*-CC_6H_5, 2H, J_{HH} = 7.5 Hz], 6.94 [t, *para*-CC_6H_5, 1H, J_{HH} = 7.2 Hz], 7.05 [t, *meta*-CC_6H_5, 2H, J_{HH} = 7.5 Hz], 7.23, 7.53 [m × 2, PC_6H_5 + CC_6H_5, 30H + 5H] ppm. FAB-MS *m/z* (abundance): 969 (2%) [M]$^+$, 856 (0.5%) [M − MI]$^+$, 767 (0.5%) [M − vinyl]$^+$, 700 (1%) [M − PPh$_3$]$^+$, 680 (5%) [M − CO − PPh$_3$]$^+$. Anal. Calc. for $C_{57}H_{46}N_2OP_2RuS{\cdot}0.25CH_2Cl_2$: C, 69.4; H, 4.7; N, 2.8%. Found: C, 68.9; H, 4.8; N, 2.7%.

Preparation of [Ru(CPh=CHPh)(κ^2-MI)(CS)(PPh$_3$)$_2$] (7)

Yellow product (101 mg, 62%) obtained by the same general procedure as for **2** from [Ru(CPh=CHPh)Cl(CS)(PPh$_3$)$_2$] (150 mg, 0.170 mmol). IR (KBr/Nujol): 1716, 1591, 1577, 1554, 1320, 1284, 1260 [ν(CS)], 967, 922 cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6D_6): 35.5 ppm; ^1H NMR (C_6D_6): 1.92 [s, CH_3, 3H], 4.40 [d, NCH, 1H, J_{HH} = 1.5 Hz], 5.36 [d, NCH, 1H, J_{HH} = 1.5 Hz], 6.40 [s, RuC=CH, 1H], 6.56 [d, *ortho*-CC_6H_5, 2H, J_{HH} = 8.1 Hz], 6.70 [d, *ortho*-CC_6H_5, 2H, J_{HH} = 7.2 Hz], 6.86 [t, *para*-CC_6H_5, 1H, J_{HH} = 7.8 Hz], 7.00 × 7.81 [m, PC_6H_5 + CC_6H_5, 30H + 5H] ppm. FAB-MS *m/z* (abundance): 961 (1) [M]$^+$, 848 (0.5) [M − MI]$^+$, 782 (0.4) [M − vinyl]$^+$, 699 (1.6) [M − PPh$_3$]$^+$, 585 (1.3) [M − MI − PPh$_3$]$^+$. Anal. Calc. for $C_{55}H_{46}N_2P_2RuS_2{\cdot}0.75CH_2Cl_2$: C, 65.3; H, 4.7; N, 2.7%. Found: C, 65.4; H, 4.7; N, 2.7%.

Preparation of [Ru{η¹-C(=O)CH=CHPh}(κ²-MI)(CO)-(PPh₃)₂] (8)

[Ru(CH=CHPh)Cl(CO)₂(PPh₃)₂] (100 mg, 0.122 mmol) and 1-methyl-2-mercaptoimidazole (15 mg, 0.131 mmol) were suspended in dichloromethane (20 mL) and treated with potassium hydroxide (7 mg, 0.125) in water (0.5 mL) and ethanol (5 mL). The reaction was stirred for 2 h. The solvent volume was concentrated under reduced pressure until precipitation of the yellow product was complete and then washed with water (5 mL), ethanol (10 mL) and hexane (10 mL). The product can be recrystallised from dichloromethane and ethanol. Yield: 72 mg (66%). IR (KBr/Nujol): 1906 [ν(CO)], 1716 [ν(C=O)], 1621, 1575, 1549, 1266, 993 cm^{-1}. IR (CH_2Cl_2): 1920 [ν(CO)], 1723 [ν(C=O)] cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 41.2 ppm; ^1H NMR (CD_2Cl_2): 2.40 [s, CH_3, 3H], 5.69 [d, NCH, 1H, J_{HH} = 1.5 Hz], 5.70 [d, =CHPh, 1H, J_{HH} = 15.3 Hz], 6.46 [d, C(=O)CH, 1H, J_{HH} = 15.3 Hz], 6.83 [d, NCH, 1H, J_{HH} = 1.5 Hz], 7.00 [m, *ortho*-CC_6H_5 + *para*-CC_6H_5, 2H + 1H], 7.17–7.51 [m, PC_6H_5 + *meta*-CC_6H_5, 30H + 2H] ppm. FAB-MS *m/z* (abundance): 899 (0.5) [M]$^+$. Anal. Calc. for $C_{50}H_{42}N_2O_2P_2RuS{\cdot}CH_2Cl_2$: C, 62.3; H, 4.5; N, 2.9%. Found: C, 62.0; H, 4.7; N, 2.7%.

