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Room-temperature cyclometallation of amines, imines and oxazolines with $[MCl_2Cp^*]_2$ (M = Rh, Ir) and $[RuCl_2(p\text{-cymene})]_2$ †

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N,*N*-Dimethylbenzylamine, alkyl and aryl imines derived from benzaldehyde, and 2-phenyl-4,4-dimethyloxazoline all undergo cyclometallation with $[IrCl_2Cp^*]_2$ ($Cp^* = \eta\text{-}C_5Me_5$) when treated with NaOAc in dichloromethane at room temperature. The imines are also cyclometallated by $[RhCl_2Cp^*]_2$ under the same conditions whilst only N-alkyl imines are cyclometallated by $[RuCl_2(p\text{-cymene})]_2$. The role of acetate in the cyclometallation is more than just as a base. X-Ray structures of cyclometallated complexes $[MCl\{C_6H_4\text{-}2\text{-}C(H)=NCH_2CH_2OMe\text{-}\kappa C,N\}(\eta\text{-ring})]$(M = Ir, Rh ring = Cp*; M = Ru, ring = *p*-cymene), $[MCl\{C_6H_4\text{-}2\text{-}C(H)=NCH_2CH_2OMe\text{-}\kappa C,N\}Cp^*]$(M = Ir, Rh), $[RuCl(\eta^2\text{-}O_2CMe)(p\text{-cymene})]$ and $[IrCl_2(NH_2Ph)Cp^*]$ are reported.

Introduction

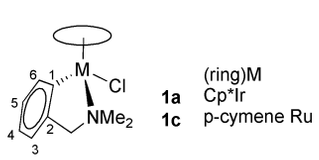
C–H activation is an extremely important process because of its potential for producing functionalised hydrocarbons.[1] Intramolecular C–H activation can lead to cyclometallated complexes;[2] such complexes of the platinum metals were first reported in 1965[3] and have since shown promise in several fields of chemistry particularly catalysis.[4] Though the chemistry of cyclometallation is well established new synthetic routes to such species which only require mild conditions and do not require an M–C bond in the starting material are still desirable. In addition, there is scope to widen the range of metal species that can undergo this process. As part of our research on half-sandwich complexes we were interested in preparing areneruthenium and Cp*M (M = Ir, Rh) complexes with cyclometallated ligands containing nitrogen donor atoms.

Arene ruthenium complexes containing cyclometallated *N*,*N*-dimethylbenzylamine (dmbaH) are known.[5] Such complexes show interesting reactivity particularly in C–C bond forming reactions with ethene,[6] and alkynes.[5] Recently η^1-aryl ruthenium complexes have been shown to be intermediates in a catalytic Heck type coupling.[7] In addition, $[RuCl(dmba)(C_6H_6)]$ has been used as an intermediate in the synthesis of a ruthenium complex for bioelectrochemical applications.[8] Arene ruthenium dmba complexes have traditionally been made by transmetallation with mercury reagents,[5,9] though a C–H activation route using NaOH as a base has recently been reported.[10] Other arene ruthenium complexes with a cyclometallated azobenzene have also been made from mercury reagents.[11] Cyclometallation of benzylideneaniline has been reported with $[RuCl_2(PMe_3)(C_6Me_6)]$ in the presence of $AgBF_4$.[12] More recently cyclometallation of a benzodiazepine has been achieved with $[RuCl_2(p\text{-cymene})]_2$ at room temperature in dichloromethane using NEt_3 as a base in the presence of $NaBPh_4$.[13] Cyclometallated nitrogen containing ligands with Cp*M (M = Rh, Ir) are much rarer, though cyclometallated phosphorus containing ligands have often been identified in C–H activation studies with Cp*M (M = Rh, Ir) complexes.[14] To our knowledge there are only two papers reporting complexes of Cp*M with a cyclometallated nitrogen donor ligand, both with iridium. Activation of an aryl C–H bond occurs in the cyclometallation of phenyl oxazolones, using $[IrCl_2Cp^*]_2$ and NaOAc,[15] whilst reaction of a diimine with $[IrCl_2Cp^*]_2$ leads to activation of a methyl group.[16]

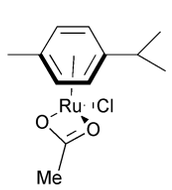
Cyclometallation in palladium chemistry is very well established and $Pd(OAc)_2$ is known to be preferable to $PdCl_2$ as a precursor. Indeed, in some cases addition of acetate to a palladium chloride complex can induce cyclometallation of the ligand.[17] We have therefore investigated the use of NaOAc to promote cyclometallation of nitrogen donor ligands in arene ruthenium and Cp*M (M = Rh, Ir) complexes. All new compounds were characterised by ^1H and ^{13}C NMR, FAB mass spectrometry and elemental analysis and X-ray diffraction in selected cases.

Results

Our intial studies used *N*,*N*-dimethylbenzylamine since the cyclometallated areneruthenium complexes with this ligand are known.[5,9] Reaction of $[IrCl_2Cp^*]_2$ with *N*,*N*-dimethylbenzylamine in dichloromethane at room temperature in the presence of NaOAc as base led to formation of complex **1a** in good yield. The ^1H NMR spectrum of **1a** clearly shows that coordination and cyclometallation of the ligand has occurred. Thus, the NMe_2 group gives rise to two singlets at δ 2.90 and 3.03 and the benzyl protons are also inequivalent giving two mutually coupled doublets at δ 3.26 and 4.38. The phenyl group shows four inequivalent protons as expected for the orthometallated product. The ^{13}C NMR spectrum shows only four arene carbons with protons attached and two signals for the NMe_2 group as expected for **1a**. The inequivalence of the methyls of the NMe_2 is consistent with the chiral centre at the metal. Moreover, it demonstrates that epimerisation at the metal and decoordination of the nitrogen must be slow on the NMR timescale.



1a (ring)M = Cp*Ir
1c (ring)M = p-cymene Ru



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† Based on the presentation given at Dalton Discussion No. 6, 9–11th September 2003, University of York, UK.

