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

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A series of vinyl, acyl and silyl complexes [Ru(R)(κ2-MI)(CO)(PPh3)2] (R = CH=CH2, CH=CHPh, CH=CHC6H4CH3-4, CH=CHFBU, CH=CHCPh2OH, C≡CPh=CHPh, C≡CPh, C≡CPh, SiMe2OEt; MI = 1-methylimidazole-2-thiolate) were prepared from either [Ru(R)Cl(CO)(PPh3)2] or [Ru(R)Cl(CO)(BTD)(PPh3)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)(PPh3)2] was prepared from [OsH(CO)(CPh=CHPh)(PPh3)2] with [RuHCl(CO)(PPh3)3] and [OsHCl(CO)(BTD)(PPh3)2], respectively. Reaction of [Ru(CH=CHPh)(κ2-MI)(CO)(PPh3)2] with 1-methyl-2-mercaptoimidazole and NaOMe without migration to yield [Ru(CH=CHPh)(κ2-MI)(CS)(PPh3)2], while treatment of [Ru(CH=CHPh)(κ2-MI)(CO)(PPh3)2] with HBF4 yielded the vinyl carbene [Ru(CH=CHPh,κ2-MI)(CO)(PPh3)2]BF4. The hydride complexes [MH(κ2-MI)(CO)(PPh3)2] (M = Ru, Os) were obtained from the reaction of HMI and KOH with [RuH(CO)(PPh3)2] and [OsH(CO)(BTD)(PPh3)2], respectively. Reaction of [Ru(CH=CHC6H4CH3-4)(κ2-MI)(CO)(PPh3)2] with excess HCl=CPH leads to isolation of the acetyl complex [Ru(C≡CPh(κ2-MI)(CO)(PPh3)2)], which is also accessible by direct reaction of [Ru(C=CPh)(CO)(BTD)(PPh3)2] with 1-methyl-2-mercaptoimidazole and NaOMe. The thiocarbonyl complex [Ru(CPh=CHPh)(κ2-MI)(CO)(PPh3)2] reacted with HMI and NaOMe without migration to yield [Ru(CPh=CHPh)(κ2-MI)(CS)(PPh3)2], while treatment of [Ru(CH=CHPh)(κ2-MI)(CO)(PPh3)2] with HMI yielded the monodentate acyl product [Ru(κγ-C≡C=O)(CH=CHPh)(κ2-MI)(CO)(PPh3)2]. The single-crystal X-ray structures of five complexes bearing vinyl, acyl, acetylide and dienyl functionality are reported.

Introduction

The coordinatively-unsaturated vinyl complexes [Ru(R)=CHR(CO)(PR3)2] (R = H, Ph etc.; R′ = PR3 Ph) have been shown to be useful starting points for the exploration of the chemistry of the vinyl ligand and has been the focus of our previous work on the addition of monodentate and tridentate ligands. This has been mirrored by recent work on the phosphoryl analogues 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 and isocyanide to [Ru(R)=CHR(CO)(PR3)2] yields coordinatively saturated compounds and even can induce migration of the vinyl group to form acyl complexes. In the last ten years, significant interest has been shown in the reactivity with polydentate donors such as pyrazolylborates and macrocyclic thioethers. However, typically these ligands have contained just one type of donor element (O, S or N). Bidentate ligands, such as carboxylate, xanthate, dithiocarbamate, S2CPCy3, alkylidithiocarbamate, alkylidithiocarboxylate, dithiobispyrazolylborate and bipyridyl 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, due to its ability to inhibit the formation of thyroid hormones. It is a biorelevant molecule and the presence of both sulfur and nitrogen donors, has been very little exploration of the coordination chemistry of such mercaptoimidazoles as ligands for metal complexes. Apart from one study in which mercaptoimidazole was used to bridge two platinum(II) centres, 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 suggests 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 [RuH(CO)(PPh3)2]. Due to the strong trans effect of the hydride ligand in the starting material, the loss of the PPh3 ligand occurs readily, creating a vacant site for coordination of the MI ligand, and the reaction is complete within 10 min (1H 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 1H 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 31P NMR spectrum indicated a mutually trans-disposition for the phosphine ligands. Three additional resonances were seen in the 1H NMR spectrum at 2.61 (s, NCH3), 5.85 (d, JMI = 1.4 Hz) and 5.67 (d, JMI = 1.4 Hz) ppm in addition to those for the PPh3 ligands. Heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond coherence
(HMBC) NMR experiments permitted the latter resonances to be assigned to the H' and H" 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.