Preparation of [Ru(CH=CHCPh₂OH)(κ²-MI)(CO)(PPh₃)₂] (9)

Yellow product (67 mg, 71%) obtained by the same general procedure as for **2** from [Ru(CH=CHPh₂OH)Cl(CO)(BTD)-(PPh₃)₂] (100 mg, 0.097 mmol). IR (KBr/Nujol): 1917 [ν(CO)], 1574, 1313, 1285, 1188, 924, 896, 843 cm^{-1}. IR (CH_2Cl_2): 1923 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 43.9 ppm. ^1H NMR ($CDCl_3$): 1.11 [s, OH, 1H], 2.41 [s, CH_3, 3H], 5.38 [d, NCH, 1H, J_{HH} = 1.6 Hz], 5.63 [d, NCH, 1H, J_{HH} = 1.6 Hz], 5.74 [d, Hβ, 1H, $J_{H\beta H\alpha}$ = 16.0 Hz], 6.83 [m, C_6H_5, 2H], 7.02 [dt, Hα, 1H, $J_{H\alpha H\beta}$ = 16.0, $J_{H\alpha P}$ = 2.7 Hz], 7.09 [m, C_6H_5, 4H], 7.19–7.95 [m, PC_6H_5 + C_6H_5, 30H + 4H] ppm. FAB-MS *m/z* (abundance): 977 (15) [M]$^+$, 960 (4) [M − OH]$^+$, 767 (4) [M − vinyl]$^+$, 715 (2) [M − PPh_3]$^+$, 697 (4) [M − OH − PPh_3]$^+$, 504 (5) [M − vinyl − PPh_3]$^+$, 477 (13) [M − vinyl − CO − PPh_3]$^+$. Anal. Calc. for $C_{56}H_{48}N_2O_2P_2RuS{\cdot}0.25CHCl_3$: C, 67.2; H, 4.8; N, 2.8%. Found: C, 67.1; H, 4.8; N, 2.5%.

Preparation of [Ru(=CHCH=CPh₂)(κ²-MI)(CO)(PPh₃)₂]BF₄ (10)

[Ru(CH=CHPh₂OH)(MI)(CO)(PPh₃)₂] (**9**) (50 mg, 0.051 mmol) was suspended in diethyl ether (5 mL) and treated with $HBF_4{\cdot}OEt_2$ (one drop, excess) causing an intense green precipitation. The reaction was stirred for 10 min and the precipitate filtered, washed with diethyl ether (10 mL) and dried. Yield: 32 mg (60%). IR (KBr/Nujol): 1958 [ν(CO)], 1572 [ν(Ru=CC=C)], 1285, 1211, 1186, 1159, 1055 [ν(B–F)], 939 cm^{-1}. IR (CH_2Cl_2): 1969 [ν(CO)], 1605 [ν(Ru=CC=C)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 36.1 ppm. ^1H NMR ($CDCl_3$): 2.28 [s, NCH_3, 3H], 6.20 [d, *ortho*-CC_6H_5, 2H, J_{HH} = 6.9 Hz], 6.29 [d, NCH, 1H, J_{HH} = 1.7 Hz], 6.39 [s(br), NCH, 1H], 7.25–7.95 [m, PC_6H_5 + CC_6H_5, 30H + 8H], 8.13 [d, Hβ, 1H, J_{HH} = 13.4 Hz], 14.81 [d, Hα, 1H, J_{HH} = 13.4 Hz] ppm. FAB-MS *m/z* (abundance): 959 (3) [M]$^+$, 696 (2) [M − PPh_3]$^+$, 553 (1) [M − CO − MI − PPh_3]$^+$, 407 (4) [M − CO − 2PPh_3]$^+$. Anal. Calc. for $C_{56}H_{45}BF_4N_2OP_2RuS$: C, 64.4; H, 4.4; N, 2.7%. Found: C, 64.7; H, 4.3; N, 2.5%.

