Reversible C–H Bond Activation Reactions of the *N*-Heterocyclic Carbene Ligands in $Ru(Ph_2PCH_2CH_2CH_2PPh_2)(IMes)(CO)H_2$ and $Ru(Ph_2AsCH_2CH_2PPh_2)(IMes)(CO)H_2$ (IMes = 1,3-Dimesityl-1,3-dihydro-2*H*-imidazol-2-ylidene)

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Abstract: Thermolysis of $Ru(IMes)(dppp)(CO)H_2$ (**1**, IMes = 1,3-dimesityl-1,3-dihydro-2*H*-imidazol-2-ylidene; dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) in the presence of trimethylvinylsilane yields Ru(IMes')(dppp)(CO)H (**2**) resulting from intramolecular $ArCH_2-H$ C–H bond activation of the *N*-heterocyclic carbene ligand. The structures of **1** and **2** have been established by X-ray crystallography. Treatment of $Ru(IMes)(arphos)(CO)H_2$ (**3**, arphos = $Ph_2AsCH_2CH_2PPh_2$) with $CH_2{=}CHSiMe_3$ at 85 °C produces a mixture of three C–H activated products **4a–c**. The C–H activated complexes **2** and **4a–c** reform their dihydride precursors upon heating under hydrogen.

Keywords: As ligands; C–H activation; hydrides; metallacycles; *N*-heterocyclic carbenes; P ligands; ruthenium

The role of *N*-heterocyclic carbenes (NHCs) as alternative ligands to tertiary phosphines in homogeneous catalysis is now well established.[1] Concomitantly, it has become increasingly apparent that carbenes (and/or their imidazolium precursors) are quite susceptible to metal induced bond activation reactions, which may be crucial to both catalytic activity and possible deactivation pathways.

Aryl C–H bond cleavage of N-bound substituents in NHCs was first described by Lappert and co-workers upon reaction of enetetramines with coordinatively unsaturated Ru(II) and Ir(I) precursors.[2] More recently, $ArCH_2-H$ activations of 1,3-dimesityl-1,3-dihydro-2*H*-imidazol-2-ylidene (IMes) and 1,3-dimesityltetrahydroimidazol-2-ylidene ($IMesH_2$) have been seen in Rh- and Ru-NHC complexes,[3,4] while activation of an sp^3 hybridised C–H bond in ICy (1,3-dicyclohexyl-1,3-dihydro-2*H*-imidazol-2-ylidene) occurs with $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$, although rapid β-hydrogen elimination affords a 1-(2-cyclohexenyl)-3-cyclohexyl-1,3-dihydro-2*H*-imidazol-2-ylidene ligand as the ultimate product.[5] C–H bond activation in imidazolium salts has been reported with Ru,[6] Ir,[7] Ni, Pd and Pt complexes,[8] including Crabtree's example of 'wrong way' attack on the imidazole ring.

We have recently reported the first example of C–C bond activation of an NHC, starting from the bis-carbene ruthenium complex $Ru(IMes)_2(PPh_3)(CO)H_2$.[9] We also showed that treatment of the mono-carbene species $Ru(IMes)(PPh_3)_2(CO)H_2$ with $CH_2{=}CHSiMe_3$, at room temperature, results in facile intramolecular C–H activation of an *ortho*-methyl group on the IMes ligand. To investigate the influence of the ancillary ligands on this process, we have prepared bidentate phosphine and phosphine-arsine precursors, which still exhibit C–H activation chemistry, albeit at higher temperatures.

