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Ring-Expanded N-Heterocyclic Carbene Complexes of Ruthenium

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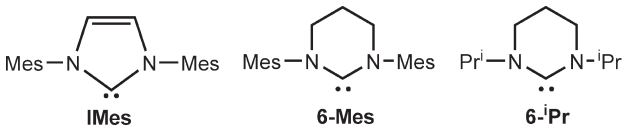
The six-membered N-heterocyclic carbene 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene (6-Mes) reacts with $Ru(PPh_3)_3(CO)HF$ to afford $Ru(6\text{-}Mes)(PPh_3)(CO)HF$ (**1**), which is converted to the five-coordinate C−H activated carbene complex $Ru(6\text{-}Mes)'(PPh_3)(CO)H$ (**2**) upon treatment with Et_3SiH. The hydride chloride precursor $Ru(PPh_3)_3(CO)HCl$ affords a mixture of products with 6-Mes, but reacts cleanly with 1,3-bis(isopropyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene (6-^{i}Pr) to give the six-coordinate activated complex $Ru(6\text{-}^i Pr)'(PPh_3)_2(CO)H$ (**3a**), in which the hydride is trans to the methylene arm of the activated NHC. This complex isomerizes in solution with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of 98.2 ± 4.6 kJ mol^{-1} and 15.5 ± 14.5 J mol^{-1} K^{-1}. The major product from the isomerization, **3b**, in which the hydride ligand is trans to carbene, can be made directly by reaction of 6-^{i}Pr with $Ru(PPh_3)_3(CO)H_2$.

Introduction

While the coordination of N-heterocyclic carbenes (NHCs) to just about every metallic element in the periodic table has now been reported,[1] the vast majority of cases have involved five-membered imidazol-ylidene- and imidazolidin-ylidene-based ligands. Only very recently have studies on six- and seven-membered-ring NHCs started to appear,[2] but it is clear already that these so-called ring-expanded carbenes exhibit quite different properties from the five-membered counterparts, particularly in terms of much higher basicity.[3] Moreover, a wider $N-C_{NHC}-N$ angle associated with ring-expanded NHCs (IMes, 101.4°;[4] 6-Mes, 114.6°:[5] see Scheme 1 for structures) results in increased steric hindrance at the metal center, which may allow specific coordination sites to be blocked or protected, a feature with obvious ramifications for catalytic applications. However, placing the N-substituents closer to the metal may also facilitate intramolecular C−H activation of the carbene ligand, which may ultimately be detrimental to catalyst performance.

Scheme 1



In light of our previous reports of intramolecular C−X (X = H, C, N) bond activation of five-membered carbenes upon reaction with various ruthenium hydride precursors,[6]

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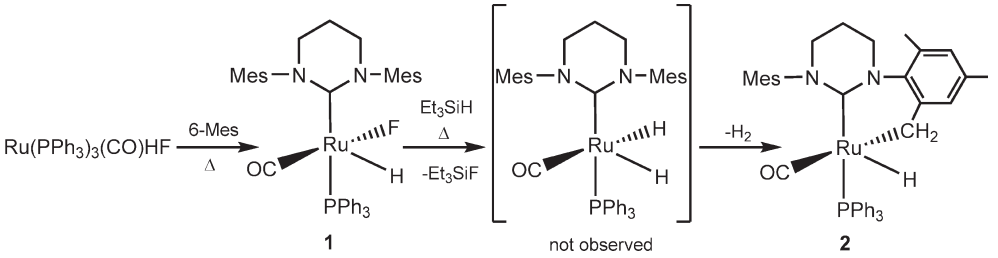
Scheme 2



we have now investigated the reactivity of the six-membered NHCs 6-Mes (1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) and 6-^{i}Pr (1,3-bis(isopropyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) toward the ruthenium hydride halide complexes $Ru(PPh_3)_3(CO)HF$ and $Ru(PPh_3)_3(CO)HCl$. We show that both of these six-membered carbenes are susceptible to intramolecular C−H activation under quite mild conditions, the first time that such reactivity has been reported in transition metal ring-expanded NHC complexes.[7]