Preparation of [Ru(CH=CHC₆H₉)(κ²-MI)(CO)(PPh₃)₂] (11)

[RuHCl(CO)(BTD)(PPh₃)₂] (130 mg, 0.157 mmol) was dissolved in tetrahydrofuran (15 mL) and treated with 1-ethynylcyclohexan-1-ol (39 mg, 0.314 mmol). The reaction was heated to reflux for 5 minutes and allowed to cool. The resulting solution was stirred and 1-methyl-2-mercaptoimidazole (18 mg, 0.158 mmol) added followed by an ethanolic solution (10 mL) of sodium methoxide (17 mg, 0.315 mmol). The reaction was stirred for 1 h and the solvent volume concentrated under reduced pressure until precipitation of the product was complete. This was recrystallised from dichloromethane and ethanol to yield a pale microcrystalline yellow product. This was filtered and washed with water (5 mL), ethanol (10 mL) and hexane (10 mL) and dried. Yield: 92 mg (67%). IR (KBr/Nujol): 1911 [ν(CO)] cm^{-1}. IR (CH_2Cl_2): 1908 [ν(CO)], 1310, 1288, 1240, 1184, 968, 919 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 42.5 ppm. ^1H NMR ($CDCl_3$): 1.41 [m, C_6H_8, 4H], 1.48 [m, C_6H_8, 2H], 1.94 [m, C_6H_8, 2H], 2.50 [s, CH_3, 3H], 4.79 [t(br), cyclohexene-C=CH, 1H, J_{HH} = 3.5 Hz], 5.63 [d, Hβ, 1H, $J_{H\beta H\alpha}$ = 16.2 Hz], 5.64 [d, NCH, 1H, J_{HH} = 1.6 Hz], 6.15 [d, NCH, 1H, J_{HH} = 1.6 Hz], 7.00 [dt, Hα, 1H, $J_{H\alpha H\beta}$ = 16.2, $J_{H\alpha P}$ = 3.3 Hz], 7.17–7.58 [m, PC_6H_5, 30H] ppm. FAB-MS *m/z* (abundance): 874 (8) [M]$^+$, 767 (3) [M − vinyl]$^+$, 612 (11) [M − PPh_3]$^+$, 584 (13) [M − CO − PPh_3]$^+$, 505 (4) [M − vinyl − PPh_3]$^+$, 477 (10) [M − vinyl − CO − PPh_3]$^+$. Anal. Calc. for $C_{49}H_{46}N_2OP_2RuS$: C, 67.3; H, 5.3; N, 3.2%. Found: C, 67.0; H, 5.1; N, 3.1%.

Preparation of [Ru(C₆H₅)(κ²-MI)(CO)(PPh₃)₂] (12)

Colourless crystalline product (51 mg, 66%) obtained by the same general procedure as for **2** from [Ru(C₆H₅)Cl(CO)(PPh₃)₃] (70 mg, 0.091 mmol). IR (KBr/Nujol): 1908 [ν(CO)], 1312, 1286, 1016, 972, 846 cm^{-1}. IR (CH_2Cl_2): 1915 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 41.2 ppm; ^1H NMR ($CDCl_3$): 2.52 [s, CH_3, 3H], 5.78 [d, NCH, 1H, J_{HH} = 1.7 Hz], 6.42 [d, NCH, 1H, J_{HH} = 1.7 Hz], 6.41 [m, *meta*-CC_6H_5 + *para*-CC_6H_5, 2H + 1H], 6.99 [d, *ortho*-CC_6H_5, 2H, J_{HH} = 6.7 Hz], 7.10–7.40 [m, PC_6H_5, 30H] ppm. FAB-MS *m/z* (abundance): 842 (25) [M]$^+$, 765 (13) [M − Ph]$^+$, 729 (6) [M − MI]$^+$, 581 (27) [M − PPh_3]$^+$, 553 (100) [M − CO − PPh_3]$^+$, 504 (7) [M − Ph − PPh_3]$^+$, 476 (20) [M − Ph − CO − PPh_3]$^+$. Anal. Calc. for $C_{47}H_{40}N_2OP_2RuS{\cdot}2/3CH_2Cl_2$: C, 63.6; H, 4.6; N, 3.1%. Found: C, 63.6; H, 4.7; N, 3.1%.

Preparation of [Ru(SiMe₂OEt)(κ²-MI)(CO)(PPh₃)₂] (13)

Pale yellow product (43 mg, 56%) obtained by the same general procedure as for **2** from [Ru(SiMe₂OEt)Cl(CO)(PPh₃)₃] (70 mg, 0.088 mmol). IR (KBr/Nujol): 1903 [ν(CO)], 1881, 1272, 1216, 1175, 923, 808 cm^{-1}. IR (CH_2Cl_2): 1906 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 45.6 ppm. ^1H NMR ($CDCl_3$): 0.07 [s, $SiCH_3$, 6H], 1.24 [t, CH_2CH_3, 3H, J_{HH} = 7.0 Hz], 2.09 [s, NCH_3, 3H], 3.69 [q, CH_2CH_3, 3H, J_{HH} = 6.8 Hz], 5.74 [d, NCH, 1H, J_{HH} = 1.6 Hz], 6.76 [d, NCH, 1H, J_{HH} = 1.6 Hz], 7.26–7.58 [m, PC_6H_5, 30H] ppm. FAB-MS *m/z* (abundance): 868 (5) [M]$^+$, 766 (17) [M − $SiMe_2OEt$]$^+$, 653 (35) [M − MI − $SiMe_2OEt$]$^+$, 625 (15) [Ru$(PPh_3)_2$]$^+$. Anal. Calc. for $C_{45}H_{46}N_2O_2P_2RuSSi$: C, 62.1; H, 5.3; N, 3.2%. Found: C, 62.4; H, 5.2; N, 3.1%.