Electronic supplementary information (ESI) available: Characterisation and crystallographic data for $[IrCl_2(NH_2Ph)Cp^*]$ (**6**), and Figures showing the structures of **3b**, **5b** and **6**. See http://www.rsc.org/suppdata/dt/b3/b303737a/

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The corresponding reactions were also attempted with $[RhCl_2Cp^*]_2$ and $[RuCl_2(p\text{-cymene})]_2$, but in neither case was the corresponding product **1b** or **1c** formed. Work up of the reaction mixtures and washing the solids formed with hexane left species which showed no signals due to *N*,*N*-dimethylbenzylamine in the ^{1}H NMR spectra. In both cases the starting dimers had reacted so the reactions of the dimers with NaOAc were investigated. Reaction of $[RhCl_2Cp^*]_2$ with NaOAc leads to a solid which shows broad signals in the ^{1}H NMR spectrum which can be assigned to Cp* protons and to acetate protons. However, the chemical shifts of the signals are not consistent between all samples, neither is their relative integration. Indeed, the integration is often not a simple ratio equivalent to one or two acetates per Cp*. In one case we were able to isolate crystals suitable for X-ray diffraction which were determined to be $[Rh(OH_2)(\eta^1\text{-}O_2CMe)_2Cp^*]\cdot H_2O$. This complex has previously been isolated by reaction of $[RhCl_2Cp^*]_2$ with AgOAc.[18,19] However, the ^{1}H NMR spectrum of this batch of crystals showed no evidence for water, as found by Merola and coworkers,[18] and the mass spectra of these samples often contain dimeric species (*m*/*z* 605) corresponding to $[Rh_2(O_2CMe)Cl_2Cp^*_2]$ showing that they still contain chloride. We believe that the solid is a mixture which, in solution, may be in dynamic equilibrium allowing exchange of chloride and acetate through dimeric species and we have made no further attempts to characterise these products.

In the case of ruthenium, the reaction of $[RuCl_2(C_6H_6)]_2$ with a large excess of NaOAc has been reported previously to give $[RuCl(O_2CMe)(C_6H_6)]$ and the corresponding *p*-cymene complex was also synthesised by a different method.[20] The ^{1}H NMR spectrum of the product from the reaction of $[RuCl_2(p\text{-cymene})]_2$ with NaOAc shows the presence of acetate and *p*-cymene in a 1 : 1 ratio and agrees with the data reported for $[RuCl(O_2CMe)(p\text{-cymene})]$. The mass spectrum also shows a peak at *m*/*z* 295 corresponding to $[Ru(O_2CMe)(p\text{-cymene})]$; however there are additional peaks at *m*/*z* 601 due to a dimer, $[Ru_2Cl_2(OAc)(p\text{-cymene})_2]$. We have managed to crystallise the product and the X-ray structure shows it to be $[RuCl(\eta^2\text{-}O_2CMe)(p\text{-cymene})]$ with a bidentate acetate as proposed previously.[20] The structure with selected bond lengths and angles is shown in Fig. 1.

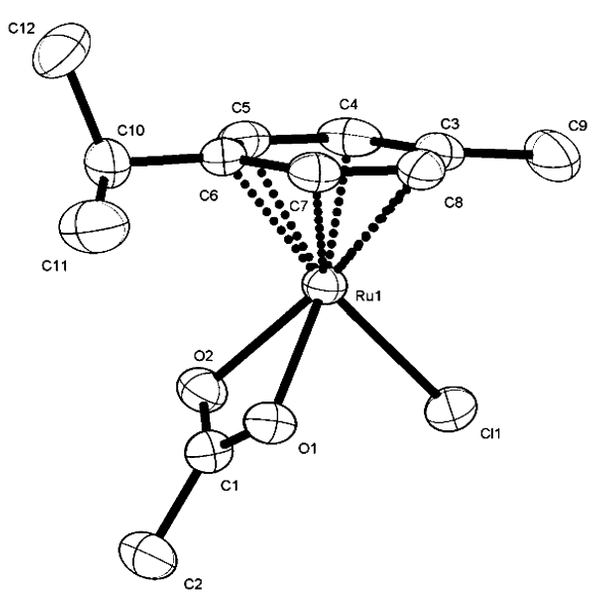
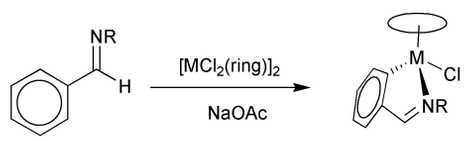


Fig. 1 Molecular structure and atom numbering scheme for **2** with 50% displacement ellipsoids and all H atoms omitted for clarity. Selected bond distances (Å) and angles (°): Ru–O(1) 2.166(2), Ru–O(2) 2.151(2), Ru–Cl 2.389(1), O(1)–C(1) 1.266(3), O(2)–C(1) 1.266(3), C(1)–C(2) 1.495(4); O(2)–Ru–O(1) 60.31(7), O(1)–Ru–Cl 84.92(5), O(2)–Ru–Cl 85.75(5).

To test the generality of the cyclometallation with Cp*Ir and further explore ligands that might cyclometallate with arene ruthenium and Cp*Rh we have tested a number of imines. Reaction of **3** or **4** with $[IrCl_2Cp^*]_2$ in the presence of NaOAc led to formation of **3a** and **4a**, respectively in good yields. The ^{1}H NMR spectra of **3a** and **4a** both show singlets at δ 1.72 and *ca*. δ 3.35 due to Cp* and OMe, respectively, with the imine proton being observed at δ 8.37 or 8.31 for **3a** or **4a**, respectively. In both complexes the NCH_2 protons are inequivalent, hence epimerisation at the metal is slow on the NMR timescale. Both complexes show the expected signals for an orthometallated phenyl group; in the ^{13}C NMR spectra the metallated carbons are observed at δ 168.73 or 168.59, for **3a** or **4a**, respectively, approximately 33 ppm downfield from the corresponding signals in the free ligands. The ν(C=N) decreases by about 50 cm^{-1} compared with the free ligand as expected for coordination of the imine. The X-ray structure of **3a** has been determined and is discussed below.



	Cp*Ir	Cp*Rh	p-cymeneRu
3 R = $(CH_2)_2OMe$	**3a**	**3b**	**3c**
4 R = $(CH_2)_2OMe$	**4a**	**4b**	**4c**
5 R = Ph	**5a**	**5b**	

The influence of the nature of the imine substituent on the course of the cyclometallation was also probed by using benzylideneaniline (**5**). In this case reaction with $[IrCl_2Cp^*]_2$ in the presence of NaOAc led to formation of a mixture of products. The ^{1}H NMR spectrum suggested the presence of the cyclometallated imine **5a** contaminated with another complex containing a non-metallated phenyl which we subsequently identified as the aniline complex $[IrCl_2(NH_2Ph)Cp^*]$ **6**.[21] Thus, during the course of the reaction some of the initial imine had hydrolysed and the resulting amine complexed to the $[IrCl_2Cp^*]_2$ to form **6**. We reasoned that if the imine is hydrolysing to form benzaldehyde and aniline then addition of excess benzaldehyde may reverse this reaction and prevent the formation of significant amounts of aniline and hence **6**. Thus, the reaction was repeated in the presence of benzaldehyde. This led to formation of solely **5a** which could be isolated in 84% yield. The structure of **5a** has been determined by X-ray diffraction and is discussed below.