Thermolysis of $Ru(PPh_3)(dppp)(CO)H_2$ with a slight excess of IMes at 100 °C for 3 weeks results in displacement of the PPh_3 ligand and formation of the mono-carbene complex $Ru(IMes)(dppp)(CO)H_2$ (**1**), which was isolated in 73% yield. The ^1H NMR spectrum in C_6D_6 showed two hydride signals at $\delta = -6.2$ and -7.1, each coupled to two ^{31}P nuclei and the other inequivalent hydride. In the $^{31}P\{^1H\}$ NMR spectrum, two doublets were observed with $J_{PP} = 24.5$ Hz, while the $^{13}C\{^1H\}$ NMR displayed two low field multiplet signals at $\delta = 205.8$ (t, $J = 9.0$ Hz) and 195.5 (dd, $J = 75.5$, 7.5 Hz), which were assigned to Ru-*C*O and Ru-*C*(IMes), respectively. The magnitude of the NMR coupling constants is consistent with the geometry shown in Scheme 1. This stereochemistry was confirmed unequivocally by the crystal X-ray structure depicted in Figure 1.[10]

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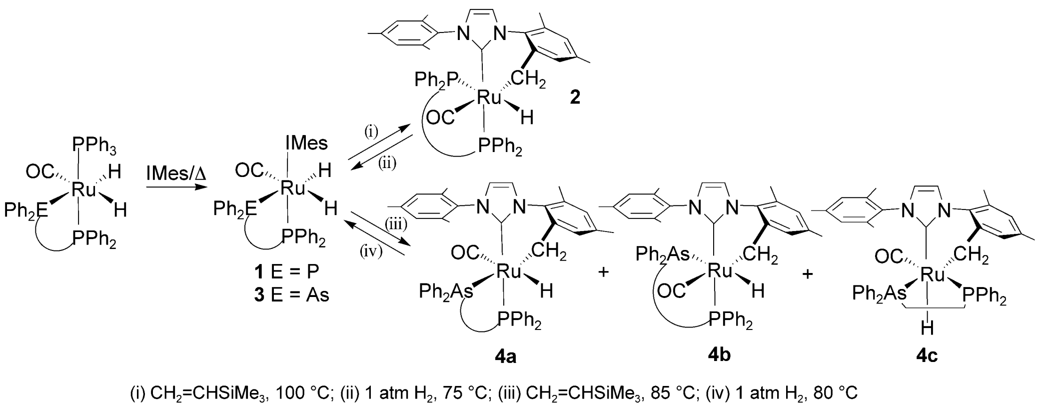

Scheme 1.

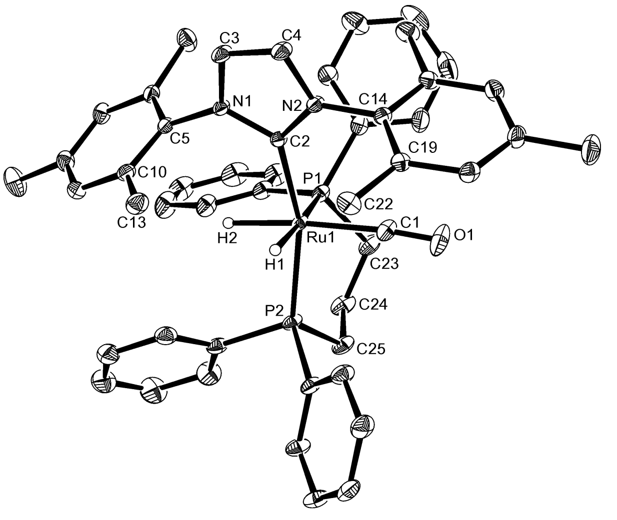

Figure 1. ORTEX diagram of Ru(IMes)(dppp)(CO)H_2 (**1**). Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (°): Ru–C(1), 1.9054(15); Ru–C(2), 2.0981(12); Ru–P(2), 2.2816(3); Ru–P(1), 2.3392(4); C(2)–Ru–P(2), 158.78(4); C(1)–Ru–P(1), 91.29(5); C(2)–Ru–P(1), 105.13(4); P(2)–Ru–P(1), 91.224(14); C(1)–Ru–C(2), 100.16(5).