Typical features were observed for the carbonyl (t, 206.1 ppm, \( J_{\text{CP}} = 15.0 \text{ Hz} \)) and triphenylphosphine ligands in the \(^{13}C\) NMR spectrum alongside four resonances for the MI ligand 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 C4 carbon and the 117.3 and 125.7 ppm resonances to the C5 and C4 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(k^2-MI)(CO)(PPh3)]\(_2\).

The 16-electron ruthenium vinyl species [RuCR=CHR(CO)(PPh3)]\(_2\) are conveniently prepared by hydreurhenation of the appropriate alkyne by [RuHCl(CO)(PPh3)]\(_2\).

Coordinatively-saturated variants are accessible from starting materials [RuHCl(CO)(L)(PPh3)] bearing weakly coordinating ligands (L) such as BTD (2,1,3-benzothiadiazole), acetonitrile, pyridine and pyrazoles. Reaction of the pale orange complex, [RuCl(CH=CH)(CO)(PPh3)] 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).

The \(^1H\) NMR spectrum of the complex showed a doublet of doublets at 4.76 ppm (\( J_{\text{HH}} = 17.5, J_{\text{CP}} = 1.3 \text{ Hz} \)) for the β-proton and another doublet of doublets at 7.38 ppm, coupling to both β-protons (\( J_{\text{HH}} = 17.5, J_{\text{HH}} = 10.0 \text{ Hz} \)) and to the two phosphorus nuclei (\( J_{\text{HP}} = 3.2 \text{ Hz} \)). Similar spectroscopic data for the MI ligand were observed to those for complex I. The new product was formulated as [RuH(CH=CH)](k^2-MI)(CO)(PPh3)]\(_2\). Under the same experimental conditions, the yellow complex, [Ru(CH=CHPh)(k^2-MI)(CO)(PPh3)]\(_2\) (3), was prepared from [Ru(CH=CHPh)(CO)(PPh3)]\(_2\). The \(^1H\) NMR spectrum of 3 showed well-defined resonances for the vinylic α- and β-protons at 7.92 (dd, \( J_{\text{HH}} = 16.2 \text{ Hz}, J_{\text{HP}} = 3.6 \text{ Hz} \)) and 5.92 ppm (\( J_{\text{HH}} = 16.2 \text{ Hz} \)). The tolyl version of this complex [Ru(CH=CHC6H4CH3-4)(k^2-MI)(CO)(PPh3)]\(_2\) (4), was isolated in an analogous fashion as a microcrystalline solid. The \(^13C\) NMR spectrum displayed resonances for the MI ligand similar to those for complex I. Two low field triplets at 154.2 (t, \( J_{\text{CP}} = 11.0 \text{ Hz} \)) and 206.5 ppm (t, \( J_{\text{CP}} = 16.1 \text{ Hz} \)) 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 \(^13C\) NMR spectrum but an HMQC experiment showed a cross peak with the Hn 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).

The complex [Ru(CH=CHBu)(k^2-MI)(CO)(PPh3)]\(_2\) (5) was obtained from [Ru(CH=CHBu)(CO)(PPh3)]\(_2\) 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)(PPh3)]\(_2\) by sequential treatment with 3,3-dimethylbut-1-yne, 1-methyl-2-mercaptoimidazole and NaOMe. Interestingly, reaction between the hydride and the MI ligand, 1, and excess terminal alkylke failed to generate vinyl complexes of the type discussed above. Although complex I 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 PPh3 ligand). However, the requirement for hydrometalation of a vacant site cis to the hydride may not be satisfied by hemiamelity 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≡CPh)(CHPh)(CO)(PPh3)]\(_2\) with 1-methyl-2-mercaptoimidazole in the presence of sodium methoxide. The presence of the vinyl ligand in the resulting yellow complex, [RuCl(C≡CPh)(CHPh)(k^2-MI)(CO)(PPh3)]\(_2\) (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 vinyl proton at 6.16 ppm.