Preparation of [Ru(C≡CPh)(κ²-MI)(CO)(PPh₃)₂] (14)

(a) Yellow product (50 mg, 65%) obtained by the same general procedure as for **2** from [Ru(C≡CPh)Cl(CO)(PPh₃)₂] (70 mg, 0.089 mmol). (b) [Ru(CH=CHC₆H₄Me-4)(MI)(CO)(PPh₃)₂] (**4**) (50 mg, 0.057 mmol) and phenylacetylene (30 mg, 0.294 mmol) were dissolved in 1,2-dichloroethane (20 mL) and heated to reflux for 3 h. All solvent was then removed under reduced pressure and the residue dissolved in dichloromethane (10 mL). Ethanol (20 mL) was added and the solvent volume concentrated under reduced pressure until precipitation of a yellow product was complete. This was washed with water (5 mL), ethanol (10 mL), hexane (10 mL) and dried. Yield: 28 g (57%). The product was recrystallised from a chloroform–ethanol mixture. IR (KBr/Nujol): 2095 [ν(C≡C)], 1958, 1940 [ν(CO)], 1595, 1319, 1288, 968, 843 cm^{-1}. IR (CH_2Cl_2): 2098 [ν(C≡C)], 1938 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 42.7 ppm; ^1H NMR ($CDCl_3$): 2.52 [s, CH_3, 3H], 5.54 [d, NCH, 1H, J_{HH} = 1.5 Hz], 5.88 [d, NCH, 1H, J_{HH} = 1.5 Hz], 6.49 [d, *ortho*-CC_6H_5, 2H, J_{HH} = 6.8 Hz], 6.96 [t, *meta*-CC_6H_5, 2H, J_{HH} = 6.8 Hz], 7.15–7.9 [m, PC_6H_5 + *para*-CC_6H_5, 30H + 1H] ppm. FAB-MS *m/z* (abundance): 866 (32) [M]$^+$, 765 (11) [M − C≡CPh]$^+$, 754 (2)

Table 1 Crystal data for compounds **4**, **7**, **11**, **12** and **14**

	4	**7**·CH_2Cl_2	**11**	**12**·$2CH_2Cl_2$	**14**
Chemical formula	$C_{50}H_{44}N_2OP_2RuS$	$C_{56}H_{48}Cl_2N_2P_2RuS_2$	$C_{49}H_{46}N_2OP_2RuS$	$C_{49}H_{44}Cl_4N_2OP_2RuS$	$C_{49}H_{40}N_2OP_2RuS$
M_r	883.94	1046.99	873.95	1013.73	867.90
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Crystal colour	Pale green	Yellow	Pale yellow	Pale yellow	Pale yellow
Crystal size/mm	0.10 × 0.05 × 0.05	0.48 × 0.32 × 0.29	0.36 × 0.33 × 0.28	0.44 × 0.12 × 0.08	0.34 × 0.29 × 0.12
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	22.696(4)	10.9391(7)	21.805(4)	23.5333(18)	14.773(3)
b/Å	17.373(3)	12.3109(7)	17.420(3)	10.4216(8)	15.086(4)
c/Å	23.941(5)	19.1341(11)	24.246(5)	19.0208(15)	19.255(5)
α/°	90.00	104.0690(10)	90.00	90.00	90.00
β/°	115.104(4)	100.5600(10)	114.296(3)	100.4770(10)	109.123(4)
γ/°	90.00	97.9500(10)	90.00	90.00	90.00
V/Å^3	8548(3)	2411.6(2)	8394(3)	4587.2(6)	4054.4(16)
Z	8	2	8	4	4
D_c/g cm^{-3}	1.374	1.442	1.383	1.468	1.422
T/K	125(2)	293(2)	150(2)	150(2)	150(2)
μ(Mo-Kα)/mm^{-1}	0.530	0.630	0.539	0.730	0.558
F(000)	3648	1076	3616	2072	1784
Reflections collected	36848	21333	72069	39496	35137
Unique reflections (R_{int})	12288 (0.1120)	11124 (0.0148)	20066 (0.0485)	10943 (0.0347)	9688 (0.0449)
R_1 ($I > 2\sigma(I)$)	0.0474	0.0378	0.0469	0.0434	0.0368
wR_2 (all data)	0.0937	0.0980	0.1159	0.1056	0.0995
$\Delta\rho_{max,\ min}$/e Å^{-3}	0.605, −0.585	1.881, −1.684	1.238, −0.976	1.276, −0.814	0.923, −0.428