The geometry at ruthenium is somewhat distorted from regular octahedral with a *trans* C(2)–Ru–P(2) angle of 158.78° (Figure 1), close to the *trans* P–Ru–P angle (160.67^0) reported in Ru(PPh_3)(dppp)(CO)H_2.[12] Thus the carbene is not significantly more sterically demanding than PPh_3. Notwithstanding the inherent difficulty in determining hydrogen atom positions crystallographically, there is some evidence for a possible intramolecular H...H interaction between the hydrido ligand H(2) and an adjacent *ortho*-C–H hydrogen H(43) of a phenyl group of one of the phosphine ligands P(1) [H...H = 2.15 Å].[13,14] A similar interaction may also prevail for H(1) with respect to one of the methyl hydrogens attached to C(13) [H...H = 2.15 Å].

Complex **1** does not react with CH_2=$CHSiMe_3$ at room temperature, but upon heating to 100 °C affords the C–H activated complex Ru(IMes')(dppp)(CO)H (**2**) (along with trimethylethylsilane) in quantitative yield (Scheme 1). The ^1H NMR spectrum of **2** displays, as expected, a single hydride resonance at $\delta = -6.7$ ($J_{HP} = 102.6$, 21.1 Hz) and two characteristic multiplets at $\delta = 0.9$ (dd, $J = 14.2$, 10.8 Hz) and 3.0 (broad triplet, $J = 10.2$ Hz) for the inequivalent methylene protons of the activated Ru-CH_2Ar group. The reaction of **2** with 1 atmosphere of H_2 at room temperature results only in very slow reformation of **1** (50% conversion after 1 week), although subsequent warming to 75 °C pushed the reaction to completion inside a further 12 h.

The X-ray crystal structure of **2** (Figure 2) displays clearly the metallated mesityl ring of the IMes ligand.[15] The activated Ru–C bond length is 2.226(2) Å, comparable to that in the PPh_3 analogue [2.235(2) Å]. The structure is severely bent around the C(2)–Ru(1)–P(2) axis [159.73(5)°], which in part reflects the phosphine bulk. A comparison of the structure of **2** with that of Ru(IMes')(PPh_3)$_2$(CO)H[9] indicates that there is alteration in the orientation of the C–H activated rings between the two structures, probably due to the variation in bulk of dppp relative to PPh_3. This effect is clearly manifested in the C(22)–Ru(1)–P(1) angle [93.38(5)°] which compares with the corresponding C–Ru–P angle of 101.10(5)^0 seen in Ru(IMes')(PPh_3)$_2$-(CO)H.

To further investigate the influence of the chelating ligand on the ease of carbene C–H activation, we prepared the potentially hemilabile system Ru(IMes)(arphos)(CO)H_2 (**3**, arphos = $Ph_2PCH_2CH_2AsPh_2$), by treatment of Ru(PPh_3)(arphos)(CO)H_2 with IMes at 80 °C for one week. The ^1H NMR spectrum of **3** recorded in C_6D_6 shows two doublet of doublets in the hydride region at −7.4 and −8.9 ppm; the magnitude of the phosphorus couplings indicates that both hydrides are *cis* to P, which itself must be *trans* to the IMes group. The hydride region in the ^1H NMR spectrum after reaction of **3** with a two-fold excess of CH_2=$CHSiMe_3$ in C_6D_6 at 85 °C for 5 days, showed three new products in a ratio 1:1:0.7 as doublets at $\delta = -6.3$, −8.5 and −8.7.