Results and Discussion

Reactivity of $Ru(PPh_3)_3(CO)HX$ (X = F, Cl) with 6-Mes. Treatment of the 18-electron hydride fluoride complex $Ru(PPh_3)_3(CO)HF$ with 2 equiv of 6-Mes (generated in situ by addition of $KN(SiMe_3)_2$ to 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate) at 343 K for 2 h resulted in formation of a single product, the five-coordinate monocarbene complex Ru(6-Mes)(PPh_3)(CO)HF (**1**). The ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{19}F NMR data are consistent with the structure shown in Scheme 2, namely, a square-based pyramid with an axial hydride ligand. The low-frequency hydride chemical shift (δ −22.8) reflects the position of Ru−H trans to a vacant coordination site.[8] The 6-Mes ligand is trans to the phosphine (demonstrated by the large C_{NHC}−P coupling of 102 Hz),[6e] with the π-acceptor CO trans to the π-donor fluoride. The ^{19}F spectrum showed a single doublet resonance at δ −239 (J_{FP} = 28 Hz), the chemical shift being characteristic of a coordinatively unsaturated Ru−F species.[9]

The enhanced σ-donor ability associated with larger ring carbenes[2c,o,10] is apparent from the ν_{CO} value of 1894 cm^{-1}, a much lower frequency than reported for the five-membered NHC analogues Ru(IMes)(PPh_3)(CO)HF (1916 cm^{-1}) and Ru(SIMes)(PPh_3)(CO)HF (1916 cm^{-1}; SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene).[9d] However, this enhancement is not reflected in the Ru−C_{NHC} distance (2.1041(18) Å) found from the X-ray crystal structure of **1** (Figure 1), which is longer than that observed in both Ru(IMes)(PPh_3)(CO)HF and Ru(SIMes)(PPh_3)(CO)HF (2.077(2) and 2.071(2) Å, respectively). In an effort to rationalize this observation, we noted that the six-membered ring of **1** is concomitant with additional tilting of the mesityl rings toward the ruthenium center, carbonyl group, and fluoride ligand (relative to the IMes/SIMes structures). In particular, the average Ru−mesityl$_{centroid}$ distances are 3.91, 4.26, and 4.23 Å in **1**, Ru(IMes)(PPh_3)(CO)HF, and Ru(SIMes)(PPh_3)(CO)HF, respectively. We suggest that these steric demands may necessitate a push of the carbene away from the metal center, thereby increasing the Ru−C_{NHC} bond distance. The six-membered NHC does not appear to impact on the trans Ru−P bond length (**1**, 2.3294(5); Ru(IMes)(PPh_3)(CO)HF, 2.3403(6); Ru(SIMes)(PPh_3)(CO)HF, 2.3494(5) Å).[2d]

In a number of cases, transition metal fluoride complexes have been successfully converted to the corresponding hydride derivatives upon treatment with alkylsilanes, the driving force for reaction being the formation of a strong Si−F bond in the R_3SiF coproduct.[9d,11] Although no reaction was