[M − MI]$^+$, 725 (2) [M − CO − MI]$^+$, 652 (5) [M − MI − C≡CPh]$^+$, 605 (29) [M − PPh_3]$^+$, 576 (28) [M − CO − PPh_3]$^+$. Anal. Calc. for $C_{49}H_{40}N_2OP_2RuS$·0.25$CHCl_3$: C, 65.9; H, 4.5; N, 3.1%. Found: C, 66.2; H, 4.6; N, 3.1%.

Preparation of [OsH(κ²-MI)(CO)(PPh_3)$_2$] (15)

Colourless product (84 mg, 90%) obtained by the same general procedure as for **2** from [OsHCl(CO)(BTD)(PPh_3)$_2$] (100 mg, 0.109 mmol). IR (KBr/Nujol): 2098 [ν(OsH)], 2060, 1888 [ν(CO)], 1309, 1292, 971, 891, 844, 812 cm^{-1}. IR (CH_2Cl_2): 2087 [ν(OsH)], 1898 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 23.0 ppm. ^1H NMR ($CDCl_3$): −15.31 [t, OsH, 1H, J_{HP} = 16.4 Hz], 2.48 [s, CH_3, 3H], 5.40 [d, NCH, 1H, J_{HH} = 1.7 Hz], 5.47 [d, NCH, 1H, J_{HH} = 1.7 Hz], 7.28, 7.62 [m × 2, PC_6H_5, 30H] ppm. FAB-MS m/z (abundance): 857 (1.3) [M]$^+$. Anal. Calc. for $C_{41}H_{36}N_2OOsP_2S$: C, 57.5; H, 4.2; N, 3.3%. Found: C, 57.3; H, 4.2; N, 3.3%.

Preparation of [Os(CH=CHPh)(CO)(κ²-MI)(PPh_3)$_2$] (16)

(a) Pale yellow product (72 mg, 77%) obtained by the same general procedure as for **2** from [Os(CH=CHPh)Cl(CO)(BTD)-(PPh_3)$_2$] (100 mg, 0.098 mmol). (b) [OsHCl(CO)(BTD)(PPh_3)$_2$] (50 mg, 0.055 mmol) and phenylacetylene (12 mg, 0.118 mmol) were dissolved in dichloromethane (20 mL) and stirred for 10 min to give a deep purple solution. A dichloromethane solution (5 mL) of 1-methyl-2-mercaptoimidazole (7 mg, 0.061 mmol) was added followed by potassium hydroxide (5 mg, 0.089 mmol) in water (0.5 mL) and ethanol (5 mL) and the reaction stirred for a further hour. Reduction in solvent volume (rotary evaporator) yielded a pale yellow product which was washed with water (5 mL), ethanol (10 mL) and hexane (10 mL). Yield: 41 mg (78%). The product can be recrystallised from dichloromethane and ethanol. IR (KBr/Nujol): 1891 [ν(CO)], 1309, 1291, 968, 954, 9001, 805 cm^{-1}. IR (CH_2Cl_2): 1897 [ν(CO)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 16.4 ppm; ^1H NMR ($CDCl_3$): 2.41 [s, NCH_3, 3H], 5.35 [d, NCH, 1H, J_{HH} = 1.8 Hz], 5.81 [d, Hβ, 1H, J_{HH} = 16.6 Hz], 6.06 [d, NCH, 1H, J_{HH} = 1.8 Hz], 6.41 [d, *ortho*-C_6H_5, 2H, J_{HH} = 7.0 Hz], 6.78 [t, *para*-C_6H_5, 1H, J_{HH} = 7.3 Hz] 6.94 [d, *meta*-C_6H_5, 2H, J_{HH} = 7.5 Hz], 7.08, 7.41 [m × 2, C_6H_5, 30H], 8.36 [dt, Hα, 1H, J_{HH} = 16.6 Hz, J_{PH} = 3.0 Hz] ppm. FAB-MS m/z (abundance): 957 (0.4) [M]$^+$, 856 (0.6) [M − vinyl]$^+$, 714 (0.5) [M − CO − vinyl − MI]$^+$. Anal. Calc. for $C_{49}H_{42}N_2OOsP_2S$: C, 61.4; H, 4.4; N, 2.9%. Found: C, 60.9; H, 4.3; N, 2.8%.