Our previous work has explored the involvement of thio-carbonyl ligands in migratory insertion reactions with organic groups. In order to explore the effect of incorporating a thio-carbonyl ligand in the system, the orange 16-electron thio-carbonyl complex [Ru(CPh=C≡CHPh)Cl(CS)(PPh3)]\(_2\) was treated...
with 1-methyl-2-mercaptoimidazole and sodium methoxide. A bright yellow solid, formulated as [Ru(CP(Ph)=CHPh)(κ²-MI)(CS)(PPh₃)] (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 firming the continuing presence of the thiocarbonyl ligand and 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.

Treatment of the coordinately-saturated, colourless complex [Ru(Cl)(CH≡CHPh)(CO)(PPh₃)] with 1-methyl-2-mercaptopimidazole 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 for migration is greater for alkyl than aryl or vinyl ligands.

Molecular structure of [Ru(CPh₂)(CO)(PPh₃)] 11

A number of examples have been reported of vinyl migration induced by addition of π-acid ligands such as carbon monoxide or isocyanide.

with dihydrobis(pyrazol-1-yl)borate to yield the acetyl complex [Ru(η²-C(=O)CH₃)(CO)(κ²-MI)(PMe₃)] 11/ and [Ru(η²-C(=O)CH₃)(CO)(PPh₃)].

Dehydration reactions

A fascinating extension of the use of conventional alkenes in hydrometallation reactions is the use of propargylic alcohols. Hydrometallation of 1,1-diphenylprop-2-yn-1-ol with [RuCl(CO)(BTD)(PPh₃)] has been shown to yield [Ru(=CHCPh₂OH)(CO)(BTD)(PPh₃)] 11/ The BTD and chloride ligands in this complex were readily replaced by the MI ligand to yield [Ru(=CHCPh₂OH)(=CH₂-MI)(CO)(PPh₃)] 11/ This complex gave rise to a molecular ion at m/z 977 in the FAB-MS spectrum along with a fragmentation for [M-OH].

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

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 ¹H 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, JHH = 10.2 Hz) for the Grubbs vinyl carbene complex [RuCl₂(=CHCH=CHPh)](PPh₃) 11/ which indicated that protonation and subsequent dehydration had occurred to yield the cation, [Ru(=CHCPh₂OH)(=CH₂-MI)(CO)(PPh₃)]BF₄ (10) (Scheme 3). The ν(CO) band at 1605 cm⁻¹ in the solid-state IR spectrum 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 deuterocloroform with HBF₄·Et₂O resulted initially 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 ¹H 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, JHH = 10.2 Hz) for the Grubbs vinyl carbene complex [RuCl₂(=CHCH=CHPh)](PPh₃) 11/ which indicated that protonation and subsequent dehydration had occurred to yield the cation, [Ru(=CHCPh₂OH)(=CH₂-MI)(CO)(PPh₃)]BF₄ (10) (Scheme 3). The ν(CO) band at 1605 cm⁻¹ in the solid-state IR spectrum 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 deuterocloroform with HBF₄·Et₂O resulted initially in a dramatic colour change to yield an intense green precipitate.

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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 CH₂ 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. 'H NMR data reported for E-(2-cyclohex-1-enyl)styrene supports this assignment with a triplet at 5.90 ppm (JHH = 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≡CHC₆H₉)₂(κ²-MI)(CO)(PPh₃)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(C₆H₅)Cl(CO)(PPh₃)₂]. This red complex undergoes rapid reaction with the deprotonated MI ligand to yield [Ru(C₆H₅)(κ²-MI)(CO)(PPh₃)₂] (12) as shown in Scheme 4.

The aryl ligand was identified in the 'H NMR spectrum from an overlapping multiplet at 6.41 ppm for the meta- and para-protons and a doublet at 6.99 ppm (JHH = 6.7 Hz) attributed to the ortho-protons. Single crystals of this complex were also obtained and a structural study undertaken (Fig. 4):
The compound [Ru(C₆H₅)Cl(CO)(PPh₃)₂] is also a versatile starting material for complexes with other σ-bonded ligands such as [Ru(SiMe₂OEt)(CO)(PPh₃)₂], which was found to react with the MI ligand in an analogous fashion to the vinyl and aryl species discussed above to give [RuHCl(CO)(κ⁻MI)(CO)(PPh₃)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 'H NMR spectrum.