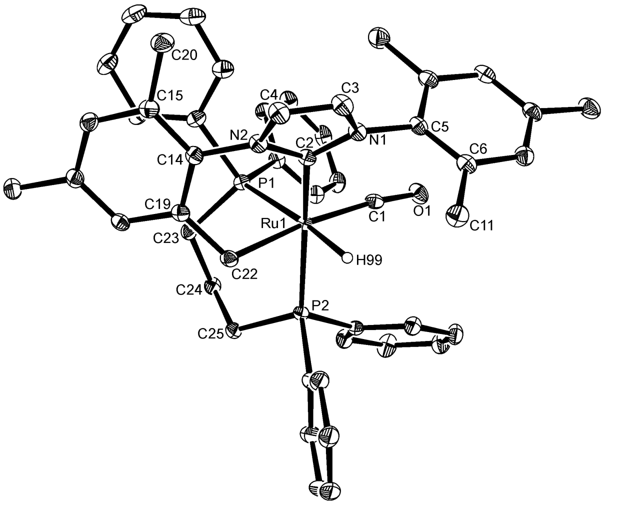

Figure 2. ORTEX diagram of Ru(IMes')(dppp)(CO)H (**2**). Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (°): Ru–C(1), 1.864(2); Ru–C(2), 2.0827(19); Ru–C(22), 2.2258(19); Ru–P(2), 2.3108(5); Ru–P(1), 2.3673(5); C(2)–Ru–P(2), 159.73(5); C(2)–Ru–C(22), 81.13(7); C(2)–Ru–P(1), 102.59(6); C(1)–Ru–C(22), 169.58(8); C(22)–Ru–P(1), 93.38(5).

The product ratio was found to be unaffected by either performing the reaction at higher temperature (100 °C), changing the solvent to THF or adding a larger excess of alkene. ^{1}H COSY and ^{1}H-^{31}P{^{1}H} HETCOR NMR experiments revealed the three complexes to be isomeric products (**4a–c**) resulting from C–H activation of the carbene. The magnitudes of the RuH-^{31}P splittings and phosphorus coupling constants to Ru-*C*(carbene), Ru-*C*O and Ru-*C*H$_2$ [from ^{13}C{^{1}H} NMR] are consistent with the structures shown in Scheme 1. Attempts to separate the mixture of isomers proved to be unsuccessful. Intriguingly, all three isomers react rapidly with H$_2$ (1 atm) at 80 °C over a period of 4 h converting back just to complex **3**.

In conclusion, intramolecular C–H bond activation of 1,3-dimesityl-1,3-dihydro-2*H*-imidazol-2-ylidene (IMes) has been found in ruthenium chelating P-P and P-As complexes. Attempts are currently underway to utilise the reversibility of the C–H activation chemistry found in the presence of H$_2$ for catalytic applications.

Experimental Section

General Remarks

Manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques with reagents dried by standard procedures. NMR spectra were recorded at 293 K on Bruker Avance 300 or Varian Mercury 400 MHz spectrometers. Coupling constants are reported in Hz. Detailed spectroscopic, analytical and crystallographic data are provided as Supporting Information

Synthesis of Ru(IMes)(dppp)(CO)H$_2$ (1)

To a solution of Ru(dppp)(PPh$_3$)(CO)H$_2$[16] (1.00 g, 1.24 mmol) in toluene (30 mL) was added 1.11 g IMes (3.72 mmol) and the mixture heated to 100 °C for 3 weeks. Removal of solvent gave a dark oily residue; addition of ethanol (30 mL) and stirring at room temperature gave a white solid. This was washed with ethanol (3 × 10 mL) and hexane (1 × 10 mL) to give **1**; yield: 0.767 g (73%). Selected NMR data (C$_6$D$_6$): ^{1}H: $\delta = -6.20$ (ddd, $J_{HP} = 22.9$, $J_{HP} = 15.5$, $J_{HH} = 5.8$ Hz, 1H, RuH), -7.07 (ddd, $J_{HP} = 79.4$, $J_{HP} = 22.9$, $J_{HH} = 5.8$ Hz, 1H, RuH); ^{31}P{^{1}H}: $\delta = 40.6$ (d, $J_{PP} = 24.5$ Hz), 28.1 (d, $J_{PP} = 24.5$ Hz).