Having found that imines derived from benzaldehyde cyclometallated easily with $[IrCl_2Cp^*]_2$ we examined the reactions of these ligands with $[RhCl_2Cp^*]_2$ and $[RuCl_2(p\text{-cymene})]_2$. In these cases hydrolysis of the ligands seemed to be more of a problem so excess benzaldehyde was used in many cases. The alkyl imines **3** and **4** cyclometallated with both rhodium and ruthenium forming **3b**,**c** and **4b**,**c** in good yields. In each case the cyclometallation was obvious from the observation of only four protons in the phenyl region in the ^{1}H NMR spectra and only four carbons with protons attached in the phenyl region of the ^{13}C spectra. The NCH_2 protons are inequivalent, as are all four aromatic protons of the *p*-cymene in **3c** and **4c**, consistent with the chiral metal centre. As found for $[IrCl_2Cp^*]_2$, reaction of benzylidene aniline with $[RhCl_2Cp^*]_2$ and NaOAc in the presence of excess benzaldehyde led to isolation of the cyclometallated product **5b**. However, the same reaction with ruthenium led only to formation of **2** by reaction with acetate.

The structures of **3a**–**c** and **5a**–**b** have been determined by X-ray crystallography and selected bond distances and angles are listed in Table 1. The structures of **3a**, **3c** and **5a** are shown in Figs. 2–4, respectively (structures of **3b** and **5b** are in the ESI †). The complexes show the expected piano-stool type

Table 1 Selected bond distances (Å) and angles (°) for **3a**–**c** and **5a**–**b**

	3a	**3b**	**3c**[a]	**5a**	**5b**
M–C(1)	2.036(3)	2.027(2)	2.043(2)	2.042(3)	2.032(3)
M–N(1)	2.078(3)	2.089(2)	2.080(2)	2.088(2)	2.115(3)
M–Cl	2.397(1)	2.398(1)	2.418(1)	2.403(1)	2.399(1)
C(1)–C(6)	1.399(5)	1.407(3)	1.418(3)	1.412(4)	1.399(5)
C(6)–C(7)	1.431(5)	1.437(3),	1.440(3)	1.433(4)	1.434(4)
C(7)–N(1)	1.290(5)	1.283(3)	1.284(3)	1.292(4)	1.281(4)
M–C(π-ring)[b]	2.148(3)	2.147(2)	2.171(2)	2.153(3)	2.123(3)
	2.155(4)	2.153(2)	2.177(2)	2.168(3)	2.149(4)
	2.159(4)	2.166(2)	2.186(2)	2.171(3)	2.150(3)
	2.252(3)	2.250(2)	2.200(2)	2.231(3)	2.250(3)
	2.279(4)	2.278(2)	2.284(2)	2.254(3)	2.250(3)
			2.288(2)		
C(1)–M–N(1)	77.84(13)	78.73(7)	77.85(7)	77.60(11)	78.33(12)
C(1)–M–Cl	85.53(11)	86.03(5)	85.37(5)	87.12(8)	89.64(10)
Cl–M–N(1)	86.09(8)	88.41(4)	87.84(5)	86.15(7)	92.06(8)

[a] Average values for two independent molecules. [b] M–C distances to Cp* (**3a**, **3b**, **5a**, **5b**) or to *p*-cymene (**3c**).

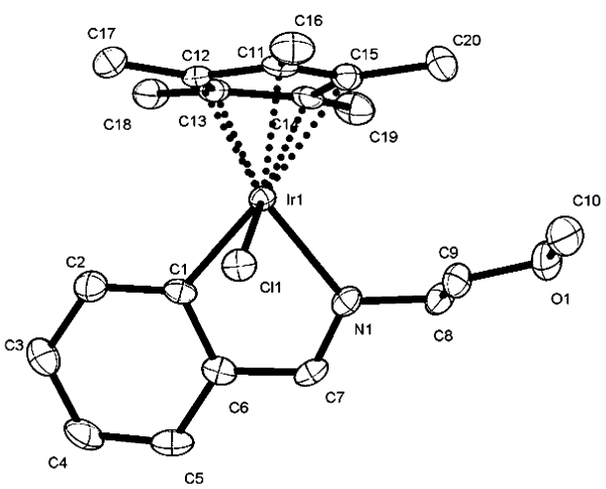


Fig. 2 Molecular structure and atom numbering scheme for **3a** with 50% displacement ellipsoids and all H atoms omitted for clarity.

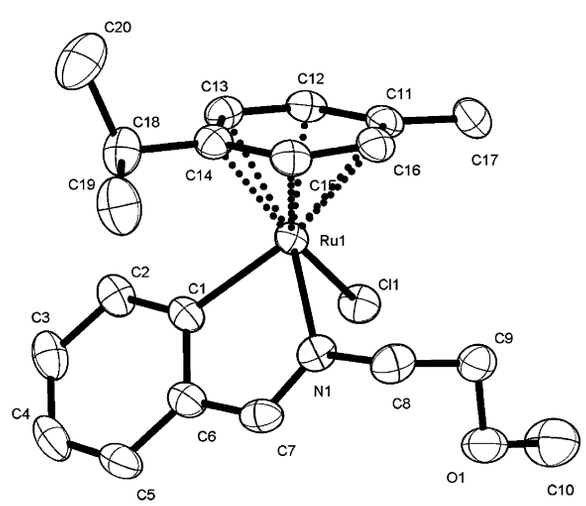


Fig. 3 Molecular structure and atom numbering scheme for one of the independent molecules of **3c** with 50% displacement ellipsoids and all H atoms omitted for clarity.

geometry. The M–$C_{(aryl)}$ bond lengths [range 2.027(2)–2.043(2) Å], the M–N bond lengths [range 2.078(3)–2.115(3) Å] and the chelate bite angles [range 77.60(11)–78.73(7)°] are similar in all the complexes. The Ir–N distances are the same as those