Crystallography

Crystals of complexes **4**, **7**, **11**, **12** and **14** were grown by slow diffusion of a dichloromethane solution of the complexes into ethanol. A single crystal of each compound 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 (**11**, **12** and **14**), 293 ± 2 K (**7**) or 125 ± 2 K (**4**). Data reduction and integration was carried out with SAINT+ and absorption corrections applied using the programme SADABS. The structures were 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.[39] See Table 1 for selected crystal data.

CCDC reference numbers 262800–262804.

See http://www.rsc.org/suppdata/dt/b5/b501906k/ for crystallographic data in CIF or other electronic format.

Acknowledgements

J. D. E. T. W.-E. gratefully acknowledges the Ramsay Memorial Trust for provision of a Fellowship. We thank the Department of Chemistry, the University of London Central Research Fund and the UCL Graduate School for consumables and Johnson Matthey Ltd for a generous loan of ruthenium salts.

References

1 H. Werner, M. A. Esteruelas and H. Otto, *Organometallics*, 1986, **5**, 2295.
2 M. R. Torres, A. Vegas, A. Santos and J. Ros, *J. Organomet. Chem.*, 1986, **309**, 169.
3 For an overview of the vinyl and acetylide chemistry of ruthenium(II), see: A. F. Hill, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 7.
4 S. Jung, K. Ilg, C. D. Brandt, J. Wolf and H. Werner, *Eur. J. Inorg. Chem.*, 2004, 469; S. Jung, C. D. Brandt, J. Wolf and H. Werner,

Dalton Trans., 2004, 375; H. Werner, S. Jung, P. Gonzalez-Herrero, K. Ilg and J. Wolf, *Eur. J. Inorg. Chem.*, 2001, 1957; S. Jung, K. Ilg, J. Wolf and H. Werner, *Organometallics*, 2001, **20**, 2121; H. Werner, W. Stüer, S. Jung, B. Weberndörfer and J. Wolf, *Eur. J. Inorg. Chem.*, 2002, 1076; H. Werner, A. Stark, P. Steinert, C. Grunwald and J. Wolf, *Chem. Ber.*, 1995, **128**, 49.

5 R. Castarlenas, M. A. Esteruelas and E. Oñate, *Organometallics*, 2001, **20**, 2294; M. A. Esteruelas, C. García-Yebra, M. Oliván, E. Oñate and M. Tajada, *Organometallics*, 2000, **19**, 5098; R. Castarlenas, M. A. Esteruelas and E. Oñate, *Organometallics*, 2000, **19**, 5454; M. L. Buil, M. A. Esteruelas, C. García-Yebra, E. Gutiérrez-Puebla and M. Oliván, *Organometallics*, 2000, **19**, 2184; C. Bohanna, M. L. Buil, M. A. Esteruelas, E. Oñate and C. Valero, *Organometallics*, 1999, **18**, 5176; C. Bohanna, B. Callejas, A. J. Edwards, M. A. Esteruelas, F. J. Lahoz, L. A. Oro, N. Ruiz and C. Valero, *Organometallics*, 1998, **17**, 373; M. A. Esteruelas, A. V. Gómez, A. M. López and E. Oñate, *Organometallics*, 1998, **17**, 3567; M. A. Esteruelas, F. Liu, E. Oñate, E. Sola and B. Zeier, *Organometallics*, 1997, **16**, 2919; M. L. Buil, S. Elipe, M. A. Esteruelas, E. Oñate, E. Peinado and N. Ruiz, *Organometallics*, 1997, **16**, 5748; M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro and E. Sola, *J. Am. Chem. Soc.*, 1996, **118**, 89; C. Bohanna, M. A. Esteruelas, J. Herrero, A. M. López and L. A. Oro, *J. Organomet. Chem.*, 1995, **498**, 199; C. Bohanna, M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro and E. Sola, *Organometallics*, 1995, **14**, 4825.