Acetylide complexes of ruthenium(II) are readily accessible by a variety of routes. For example, the complex [Ru(C≡CPh)Cl(CO)(BTD)(PPh₃)₂] can be conveniently prepared from [RuHCl(CO)(BTD)(PPh₃)₂] and H₂[C≡CPh] (14), however it is worth noting that [RuHCl(CO)(PPh₃)₂] reacts with mercury bis(acetylides) to yield the but-3-en-1-yn-3-yl complexes, [Ru(C≡CPh)Cl(CO)(PPh₃)₂], rather than products bearing an acetylide ligand. Treatment of [Ru(C≡CPh)Cl(CO)(BTD)(PPh₃)₂] with 1-methyl-2-mercaptoimidazole and base yields [Ru(C≡CPh)(κ⁻MI)(CO)(PPh₃)₂] (14) in moderate yield as shown in Scheme 5:

Scheme 5 Reagents and conditions: (i) excess HC≡CPh, heat; (ii) HCl=CC₆H₄Me-4; (iii) MI, NaOMe, (iv) Hg(C≡CPh), heat.

The retention of the acetylide functionality was indicated by a ν(C≡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 '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 and that of others has shown an acetylide ligand can be generated by heating vinyl species with excess alkylene. Thus, heating [Ru(CH≡CHC₆H₄Me-4)(κ⁻MI)(CO)(PPh₃)₂] (4) with excess phenylacetylene in 1,2-dichloroethane yielded the acetylide complex [Ru(C≡CPh)(κ⁻MI)(CO)(PPh₃)₂] (14) by a second route. The mechanism of this reaction is unclear but a plausible suggestion is the formation of a Ru(tv) intermediate from oxidative addition of the H–C bond of the alkylene followed by reductive elimination of H,Cl=CHC₆H₄Me-4 (detected by '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., PPh₃) or by opening of the MI chelate. No free triphenylphosphine was detected in samples of the reaction mixture analysed by ³¹P 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 [OsHCl(CO)(BTD)(PPh₃)₂] 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)(PPh₃)₂] is not sufficient to labilise a phosphine and generate a vacant coordination site, in contrast to the ruthenium analogue.

Reaction of [OsHCl(CO)(BTD)(PPh₃)₂] with the HMI ligand in the presence of potassium hydroxide led to isolation of [OsH(κ⁻MI)(CO)(PPh₃)₂] (15) in good yield (Scheme 6). A high field triplet resonance was observed at −15.31 ppm (Jₚₚ = 16.4 Hz) in the 'H NMR spectrum for the hydride. Hydroosmation of phenylacetylene by [OsHCl(CO)(BTD)(PPh₃)₂] provides the purple complex [Os(CH≡CPhHCl(CO)(BTD)(PPh₃)₂] which was found to be dissociative on heating with 1-methyl-2-mercaptoimidazole and base yields [OsHCl(CO)(κ⁻MI)(CO)(PPh₃)₂] (14) in moderate yield as shown in Scheme 5:

Scheme 6 Reagents: (i) NaOMe, (ii) HC≡CPh.
of all the structures discussed here, the acetylide complex 
\[\text{Ru}(\text{C}=\text{CH})\left(\kappa^2\text{-MI}\right)\left(\text{CO}\right)(\text{PPh}_3)_2\] (14) is unique by virtue of the \(\sigma\)-organyl ligand being \textit{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 \textit{trans} influence of the acetylide ligand.\(^1\) Recently the structure of the acetylide complex \([\text{Ru}(\text{C}=\text{BH})\text{Cl}(\kappa^2\text{-Me}-\text{bipy})\text{(PPh}_3)_2]\) \(\text{(Me}_{\text{bipy}} = \text{dimethylbipyridyl)}\) has been reported.\(^2\) In this structure, the \textit{trans} influence of the \textit{C}=\text{BH} ligand results in Ru–N bond lengths of 2.120(4) \(\text{Å}\) \(\text{(trans to acetylide)}\) and 2.051(3) \(\text{Å}\) \(\text{(trans to chloride)}\). This compares well with the Ru1–N1 distance of 2.1441(18) \(\text{Å}\) in complex 14. The Ru1–C2 bond length of 2.019(2) \(\text{Å}\) in 14 is similar to the same feature in \([\text{Ru}(\text{C}=\text{BH})\text{Cl}(\kappa^2\text{-Me}-\text{bipy})\text{(PPh}_3)_2]\) of 2.053(5) \(\text{Å}\), while the C2–C3 triple bond is slightly longer \(\left(2.046(3)\right)\) \(\text{Å}\) in 14 than the distance found in \([\text{Ru}(\text{C}=\text{BH})\text{Cl}(\kappa^2\text{-Me}-\text{bipy})\text{(PPh}_3)_2]\) of 1.174(6) \(\text{Å}\). The acetylide ligand is essentially linear in both complexes.

**Conclusion**

This report has demonstrated the 1-methylimidazol-2-thiolate (MI) ligand to be an effective bidentate mixed-donor chelate for complexes of ruthenium(ii) bearing a wide range of \(\sigma\)-organyl and \(\sigma\)-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 \(\left(80\,^{\circ}\text{C}\right)\) 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\(_2\text{Cl}_2\) 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’ indicates a virtual triplet nuclear magnetic resonance. NMR spectroscopy was carried out at 25 \(^{\circ}\text{C}\) using Bruker AMX-300 (\(1^H: 299.87\) MHz, \(13C: 75.40\) MHz) or Bruker DRX-500 (\(1^H: 501.13\) MHz, \(13C: 125.77\) MHz) spectrometers. FAB-MS spectra (nitrobenzyl alcohol matrices) were measured using a VG 70-5B 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 \(^1\text{H}\) NMR spectra of the complexes. The complexes \([\text{Ru}(\text{CH}=\text{CH})(\kappa^2\text{-MI})(\text{CO})(\text{PPh}_3)_2]\).\(^{17}\) \([\text{Ru}(\text{CH}=\text{CH})(\kappa^2\text{-MI})(\text{CO})(\text{PPh}_3)_2]\).\(^{17}\) \([\text{Ru}(\text{CH}=\text{CH})(\kappa^2\text{-MI})(\text{CO})(\text{PPh}_3)_2]\).\(^{17}\) \([\text{Ru}(\text{CH}=\text{CH})(\kappa^2\text{-MI})(\text{CO})(\text{PPh}_3)_2]\).\(^{17}\) \([\text{Ru}(\text{CH}=\text{CH})(\kappa^2\text{-MI})(\text{CO})(\text{PPh}_3)_2]\).\(^{17}\)

**Preparation of \([\text{Ru}(\kappa^2\text{-MI})(\text{CO})(\text{PPh}_3)_2]\) (1)**

\([\text{Ru}(\text{CH}=\text{CH})(\kappa^2\text{-MI})(\text{CO})(\text{PPh}_3)_2]\) \(200\,\text{mg}, 0.210\,\text{mmol}\) and 1-methyl-2-mercaptomidazole \(26\,\text{mg}, 0.228\,\text{mmol}\) 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 (CHCl₃): 1973 (sh) [ν(RuH)] 1919 [ν(CO)] cm⁻¹. ³¹P[H] NMR (CDCl₃): 49.9 ppm. H NMR (CDCl₃): –13.05 [t, RuH, 1H, J = 19.4 Hz], 2.61 [d, CH₃, 3H], 5.58 [d, NCH, 1H, J = 1.4 Hz], 5.67 [d, NCH, 1H, J = 1.4 Hz], 7.25, 7.62 [m, 2 × C₆H₅, 30H] ppm. ¹³C[H] NMR (CDCl₃): 30.2 [s, CH₃], 117.3 [s, NCH], 125.7 [s, NCH], 127.9 [t, ν(m-PCH₃), J = 5.9 Hz], 129.7 [s, ν(p-PCH₃), J = 4.6 Hz], 135.4 [t, ipso-PCH₃, J = 20.7 Hz], 156.5 [s, NCH], 206.1 [t, CO, J = 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 C₂₀H₂₀N₄OPRu: C, 63.6%; H, 4.8% N, 3.0%.