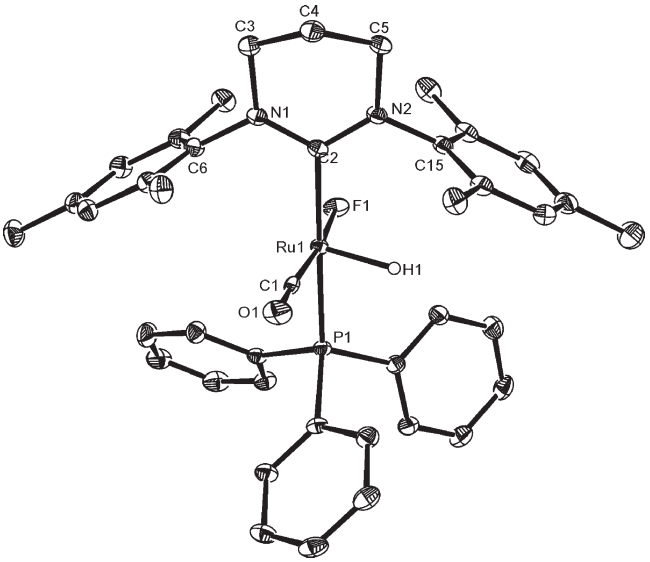


Figure 1. X-ray crystal structure of Ru(6-Mes)(PPh_3)(CO)HF (**1**). Thermal ellipsoids are set at 30% probability. Hydrogen atoms (except Ru−H) and minor disordered components have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−C(1) 1.821(7), Ru(1)−C(2) 2.1041(18), Ru(1)−P(1) 2.3294(5), Ru(1)−F(1) 2.0418(11), C(2)−Ru(1)−P(1) 177.82(5), C(1)−Ru(1)−F(1) 172.92(13), N(1)−C(2)−N(2) 117.17(16).

(7) Intramolecular C−H insertion of a free six-membered diamidocarbene has recently been described (Hudnall, T. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2009**, *131*, 16039), while we have found very recently that heating 6-Mes (or the seven-membered analogue 7-Mes) alone (343 K, ≥12 h) leads to insertion of the carbenic carbon into an ortho-methyl C−H bond. Holdroyd, R. S.; Page, M. J.; Warren, M. R.; Whittlesey, M. K. *Tetrahedron Lett.* **2010**, *51*, 557.

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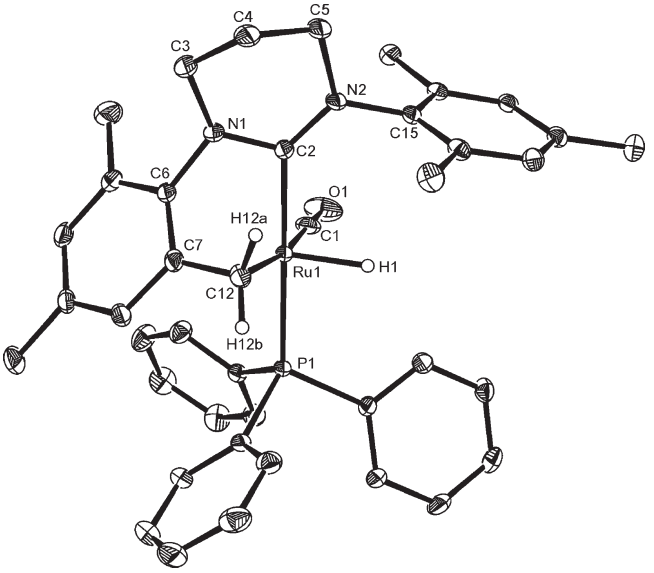

Figure 2. X-ray crystal structure of Ru(6-Mes)′(PPh_3)(CO)H (**2**). Thermal ellipsoids are set at 30% probability. Hydrogen atoms (except for Ru−H and Ru−CH_2) have been omitted for clarity, as have the solvent and the minor disordered components present. Selected bond lengths (Å) and angles (deg): Ru(1)−C(1) 1.847(3), Ru(1)−C(2) 2.063(2), Ru(1)−C(12) 2.228(2), Ru(1)−P(1) 2.3339(6), C(2)−Ru(1)−P(1) 178.11(7), C(1)−Ru(1)−C(12) 171.45(10), N(1)−C(2)−N(2) 118.7(2).

detected between **1** and 5 equiv of Et_3SiH at room temperature, quantitative conversion of Et_3SiH to Et_3SiF was found upon heating the mixture at 343 K for 12 h (Scheme 2). A single ruthenium-containing product was formed, which was identified as the C−H activated carbene complex Ru(6-Mes)′(PPh_3)(CO)H (**2**) due to the appearance of five different methyl resonances in the ^{1}H NMR spectrum, along with two multiplets for the diastereotopic protons of the coordinated methylene group.[12]