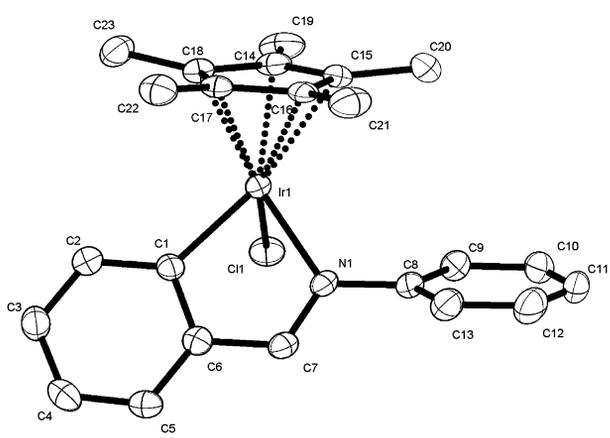
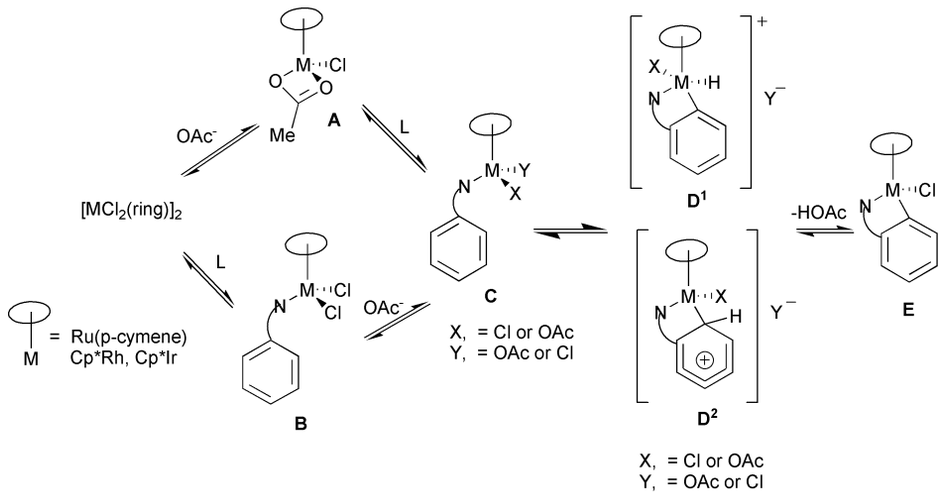


Fig. 4 Molecular structure and atom numbering scheme for **5a** with 50% displacement ellipsoids and all H atoms omitted for clarity.

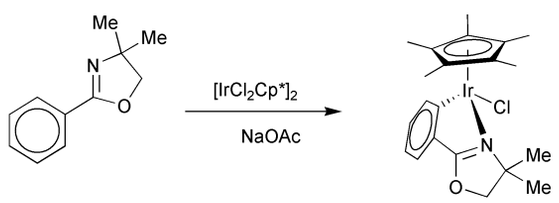
in related Cp*Ir cyclometallated diazabutadiene complexes[16] though the Ir–C distances are slightly shorter in **3a** and **5a** consistent with a bond to an sp^2 carbon rather than sp^3. The Ru–C and Ru–N bond lengths are similar to those in the related (*p*-cymene)ruthenium complex with a cyclometallated benzodiazepine.[13] Complex **3c** shows two independent molecules in the unit cell, the only major difference between these being the orientation of the $(CH_2)_2OMe$ chain and a lengthening of the Ru–Cl bond in one molecule. In **5a** the phenyl substituent on nitrogen is rotated out of the plane of the cyclometallated fragment (dihedral angle C(7)–N(1)–C(8)–C(9) = 128.6°) and is approximately parallel to the Cp*; presumably this is to minimise unfavourable steric interactions with the Cp*. The rhodium complex **5b** shows a similar orientation. All the complexes show significant variations in the M–C bond lengths to the π-bound ring. Thus, the Cp* complexes (**3a**,**b** and **5a**,**b**) show an η^3–η^2 coordination with three short M–C bonds: 2.123(3)–2.171(3) Å, and two longer ones: 2.231(3), 2.279(4) Å. Similarly the *p*-cymene ruthenium complex shows an η^4–η^2 distortion with four short bonds: 2.171(2)–2.200(2) Å, and two longer bonds: 2.284(2)–2.288(2) Å. In all cases the longer bonds are approximately *trans* to the M–C σ-bond.

We have also examined cyclometallation of phenyl oxazoline **7**. Reaction of **7** with $[IrCl_2Cp^*]_2$ and NaOAc led to formation of **7a**. The ^{1}H NMR spectrum shows two singlets at δ 1.50 and 1.53, two mutually coupled doublets at δ 4.43 and 4.55 due to the oxazoline and only four protons in the phenyl region as expected for cyclometallation. Similar reactions with $[RhCl_2Cp^*]_2$ and $[RuCl_2(p\text{-cymene})]_2$ at room temperature failed to



Scheme 1 Proposed mechanism

give cyclometallated products. This is not due to lack of stability of the product, at least for ruthenium, since we have previously synthesised this compound *via* a mercury reagent.[22]



7 **7a**

Discussion

The results described above show that acetate can promote cyclometallation of amines, imines and oxazolines with $[IrCl_2Cp^*]_2$ even at room temperature. The corresponding reactions work for fewer substrates with Cp*Rh and fewer still with areneruthenium under the same conditions. The greater facility for cyclometallation with Cp*Ir rather than rhodium has been noted previously for benzoate complexes.[23] The detailed mechanism and role(s) of acetate in these reactions is not yet clear, however, some key intermediates are presented in Scheme 1 and are discussed further below.

Our attempts to isolate a complex of type **B** (Scheme 1) by direct reaction of the dimers with these ligand have so far failed; there is no reaction or in the case of imines hydrolysis occurs to give primary amine complexes *e.g.* **6**. Notably, there is no reaction between **1** and $[IrCl_2Cp^*]_2$ using NEt_3 as base in place of NaOAc. This suggests that acetate may help facilitate break up of the dimer and exchange of a chloride ligand. This is further evidenced by the fact that all the dimers will react with acetate. In the case of ruthenium we isolated the known complex **2**, a species of type **A** (Scheme 1), which can cyclometallate **3** to form **3c** in the absence of added acetate. Another special feature of acetate may be its ability to act as an intramolecular base as has been proposed in palladium cyclometallation reactions.[1c] The intramolecular hydrogen bonding observed in $[Rh(OH_2)(\eta^1\text{-}O_2CMe)_2Cp^*]\cdot H_2O$ shows this may also be possible for these half-sandwich cyclometallations.