Preparation of [Ru(CHO=CH)₂(C₆H₅)(CO)(PPh₃)](5)

Pale yellow microcrystalline product (73 mg, 66%) obtained by the same general procedure as for 2 from [Ru(CHO=CH-Bu)(C₆H₅)(CO)(PPh₃)](5) (100 mg, 0.130 mmol). IR (KBr/Nujol): 1909 [ν(C=O), 1572, 1320, 1288, 1258, 970 cm⁻¹ IR (CHCl₃): 1900 [ν(C=O)] cm⁻¹. ³¹P[H] NMR (CDCl₃): 43.6 ppm. H NMR (CDCl₃): 0.42 [s, CMe₃, 9H], 2.49 [s, CH₃, 3H], 5.92 [d, H₂, J = 15.9 Hz], 5.51 [d, NCH, 1H, J = 1.7 Hz], 6.05 [d, NCH, 1H, J = 1.6 Hz], 7.64 [dt, H₀, 1H, J = 15.9, J = 3.3 Hz], 7.23–7.96 [m, PC₆H₅, 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 – PPh₃], 560 (57) [M – CO – PPh₃], 505 (16) [M – vinyl – PPh₃], 487 (52) [M – vinyl – CO – PPh₃]. Anal. Calc. for C₂₀H₂₀N₄OPRu: C, 63.9%; H, 5.3%; N, 3.1%. Found: C, 64.0%; H, 5.2%; N, 3.1%.

Preparation of [Ru(C≡CPh)(PPh₃)](6)

Yellow product (69 mg, 64%) obtained by the same general procedure as for 2 from [Ru(C≡CPh)(PPh₃)](6) (100 mg, 0.112 mmol). IR (KBr/Nujol): 2150 [ν(C≡C), 1921 [ν(C≡C), 1653, 1308, 1297, 905 cm⁻¹ IR (CHCl₃): 2160 [ν(C≡C), 1924 [ν(C≡C)] cm⁻¹. ³¹P[H] NMR (CDCl₃): 40.7 ppm. H NMR (CDCl₃): 2.42 [s, CH₃, 3H], 5.72 [d, NCH, 1H, J = 1.6 Hz], 6.16 [d, NCH, 1H, J = 1.6 Hz], 7.62 [d, ν(o-C₆H₄), 2H], 7.19 [dt, ν(o-C₆H₄), 2H, J = 7.5 Hz], 6.94 [t, ν(par-C₆H₄), 1H, J = 7.5 Hz], 7.05 [t, ν meta-C₆H₄, 2H, J = 7.5 Hz], 7.23, 7.53 [m × 2, PC₆H₅, 30H], 128.3 [s, ν(CO), J = 3.2 Hz] ppm. FAB-MS m/z (abundance): 869 (1.5) [M⁺], 765 (0.25) [M – vinyl], 607 (2) [M – PPh₃], 579 (1) [M – CO – PPh₃]. Anal. Calc. for C₂₆H₂₄N₄OPRu: C, 67.7; H, 4.9%; N, 3.2%. Found: C, 67.3; H, 4.9; N, 3.2%.

Preparation of [Ru(CHO=CH-C₆H₅)(CO)(PPh₃)](7)

Yellow product (101 mg, 65%) obtained by the same general procedure as for 2 from [Ru(CHO=CH-C₆H₅)(CO)(PPh₃)](7) (150 mg, 0.170 mmol). IR (KBr/Nujol): 1716, 1591, 1577, 1554, 1320, 1284, 1260 [ν(C≡C)], 967, 922 cm⁻¹. ³¹P[H] NMR (CDCl₃): 35.5 ppm. H NMR (CDCl₃): 1.92 [s, CH₃], 4.40 [d, NCH, 1H, J = 1.5 Hz], 5.36 [d, NCH, 1H, J = 1.5 Hz], 6.10 [d, ortho-C₆H₄, 2H], 6.86 [t, ν(par-C₆H₄), 1H, J = 1.6 Hz], 7.00 × 7.81 [m, PC₆H₅, 30H], 30H + 5H] ppm. FAB-MS m/z: (abundance): 1068 (1) [M⁺], 848 (0.5) [M – MI], 702 (0.4) [M – vinyl], 649 (1.6) [M – PPh₃], 585 (1.3) [M – CO – PPh₃]. Anal. Calc. for C₂₆H₂₄N₄OPRu: C, 65.3; H, 4.7; N, 2.7%. Found: C, 65.4; H, 4.7; N, 2.7%.
Preparation of $[\text{Ru}([\text{CH}_2\text{C}(\text{O})(\text{C}_6\text{H}_5)\text{Cl}]{\text{PPh}_3})_2\text{]}$ (10)