Synthesis of Ru(IMes')(dppp)(CO)H (2)

A solution of **1** (0.066 g, 0.077 mmol) in C$_6$D$_6$ (0.5 mL) in a J. Young's resealable NMR tube containing 1.2 equivalents of CH$_2$=CHSiMe$_3$ (15 μL) was heated at 100 °C for 24 h. ^{31}P{^{1}H} NMR spectroscopy showed formation of **2** (98% conversion by NMR) and CH$_3$CH$_2$SiMe$_3$. Removal of the solvent and recrystallisation from toluene/hexane (1:4) afforded **2** as pale yellow crystals; yield: 0.054 g (89%). Selected NMR data (C$_6$D$_6$): ^{1}H: $\delta = 3.02$ (br 't', 1H, $J_{HH} = 11.0$, $J_{HP} = 10.1$ Hz, CH$_2$), 0.88 ('t', 1H, $J_{HH} = 11.0$, $J_{HP} = 11.7$ Hz, CH$_2$), -6.71 (dd, 1H, $J_{HP} = 102.6$, $J_{HP} = 21.1$ Hz, RuH); ^{31}P{^{1}H}: $\delta = 39.6$ (d, $J_{PP} = 25.6$ Hz), 15.2 (d, $J_{PP} = 25.6$ Hz).

Synthesis of Ru(IMes)(arphos)(CO)H$_2$ (3)

The title compound was purified as for **1** after reaction of Ru(PPh$_3$)(arphos)(CO)H$_2$[16] with IMes in toluene at 80 °C for 1 week. Selected NMR data (C$_6$D$_6$): ^{1}H: $\delta = -7.44$ (dd, $J_{HP} = 25.9$, $J_{HH} = 3.3$ Hz, 1H, RuH), -8.91 (dd, $J_{HP} = 25.9$, $J_{HH} = 3.3$ Hz, 1H, RuH); ^{31}P{^{1}H}: $\delta = 88.7$ (s).

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[10] Crystal data for **1**: $C_{49}H_{52}N_2OP_2Ru$, $M = 847.94$, triclinic, $a = 10.8200(1)$, $b = 11.6180(1)$, $c = 18.9160(2)$ Å, $\alpha = 97.73°$, $\beta = 109.018(1)°$, $\gamma = 115.29°$, $V = 2125.53(4)$ Å^3, $T = 150$ K, space group P-1, $Z = 2$, μ(Mo-Kα) = 0.71073 mm^{-1}, 49324 data were collected of which 16064 were unique ($R_{int} = 0.0543$), 13923 had $F_o > 4\sigma(F_o)$, $7.10 < 2\theta < 66.24°$. $R1 = 0.0342$ (for 4σ data), $wR2 = 0.0917$, $S = 1.023$ (for all data). The hydrides (H1, H2) were located and refined at a distance of 1.6 Å from the central metal. The structure was solved using SHELXS and all non-hydrogen atoms were refined anisotropically using full-matrix least-squares on F^2 (SHELXL-97). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 208705.

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[15] Crystal data for **2**: $C_{49}H_{50}N_2OP_2Ru$, $M = 845.92$, monolinic, $a = 20.8160(2)$, $b = 12.3860(1)$, $c = 16.0930(2)$ Å, $\beta = 99.616(1)°$, $V = 4090.91(7)$ Å^3, $T = 150$ K, space group $P2_1/c$, $Z = 4$, μ(Mo-Kα) = 0.71073 mm^{-1}, 74811 data were collected of which 9439 were unique ($R_{int} = 0.0512$), 7774 had $F_o > 4\sigma(F_o)$, $7.18 < 2\theta < 54.96°$. $R1 = 0.0314$ (for 4σ data), $wR2 = 0.0791$, $S = 1.070$ (for all data). The hydride (H99) was located and freely refined. The structure was solved using SHELXS and all non-hydrogen atoms were refined anisotropically using full-matrix least-squares on F^2 (SHELXL-97). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 208704.

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