In order for C–H activation to occur a vacant site is needed therefore loss of an anion from **C** is likely to be necessary as found in a related Cp*Ir system.[24] The two most likely mechanisms for the C–H activation step are; oxidative addition of the aryl C–H bond to give M^V (M = Ir, Rh) or Ru^{IV} cations followed by reductive elimination of HX (*i.e. via* $\mathbf{D^1}$), or electrophilic attack of the metal on the arene (*i.e. via* a Wheland intermediate $\mathbf{D^2}$) followed by loss of a proton. These two alternatives have different requirements for electron density at the metal. Electrophilic attack is favoured by electron poor metal centres whilst oxidative addition is favoured by electron-rich metal centres. The failure of **1**, a good σ-donor ligand but with no π-acceptor character, to cyclometallate with $[RhCl_2Cp^*]_2$ and $[RuCl_2(p\text{-cymene})]_2$ would be consistent with an electrophilic mechanism. In agreement with that, cyclometallation of **1** is possible starting with a more electrophilic, cationic ruthenium complex, though with a stronger base *viz*. NaOH;[10] and is more efficient with $[RuCl_2(C_6H_6)]_2$ rather than the more electron donating *p*-cymene dimer.[5] However, Bergman *et al.* have shown that intermolecular C–H activation with [IrMe(OTf)(L)Cp*] (L = PMe_3 or $P(OMe)_3$) proceeds *via* dissociation of triflate which is favoured by electron donating ligands, *i.e.* the rate with PMe_3 is faster than with $P(OMe)_3$.[24] Similar increased rates of C–H activation with more electron donating substituents have been observed for platinum diimine systems.[25] This is in agreement with our observations that the alkyl-substituted imines **3** and **4** cyclometallate more easily than the aryl-substituted one **5**, and with the reduced reactivity of the oxazoline **7** containing the electron withdrawing oxygen atom. Thus, electron donating ligands may help in promoting loss of an anion and creating a vacant coordination site, however too much donation may then be detrimental in reducing the electrophilicity of the metal for the C–H activation step. Further studies to probe the electronic requirements of the ligands to facilitate C–H activation, the precise role(s) of acetate and C–C bond forming reactivity of some of the resultant complexes are currently under investigation.

Experimental

Dichloromethane, *N*,*N*-dimethylbenzylamine, benzylideneaniline and sodium acetate were used as supplied. The dimers $[MCl_2Cp^*]_2$ (M = Rh, Ir)[26] or $[RuCl_2(p\text{-cymene})]_2$,[27] and oxazoline **7**[28] were prepared by literature methods. The methoxy-alkyl imines **3** and **4** were prepared by the same procedure as a similar hydroxyethyl imine.[29] The reactions described were carried out under nitrogen; however, once isolated as pure solids the compounds are air-stable and precautions for their storage are unnecessary. ^1H and ^{13}C NMR spectra were obtained using Bruker spectrometers, at 250 MHz in $CDCl_3$ unless stated otherwise, chemical shifts were recorded in ppm (referenced to tetramethylsilane or residual protons in the NMR solvent). FAB mass spectra were obtained on a Kratos Concept mass spectrometer using an NOBA matrix. Infrared spectra were run as solids in a diamond ATR cell using a Perkin Elmer Spectrum 1 instrument. Microanalyses were performed by the elemental analysis service of the University of North London.

General procedure for cyclometallation reactions

Sodium acetate and the appropriate dimer $[MCl_2Cp^*]_2$ (M = Rh, Ir) or $[RuCl_2(p\text{-cymene})]_2$ were added to a solution of the ligand in dichloromethane (15–20 ml). The mixture was stirred for several hours, then filtered through Celite. The filtrate was evaporated to dryness and then washed with hexane to remove excess ligand to give the cyclometallated products. These were usually pure at this stage but the compounds could be recrystallised from dichloromethane–hexane. Details of individual reactions are shown below.

[IrCl{C_6H_4-2-CH_2NMe_2-κ*C*,*N*}Cp*] (1a)

This was prepared from NaOAc (50 mg, 0.61 mmol), $[IrCl_2Cp^*]_2$ (200 mg, 0.25 mmol), and *N*,*N*-dimethylbenzylamine (85 mg, 0.63 mmol); after stirring for 20 h, **1a** was isolated as an orange precipitate (177 mg, 71%). Calc. for $C_{19}H_{27}ClIrN$: C, 45.91, H, 5.47, N, 2.82. Found: C, 45.87, H, 5.56, N, 2.79%. ^{1}H NMR: δ 1.63 (s, 15H, Cp*), 2.90 (s, 3H, NMe), 3.03 (s, 3H, NMe′), 3.26 (d, 1H, *J* 13, NCH), 4.38 (d, 1H, *J* 13, NCH′), 6.86 (dt, 1H, *J* 7, 1, H^4), 6.98 (t, 1H, *J* 7, H^5), 7.05 (d, 1H, *J* 7, H^3), 7.61 (d, 1H, *J* 7, H^6). ^{13}C NMR: δ 9.47 (C_5Me_5), 51.81, 57.47 (2 × NMe), 73.72 (NCH_2), 87.61 (C_5Me_5), 121.56, 122.38, 126.47, 134.65 (C^3, C^4, C^5, C^6), 148.30 (C^2), 151.38 (C^1Ir). MS (FAB): *m*/*z* 497 $[M]^+$, 460 $[M - Cl - H_2]^+$.

Reaction of *N*,*N*-dimethylbenzylamine with $[RhCl_2Cp^*]_2$

A mixture of *N*,*N*-dimethylbenzylamine (87 mg, 0.65 mmol), NaOAc (55 mg, 0.67 mmol), and $[RhCl_2Cp^*]_2$ (200 mg, 0.32 mmol), was stirred in dichloromethane for 20 h. The mixture was filtered through Celite and evaporated to dryness. The ^{1}H NMR spectrum showed a broad resonance at *ca*. δ 1.7 due to Cp* and another signal at *ca*. δ 1.95. The mass spectrum showed ions at *m*/*z* 237 [RhCp*], 297 [Rh(OAc)Cp*], 545 $[Rh_2Cl_2Cp^*_2 - H]$, 581 $[Rh_2Cl_3Cp^*_2]$, 605 $[Rh_2Cl_2(OAc)Cp^*_2]$. Crystals were grown by diffusion of hexane into a dichloromethane solution. The X-ray structure showed the crystals to be $[Rh(OH_2)(\eta^1\text{-}O_2CMe)_2Cp^*]\cdot H_2O$.

Reaction of *N*,*N*-dimethylbenzylamine with $[RuCl_2(p\text{-cymene})]_2$

A mixture of *N*,*N*-dimethylbenzylamine (88 mg, 0.66 mmol), NaOAc (67 mg, 0.82 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (200 mg, 0.33 mmol), was stirred in dichloromethane for 20 h. The mixture was filtered through Celite and evaporated to dryness. The ^{1}H NMR spectrum showed the presence of $[RuCl(\eta^2\text{-}O_2CMe)(p\text{-cymene})]$ (**2**) by comparison with literature data.[20] This was further characterised by X-ray diffraction.