6 B. Gómez-Lor, A. Santos, M. Ruiz and A. M. Echavarren, *Eur. J. Inorg. Chem.*, 2001, 2305; A. M. Castaño, A. M. Echavarren, J. López and A. Santos, *J. Organomet. Chem.*, 1989, **379**, 171; J. Montoya, A. Santos, A. M. Echavarren and J. Ros, *J. Organomet. Chem.*, 1990, **390**, C57; H. Loumrhari, J. Ros, M. R. Torres, A. Santos and A. M. Echavarren, *J. Organomet. Chem.*, 1991, **411**, 255; J. Montoya, A. Santos, J. López, A. M. Echavarren, J. Ros and A. Romero, *J. Organomet. Chem.*, 1992, **426**, 383; J. López, A. Romero, A. Santos, A. Vegas, A. M. Echavarren and P. Noheda, *J. Organomet. Chem.*, 1989, **373**, 249.

7 A. Pedersen, M. Tilset, K. Folting and K. G. Caulton, *Organometallics*, 1995, **14**, 875; A. V. Marchenko, H. Gérard, O. Eisenstein and K. G. Caulton, *New. J. Chem.*, 2001, **25**, 1244; A. V. Marchenko, H. Gérard, O. Eisenstein and K. G. Caulton, *New. J. Chem.*, 2001, **25**, 1382.

8 (*a*) A. F. Hill, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Organometallics*, 1998, **17**, 4249; (*b*) N. W. Alcock, A. F. Hill and R. P. Melling, *Organometallics*, 1991, **10**, 3898; (*c*) A. F. Hill and J. D. E. T. Wilton-Ely, *J. Chem. Soc., Dalton Trans.*, 1999, 3501; (*d*) J. C. Cannadine, A. F. Hill, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Organometallics*, 1996, **15**, 5409; (*e*) A. F. Hill, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, unpublished results; (*f*) A. F. Hill, C. T. Ho and J. D. E. T. Wilton-Ely, *Chem. Commun.*, 1997, 2207; (*g*) J. Cannadine, A. Hector and A. F. Hill, *Organometallics*, 1992, **11**, 2323.

9 R. B. Bedford, A. F. Hill and C. Jones, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 547; R. B. Bedford, A. F. Hill, C. Jones, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *J. Chem. Soc., Dalton Trans.*, 1997, 139; R. B. Bedford, A. F. Hill, C. Jones, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Chem. Commun.*, 1997, 179; A. F. Hill, C. Jones, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Chem. Commun.*, 1998, 367; A. F. Hill, C. Jones, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *J. Chem. Soc., Dalton Trans.*, 1998, 1419; R. B. Bedford, A. F. Hill, C. Jones, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Organometallics*, 1998, **17**, 4744; A. F. Hill, C. Jones and J. D. E. T. Wilton-Ely, *Chem. Commun.*, 1999, 451.

10 The BTD complexes were prepared using the same procedure reported for the BSD (2,1,3-benzoselenadiazole) analogues, in M. C. J. Harris and A. F. Hill, *Organometallics*, 1991, **10**, 3903.

11 (*a*) J. Montoya, A. Santos, A. M. Echavarren and J. Ros, *J. Organomet. Chem.*, 1990, **390**, C57; (*b*) H. Loumrhari, J. Ros, M. R. Torres, A. Santos and A. M. Echavarren, *J. Organomet. Chem.*, 1991, **411**, 255; (*c*) J. Montoya, A. Santos, J. López, A. M. Echavarren, J. Ros and A. Romero, *J. Organomet. Chem.*, 1992, **426**, 383; (*d*) C. Bohanna, M. A. Esteruelas, F. J. Lahoz, E. Oñate and L. A. Oro, *Organometallics*, 1995, **14**, 4685; (*e*) G. Bellachioma, G. Cardaci, V. Gramlich, A. Macchioni, F. Pieroni and L. M. Venanzi, *J. Chem. Soc., Dalton Trans.*, 1998, 947; (*f*) C. Bohanna, M. A. Esteruelas, F. J. Lahoz, E. Oñate and L. A. Oro, *Organometallics*, 1995, **14**, 4685.

12 (*a*) H. Loumrhari, L. Matas, J. Ros, M. R. Torres and A. Perales, *J. Organomet. Chem.*, 1991, **403**, 373; (*b*) M. R. Torres, A. Perales, H. Loumrhari and J. Ros, *J. Organomet. Chem.*, 1990, **384**, C61; (*c*) M. R. Torres, A. Perales, H. Loumrhari and J. Ros, *J. Organomet. Chem.*, 1990, **385**, 379.