$[\text{Ru}(\text{CH}=\text{CH}\text{P}h)(\text{C}=\text{M}i)(\text{CO})(\text{PPh}_3)_2]$ (50 mg, 0.051 mmol) was suspended in diethyl ether (5 mL) and treated with HBF$_4$·OEt$_2$ (one drop, excess) causing an intense green precipitate. 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): 1915 [v(CO)] cm$^{-1}$. Anal. Calc. for C$_{49}$H$_{41}$N$_2$O$_2$P$_2$Ru: C, 67.3; H, 5.3; N, 3.1%. Found: C, 66.7; H, 5.1; N, 3.1%.

Preparation of $[\text{Ru}(\text{C}_6\text{H}_5\text{CM})(\text{CO})(\text{PPh}_3)_2]$ (11)

$[\text{Ru}([\text{CH}_2\text{H}]\text{C}(\text{H})(\text{C}=(\text{M}i)(\text{CO})(\text{PPh}_3)_2]$ (70 mg, 0.089 mmol) IR (KBr/Nujol): 1967 [v(CO)] cm$^{-1}$. IR (CHCl$_3$): 1880 [v(CO)] cm$^{-1}$. Anal. Calc. for C$_{48}$H$_{39}$N$_2$O$_2$P$_2$Ru: C, 67.0; H, 4.9; N, 3.1%. Found: C, 66.5; H, 5.0; N, 3.1%.

Preparation of $[\text{Ru}(\text{C}_6\text{H}_5\text{CM})(\text{CO})(\text{PPh}_3)_2]$ (12)

Yield: 28 g (57%). The product was recrystallised from chloroform–ethanol mixture. C$_{56}$H$_{48}$N$_2$O$_2$P$_2$RuS: Anal. Calc. for C, 62.1; H, 4.8; N, 2.5%. Found: C, 61.8; H, 4.7; N, 2.6%.

Preparation of $[\text{Ru}(\text{C}_6\text{H}_5\text{CM})(\text{CO})(\text{PPh}_3)_2]$ (13)

Yield: 28 g (57%). The product was recrystallised from chloroform–ethanol mixture. C$_{49}$H$_{41}$N$_2$O$_2$P$_2$RuS: Anal. Calc. for C, 62.1; H, 4.8; N, 2.5%. Found: C, 61.8; H, 4.7; N, 2.6%.

Preparation of $[\text{Ru}(\text{C}_6\text{H}_5\text{CM})(\text{CO})(\text{PPh}_3)_2]$ (14)

Yield: 28 g (57%). The product was recrystallised from a chloroform–ethanol mixture. IR (KBr/Nujol): 2095 [v(C=C)], 1958, 1940 [v(CO)], 1595, 1319, 1288, 988, 843 cm$^{-1}$. IR (CH$_2$Cl$_2$): 2098 [v(C=C)], 1938 [v(CO)] cm$^{-1}$. Anal. Calc. for C$_{49}$H$_{41}$N$_2$O$_2$P$_2$RuS: C, 62.1; H, 4.8; N, 2.5%. Found: C, 61.8; H, 4.7; N, 2.6%.

Anal. Calc. for C49H42N2OOP2RuS: 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 geometrical and intensity data were taken from this sample on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073 \text{ Å}$) 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. See Table 1 for selected crystal data.

CCDC reference numbers 262800–262804. See http://www.rsc.org/supdata/dt/b5/b501906k/ for crystallographic data in CIF or other electronic format.

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References