[IrCl{C_6H_4-2-C(H)=N(CH_2)$_2$$OCH_3$-κ*C*,*N*}Cp*] (3a)

This was prepared from NaOAc (70 mg, 0.85 mmol), $[IrCp^*Cl_2]_2$ (200 mg, 0.25 mmol), and imine **3** (80 mg, 0.50 mmol); after stirring for 5 h, **3a** was isolated as an orange precipitate (255 mg, 96%). Calc. for $C_{20}H_{27}ClIrNO$: C, 45.75, H, 5.18, N, 2.67. Found: C, 45.65, H, 5.18, N, 2.62%. ^{1}H NMR: δ 1.72 (s, 15H, Cp*), 3.37 (s, 3H, OMe), 3.85 (m, 2H, CH_2O), 4.19 (m, 2H, NCH_2), 6.97 (dt, 1H, *J* 7.5, 1, H^4), 7.15 (dt, 1H, *J* 7.5, 1.5, H^5), 7.52 (dd, 1H, *J* 7.5, 1 Hz, H^3), 7.76 (d, 1H, *J* 7.5, H^6), 8.37 (s, 1H, HC=N). ^{13}C NMR: δ 9.25 (C_5Me_5), 59.00 (OMe), 61.89 (CH_2O), 70.34 (NCH_2), 88.88 (C_5Me_5), 121.97, 128.52, 131.71, 134.71 (C^3, C^4, C^5, C^6), 146.42 (C^2), 168.73 (C^1Ir), 176.31 (HC=N). MS (FAB): *m*/*z* 525 $[M]^+$, 490 $[M - Cl]^+$. IR: ν(C=N) 1596 cm^{-1}.

[RhCl{C_6H_4-2-C(H)=N(CH_2)$_2$OMe-κ*C*,*N*}Cp*] (3b)

This was prepared from NaOAc (33 mg, 0.40 mmol), $[RhCl_2Cp^*]_2$ (100 mg, 0.16 mmol), imine **3** (53 mg, 0.32 mmol) and benzaldehyde (33 mg, 0.31 mmol); after stirring for 5 h, **3b** was isolated as a red solid (125 mg, 89%). Calc. for $C_{20}H_{27}ClNORh$: C, 55.12, H, 6.24, N, 3.21. Found: C, 54.92, H, 6.39, N, 3.15%. ^{1}H NMR: δ 1.66 (s, 15H, Cp*), 3.38 (s, 3H, OMe), 3.87 (m, 2H, CH_2O), 4.01 (m, 1H, NC*H*H′), 4.20 (m, 1H, NCH*H*′), 7.00 (dt, 1H, *J* 7.5, 1, H^4), 7.21 (dt, 1H, *J* 7.5, 1.5, H^5), 7.42 (dd, 1H, *J* 7.5, 1.5, H^3), 7.77 (d, 1H, *J* 7.5, H^6), 8.16 (d, 1H, J_{RhH} 4, HC=N). ^{13}C NMR: δ 9.49 (C_5Me_5), 59.11 (OMe), 60.75 (CH_2O), 70.62 (NCH_2), 96.03 (d, J_{RhC} 6, C_5Me_5), 122.67, 128.46, 130.95, 136.01 (C^3, C^4, C^5, C^6), 145.49 (C^2), 173.97 (HC=N), 184.03 (d, J_{RhC} 33, C^1Rh). MS (FAB): *m*/*z* 435 $[M]^+$, 400 $[M - Cl]^+$. IR: ν(C=N) 1606 cm^{-1}.

[RuCl{C_6H_4-1-C(H)=N(CH_2)$_2$$OCH_3$-κ*C*,*N*}(*p*-cymene)] (3c)

This was prepared from NaOAc (67 mg, 0.82 mmol), $[RuCl_2(p\text{-cymene})]_2$ (200 mg, 0.33 mmol), and imine **3** (107 mg, 0.66 mmol) and benzaldehyde (35 mg, 0.33 mmol); after stirring for 5 h, **3c** was isolated as a brown solid (230 mg, 82%). Calc. for $C_{20}H_{26}ClNORu$: C, 55.48, H, 6.05, N, 3.24. Found: C, 55.54, H, 6.05, N, 3.29%. ^{1}H NMR: δ 0.83 (d, 3H, *J* 7, CH*Me*Me′), 1.06 (d, 3H, *J* 7, CHMe*Me*′), 2.07 (s, 3H, Cy-*Me*), 2.49 (sept, 1H, *J* 7 Hz, C*H*MeMe′), 3.39 (s, 3H, OMe), 3.98 (m, 2H, CH_2O), 4.26 (m, 2H, NCH_2), 4.82 (d, 1H, *J* 6, Cy), 4.99 (d, 1H, *J* 6, Cy), 5.58 (d, 1H, *J* 6, Cy), 5.62 (d, 1H, *J* 6, Cy), 6.95 (t, 1H, *J* 7, H^4), 7.12 (dt, 1H, *J* 7.5, 1.5, H^5), 7.41 (dd, 1H, *J* 7.5, 1, H^3), 8.05 (s, 1H, HC=N), 8.12 (d, 1H, *J* 7.5, H^6). ^{13}C NMR: δ 18.96 (MeC_6H_4), 21.42 ($CH(^iPr)$), 23.21, 31.04 (2 × $Me(^iPr)$), 58.97 (OMe), 65.30 (CH_2O), 70.69 (NCH_2), 80.17, 80.89, 90.07, 91.24 (CH (C_6H_4 Cy)), 101.89, 102.62 (C (C_6H_4 Cy)), 122.33, 128.90, 129.71, 139.07 (C^3, C^4, C^5, C^6), 145.38 (C^2), 173.69 (HC=N), 188.48 (C^1Ru). MS (FAB): *m*/*z* (%) 433 $[M]^+$, 398 $[M - Cl]^+$. IR: ν(C=N) 1601 cm^{-1}.

[IrCl{C_6H_4-2-C(H)=N(CH_2)$_3$$OCH_3$-κ*C*,*N*}Cp*] (4a)

This was prepared from NaOAc (70 mg, 0.85 mmol), $[IrCl_2Cp^*]_2$ (200 mg, 0.25 mmol), and imine 4 (90 mg, 0.50 mmol); after stirring for 5 h, **4a** was isolated as an orange precipitate (260 mg, 96%). Calc. for $C_{21}H_{29}ClIrNO$: C, 46.78, H, 5.42, N, 2.60. Found: C, 46.80, H, 5.46, N, 2.68%. ^{1}H NMR: δ 1.72 (s, 15H, Cp*), 2.17 (m, 2H, CH_2), 3.33 (s, 3H, OMe), 3.43 (m, 2H, CH_2O), 4.13 (m, 2H, NCH_2), 6.98 (dt, 1H, *J* 7.5, 1, H^4), 7.16 (dt, 1H, *J* 7.5 and 1.5, H^5), 7.52 (dd, 1H, *J* 7.5, 1, H^3), 7.76 (d, 1H, *J* 7.5, H^6), 8.31 (s, 1H, HC=N). ^{13}C NMR: δ 9.20 (C_5Me_5), 29.02 (CH_2), 58.75 (OMe), 59.81 (CH_2O), 69.75 (NCH_2), 88.87 (C_5Me_5), 121.96, 128.16, 131.61, 134.73 (C^3, C^4, C^5, C^6), 146.27 (C^2), 168.59 (C^1Ir), 175.55 (HC=N); MS (FAB): *m*/*z* 539 $[M]^+$, 502 $[M - Cl - H_2]^+$. IR: ν(C=N) 1593 cm^{-1}.