13 H. Loumrhari, J. Ros and M. R. Torres, *Polyhedron*, 1991, **10**, 421.

14 R. B. Bedford and C. S. J. Cazin, *J. Organomet. Chem.*, 2000, **598**, 20.

15 A. L. Hector and A. F. Hill, *J. Organomet. Chem.*, 1993, **447**, C7.

16 H. Loumrhari, J. Ros, R. Yáñez and M. R. Torres, *J. Organomet. Chem.*, 1991, **408**, 233.

17 H. Adams, P. E. McHugh, M. J. Morris, S. E. Spey and P. J. Wright, *J. Organomet. Chem.*, 2001, **619**, 209.

18 J. López, A. Santos, A. Romero and A. M. Echavarren, *J. Organomet. Chem.*, 1993, **443**, 221.

19 A. Santos, J. López, A. Galán, J. J. González, P. Tinoco and A. M. Echavarren, *Organometallics*, 1997, **16**, 3482.

20 U. Bandyopadhyay, K. Biswas and R. K. Banerjee, *Toxicol. Lett.*, 2002, **128**, 117; A. D. Toft, *N. Engl. J. Med.*, 2001, **345**, 512; D. S. Cooper, *N. Engl. J. Med.*, 1984, **311**, 1353; E. C. Bartels and R. W. Sjogren, *Clin. Endocrinol.*, 1951, **11**, 1057.

21 (*a*) D. Li, Y-F. Luo, T. Wu and S. W. Ng, *Acta Crystallogr., Sect. E*, 2004, **60**, 726; (*b*) A. Silvestri, G. Ruisi and M. A. Girasolo, *J. Inorg. Biochem.*, 2002, **92**, 171; (*c*) G. Lowe, S. A. Ross, M. Probert and A. Cowley, *Chem. Commun.*, 2001, 1288; (*d*) J. Jolley, W. I. Cross, R. G. Pritchard, C. A. McAuliffe and K. B. Nolan, *Inorg. Chim. Acta.*, 2001, **315**, 36; (*e*) R. S. Balestrero, D. M. Forkey and J. G. Russell, *Magn. Reson. Chem.*, 1986, **24**, 651; (*f*) R. A. McAllister, *Nature*, 1952, **169**, 708.

22 The BTD complexes were prepared using the same procedure reported for the BSD (2,1,3-benzoselenadiazole) analogues, in N. W. Alcock, A. F. Hill and M. S. Roe, *J. Chem. Soc., Dalton Trans.*, 1990, 1737.

23 J. López, A. Romero, A. Santos, A. Vegas, A. M. Echavarren and P. Noheda, *J. Organomet. Chem.*, 1989, **373**, 249.

24 (*a*) A. Romero, A. Santos, J. López and A. M. Echavarren, *J. Organomet. Chem.*, 1990, **391**, 219; (*b*) M. R. Torres, A. Santos, A. Perales and J. Ros, *J. Organomet. Chem.*, 1988, **353**, 221.

25 A. F. Hill, M. C. J. Harris and R. P. Melling, *Polyhedron*, 1992, **11**, 781.

26 S. T. Nguyen, L. K. Johnson, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1992, **114**, 3974.

27 M. C. J. Harris and A. F. Hill, *J. Organomet. Chem.*, 1992, **438**, 209.

28 I. M. Lyapkalo, M. Webel and H.-U. Reiβig, *Eur. J. Org. Chem.*, 2002, 3646; R. Tamura, M. Kato, K. Saegusa, M. Kakihana and D. Oda, *J. Org. Chem.*, 1987, **52**, 4121.

29 W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1977, **142**, C1; C. E. F. Rickard, W. R. Roper, G. E. Taylor, J. M. Waters and L. J. Wright, *J. Organomet. Chem.*, 1990, **389**, 375.

30 S. M. Maddock, C. E. F. Rickard, W. R. Roper and L. J. Wright, *Organometallics*, 1996, **15**, 1793.

31 R. B. Bedford, A F. Hill, A. R. Thompsett, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1996, 1059.

32 A. F. Hill and R. P. Melling, *J. Organomet. Chem.*, 1990, **396**, C22.

33 L. Vaska, *J. Am. Chem. Soc.*, 1964, **86**, 1943.

34 A. Coto, I. de los Ríos, M. Jiménez Tenorio, C. Puerta and P. Valerga, *J. Chem. Soc., Dalton Trans.*, 1999, 4309.

35 N. Kuhnert, N. Burzlaff, E. Dombrowski and W. A. Schenk, *Z. Naturforsch., Teil B*, 2002, **57**, 259.

36 C. J. Adams and S. J. A. Pope, *Inorg. Chem.*, 2004, **43**, 3492.

37 K. R. Laing and W. R. Roper, *J. Chem. Soc. A*, 1970, 2149.

38 M. R. Torres, A. Vegas, A. Santos and J. Ros, *J. Organomet. Chem.*, 1987, **326**, 413.

39 *SHELTXTL V 6.10 Bruker AXS*, 2000.