[RhCl{C_6H_4-2-C(H)=N(CH_2)$_3$$OCH_3$-κ*C*,*N*}Cp*] 4b

This was prepared from NaOAc (66 mg, 0.81 mmol), $[RhCl_2Cp^*]_2$ (200 mg, 0.32 mmol), and imine **4** (115 mg, 0.65 mmol); after stirring for 5h, **4b** was isolated as a red solid (275 mg, 95%). Calc. for $C_{21}H_{29}ClNORh$: C, 56.07, H, 6.50, N, 3.11. Found: C, 55.98, H, 6.44, N, 3.15%. ^{1}H NMR (300 MHz): δ 1.66 (s, 15H, Cp*), 2.21 (m, 2H, –CH_2), 3.32 (s, 3H, OMe), 3.44 (m, 2H, –CH_2O), 3.93 (m, 1H, NC*H*H′), 4.12 (m, 1H, NCH*H*′), 7.01 (dt, 1H, *J* 7.5, 1, H^4), 7.22 (dt, 1H, *J* 7.6, 1.5, H^5), 7.41 (dd, 1H, *J* 7.5, 1.5, H^3), 7.77 (d, 1H, *J* 7, H^6), 8.11 (d, 1H, J_{RhH} 4, HC=N). ^{13}C NMR: δ 9.41 (C_5Me_5), 29.32 (CH_2), 58.64 (CH_2O), 58.75 (OMe), 69.72 (NCH_2), 95.98 (d, J_{RhC} 6, C_5Me_5), 122.62, 128.08, 130.81, 136.01 (C^3, C^4, C^5, C^6), 145.32 (C^2), 172.97 (HC=N), 183.93 (d, J_{RhC} 33, C^1Rh). MS (FAB): *m*/*z* 449 $[M]^+$, 414 $[M - Cl]^+$, 412 $[M - Cl - H_2]^+$. IR: ν(C=N) 1604 cm^{-1}.

[RuCl{C_6H_4-1-C(H)=N(CH_2)$_3$$OCH_3$-κ*C*,*N*}(*p*-cymene)] 4c

This was prepared from NaOAc (35 mg, 0.43 mmol), $[RuCl_2(p\text{-cymene})]_2$ (100 mg, 0.16 mmol), and imine **4** (58 mg, 0.33 mmol) and benzaldehyde (18 mg, 0.17 mmol); after stirring for 5 h, **4c** was isolated as a red solid (123 mg, 84%). Calc. for

$C_{21}H_{28}ClNORu$: C, 56.43, H, 6.31, N, 3.13. Found: C, 56.61, H, 6.22, N, 3.13%. ^{1}H NMR: δ 0.80 (d, 3H, J 7, CH*Me*Me′), 1.06 (d, 3H, J 7, CHMe*Me′*), 2.10 (s, 3H, Cy–Me), 2.37 (m, 2H, CH_2), 2.49 (sept, 1H, J 7, C*H*MeMe′), 3.36 (s, 3H, OMe), 3.47 (m, 2H, CH_2O), 4.17 (m, 2H, NCH_2), 4.82 (d, 1H, J 6.5, Cy), 4.95 (d, 1H, J 6, Cy), 5.64 (d, 2H, J 6.5, Cy), 6.96 (dt, 1H, J 7.5, 1, H^4), 7.13 (dt, 1H, J 7.5, 1.5, H^5), 7.41 (dd, 1H, J 7.5, 1, H^3), 8.01 (s, 1H, HC=N), 8.12 (d, 1H, J 7.5, H^6). ^{13}C NMR: δ 18.98 (*Me*C_6H_4), 21.23 (CH (^{i}Pr)), 23.49 (Me (^{i}Pr)), 29.53 (CH_2), 31.04 (Me (^{i}Pr)), 58.83 (OMe), 62.97 (CH_2O), 69.82 (NCH_2), 79.58, 81.26, 89.79, 91.71 (CH (C_6H_4 Cy)), 101.21, 103.31 (C (C_6H_4 Cy)), 122.34, 128.61, 129.68, 139.07 (C^3, C^4, C^5, C^6), 145.19 (C^2), 172.77 (HC=N), 188.31 (C^{1}Ru). MS (FAB): *m*/*z* 447 [M]$^+$, 410 [M − Cl − H$_2$]$^+$. IR: ν(C=N) 1602 cm^{-1}.

[IrCl{C_6H_4-2-C(H)=NPh-κ*C*,*N*}Cp*] 5a

This was prepared from NaOAc (13 mg, 0.16 mmol), [$IrCl_2$-Cp*]$_2$ (50 mg, 0.06 mmol), dibenzylideneaniline (23 mg, 0.13 mmol) and benzaldehyde (7 mg, 0.07 mmol); after stirring for 5 h, **5a** was isolated as a red precipitate (57 mg, 84%). Calc. for $C_{23}H_{25}ClIrN$: C, 50.86, H, 4.64, N, 2.58. Found: C, 50.78, H, 4.68, N, 2.59%. ^{1}H NMR: δ 1.47 (s, 15H, Cp*), 7.02 (dt, 1H, J 7.5, 1, H^4), 7.20 (dt, 1H, J 7.5, 1.5, H^5), 7.30 (m, 1H, Ph), 7.40 (t, 2H, J 7.5, Ph), 7.57 (m, 2H, Ph), 7.62 (dd, 1H, J 7.5, 1, H^3), 7.85 (d, 1H, J 7.5, H^6), 8.31 (s, 1H, HC=N). ^{13}C NMR: δ 8.90 (C_5Me_5), 89.39 (C_5Me_5), 122.14, 122.67, 127.43, 129.16, 129.75, 132.62, 135.29 (C^3, C^4, C^5, C^6 and Ph), 147.15 (C^2), 152.00 (Ph), 170.68 (C^{1}Ir), 175.58 (HC=N). MS (FAB): *m*/*z* 543 [M]$^+$, 508 [M − Cl]$^+$. IR: ν(C=N) 1582 cm^{-1}.

[RhCl{C_6H_4-2-C(H)=NPh-κ*C*,*N*}Cp*] 5b

This was prepared from NaOAc (66 mg, 0.80 mmol), [$RhCl_2$-Cp*]$_2$ (200 mg, 0.32 mmol), dibenzylideneaniline (120 mg, 0.65 mmol) and benzaldehyde (35 mg, 0.33 mmol); after stirring for 5 h, **5b** was isolated as a red precipitate (178 mg, 71%). Calc. for $C_{23}H_{25}ClNRh$: C, 60.87, H, 5.55, N, 3.09. Found: C, 60.63, H, 5.85, N, 3.00%. ^{1}H NMR: δ 1.43 (s, 15H, Cp*), 7.06 (t, 1H, J 7.5, H^4), 7.27 (t, 1H, J 7.5, H^5), 7.30 (t, 1H, J 7.5, Ph), 7.42 (t, 2H, J 7.5, Ph), 7.54 (dd, 1H, J 7.5, 1, H^3), 7.62 (d, 2H, J 8, Ph), 7.85 (d, 1H, J 8, H^6), 8.18 (d, 1H, J_{RhH} 4, HC=N). ^{13}C NMR: δ 9.10 (C_5Me_5), 96.42 (d, J_{RhC} 6.5, C_5Me_5), 122.32, 122.89, 127.42, 129.28, 129.58, 131.64, 136.58 (C^3, C^4, C^5, C^6 and Ph), 146.32 (C^2), 151.24 (Ph), 172.50 (HC=N), 185.55 (d, J_{RhH} 33, C^{1}Rh). MS (FAB): *m*/*z* 453 [M]$^+$, 418 [M − Cl]$^+$. IR: ν(C=N) 1598 cm^{-1}.

[IrCl{C_6H_4-2-Me$_2$oxaz)-κ*C*,*N*}Cp*] 7a

This was prepared from NaOAc (16 mg, 0.20 mmol), [$IrCl_2$Cp*]$_2$ (63 mg, 0.08 mmol), and oxazoline **7** (28 mg, 0.16 mmol); after stirring for 5 h, **7a** was isolated as an orange precipitate (62 mg, 74%). Calc. for $C_{21}H_{27}ClIrNO$: C, 46.96, H, 5.07, N, 2.61. Found: C, 46.72, H, 4.89, N, 2.54%. ^{1}H NMR: δ 1.50 (s, 3H, Me), 1.53 (s, 3H, Me), 1.79 (s, 15H, Cp*), 4.43 (d, 1H, J 8, OCHH′), 4.55 (d, 1H, J 8, OCHH′), 6.99 (dt, 1H, J 7.5, 1, H^4), 7.24 (dt, 1H, J 7.5, 1.5, H^5), 7.42 (dd, 1H, J 7.5, 1, H^3), 7.75 (d, 1H, J 7.5, H^6). ^{13}C NMR: δ 10.14 (C_5Me_5), 26.54 (Me), 28.87 (Me), 67.51 (CMe_2), 82.95 (OCH_2), 88.05 (C_5Me_5), 121.89, 126.51, 132.35, 135.37 (C^3, C^4, C^5, C^6), 162.81 (C^2), 178.17 (C^{1}Ir). MS (FAB): *m*/*z*. 537 [M]$^+$, 502 [M − Cl]$^+$. IR: ν(C=N) 1623 cm^{-1}.

X-Ray crystal structure determinations

Details of the structure determinations of crystals of **2**, **3a**–**c** and **5a**–**b** are given in Table 2, those for **6** are in the ESI.† Data were collected on a Bruker Apex 2000 CCD diffractometer using graphite monochromated Mo-Kα radiation, λ = 0.7107 Å at 150 K. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections (SADABS)[30] were

Table 2 Crystallographic data for **2**,**3a**–**c** and **5a**,**b**

	2	3a	3b	3c	5a	5b
Empirical formula	$C_{12}H_{17}ClO_2Ru$	$C_{20}H_{27}ClIrNO$	$C_{20}H_{27}ClNORh$	$C_{20}H_{26}ClNORu$	$C_{23}H_{25}ClIrN$	$C_{23}H_{25}ClRhN$
M	329.77	525.08	435.79	432.94	543.09	453.80
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$Pna2_1$
a/Å	15.2250(9)	7.5629(4)	7.5479(14)	14.006(3)	7.4282(6)	17.160(3)
b/Å	12.5502(7)	14.6554(8)	14.691(3)	14.321(3)	15.3106(11)	14.260(2)
c/Å	14.5795(8)	17.0530(9)	17.096(3)	19.188(4)	17.4949(13)	7.9550(13)
β/°	109.238(1)	95.795(1)	95.536(3)	92.75(3)	99.686(1)	90
U/Å^3	2630.2(3)	1880.45(17)	1886.9(6)	3844.3(13)	1961.3(3)	1946.7(5)
Z	8	4	4	8	4	4
μ/mm^{-1}	1.378	7.249	1.053	0.961	6.950	1.021
F(000)	1328	1024	896	1776	1056	928
Crystal size/mm	0.26 × 0.20 × 0.12	0.38 × 0.35 × 0.31	0.29 × 0.22 × 0.14	0.40 × 0.38 × 0.25	0.33 × 0.32 × 0.06	0.42 × 0.16 × 0.10
Reflections collected	9970	14418	13365	29014	15995	9604
Unique reflections (R_{int})	2581 (0.0193)	3692 (0.0298)	3310 (0.0341)	7550 (0.0244)	4287 (0.0390)	3708(0.0322)
Data/restraints/parameters	2581/0/148	3692/0/223	3310/0/223	7550/0/441	4287/0/240	3708/1/240
Goodness-of-fit on F^2	1.099	1.237	1.058	1.033	0.975	1.034
$R1$ indices [I>2σ(I)]	0.0259	0.0215	0.0207	0.0244	0.0205	0.0268
$wR2$ (all data)	0.0660	0.0508	0.0535	0.0653	0.0484	0.0680
Largest diff. peak, hole/e Å^{-3}	0.993, −0.272	0.568, −1.282[a]	0.528, −0.395	0.587, −0.510	1.981[b], −0.588	0.535, −0.273

[a] 0.96 Å from Ir. [b] 0.82 Å from Ir.

applied in all cases. The structures were solved by Patterson methods and refined by full-matrix least squares on F^2 using the program SHELXTL-PC.[31] All hydrogen atoms bonded to carbon were included in calculated positions (C–H = 0.96 Å) using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters without positional restraints. Complex **3c** has two independent molecules in the unit cell the only significant differences are the orientation of the CH_2CH_2OMe chain and the Ru–Cl bond distance.

CCDC reference numbers 207506–207512.

See http://www.rsc.org/suppdata/dt/b3/b303737a/ for crystallographic data in CIF or other electronic format.

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