The molecular structure of **2** was confirmed by X-ray diffraction, as shown in Figure 2. The complex adopts the expected square-pyramidal geometry at ruthenium, with the base of the pyramid defined by the phosphorus atom, the carbonyl carbon, the carbene carbon, and the activated CH_2 of the mesityl ring. The C(7)−C(12)−Ru(1) angle of 77.42(14)° reflects the level of distortion from metrics pertaining to an idealized sp^3-hybridized methylene group. The net effect of the tension resulting from activation of C(12) is a dramatic tilt of the carbene ring, which is evidenced by the difference in the N(1)−C(2)−Ru−(1) and N(2)−C(2)−Ru(1) angles (105.73(16)° and 135.36(17)°, respectively). The internal strain in **2** may also contribute to the shortening of the Ru−C_{NHC} distance (2.063(2) Å) compared to that in **1** (2.1041(18) Å) as well as to the high-frequency shift of 8 ppm seen for the hydride resonance of **2** (again relative to **1**) despite it still being trans to a vacant coordination site.

At no stage of the reaction of **1** with Et_3SiH were we able to detect the dihydride complex Ru(6-Mes)(PPh_3)(CO)H_2 shown in Scheme 2 that must be formed initially, implying that C−H activation is a very facile process. The failure to observe Ru(6-Mes)(PPh_3)(CO)H_2 is perhaps not surprising given that there is very limited experimental evidence for d^6-ML_5 dihydride species, even though DFT calculations suggest that such compounds should be isolable.[13] Attempts to convert **2** to the dihydride with either H_2 or EtOH were unsuccessful, although addition of D_2 resulted in H/D exchange into the *ortho*-methyl positions of the mesityl rings of **2** (very little deuterium labeling was apparent at the hydride position by either ^{2}H or ^{1}H NMR spectroscopy) over a period of hours at room temperature, indicating that Ru(6-Mes)(PPh_3)(CO)H_2 has at least a transient existence on the reaction pathway.[14]

The reactivity of the hydride chloride complex Ru(PPh_3)$_3$(CO)HCl with 6-Mes (4 equiv) proved to be quite different from that of the hydride fluoride precursor in yielding the C−H activated complex **2** without the need for alkylsilane as the major product following reaction in C_6D_6 at 343 K overnight. Smaller amounts of the known all-phosphine dihydride compound Ru(PPh_3)$_3$(CO)H_2 and what we assign as the hydride chloride complex Ru(6-Mes)(PPh_3)(CO)HCl (based on the similarity of the hydride and phosphorus chemical shifts to those of **1**; ^{1}H: δ −23.60 cf. δ −22.83 in **1**; ^{31}P: δ 45.0 cf. δ 42.8 in **1**) were also formed. When the reaction was repeated but with a 1:1 ratio of Ru(PPh_3)$_3$(CO)HCl and 6-Mes, Ru(6-Mes)(PPh_3)(CO)HCl was formed as the major product,[15] with only a minimal amount of **2** (see Conclusions section).

Reactivity of Ru(PPh_3)$_3$(CO)HX (X = Cl, F) and Ru(PPh_3)$_3$(CO)H_2 with 6-^{i}Pr. In contrast to 6-Mes, the N-isopropyl-substituted carbene 6-^{i}Pr (generated in situ as for 6-Mes by reaction of the corresponding tetrahydropyrimidinium salt with KN($SiMe_3$)$_2$) gave cleaner reactions with Ru(PPh_3)$_3$(CO)HCl than with Ru(PPh_3)$_3$(CO)HF. The combination of Ru(PPh_3)$_3$(CO)HCl with 6 equiv of 6-^{i}Pr in benzene at room temperature resulted in complete conversion to the C−H activated complex Ru(6-^{i}Pr)′(PPh_3)$_2$(CO)H (**3a**) over the course of only 20 min. The lesser bulk of 6-^{i}Pr relative to 6-Mes allows **3a** to attain an 18-electron configuration by coordination of a second PPh_3 ligand. 1-D and 2-D NMR spectra established the geometry of **3a** as that shown in Scheme 3. The appearance of only a singlet in the ^{31}P{^{1}H} spectrum implies a trans PPh_3−Ru−PPh_3 arrangement,[16] while the presence of a strong NOE correlation between the Ru-hydride and the methine proton of the unactivated isopropyl substituent at δ 6.08 supports their close proximity.

(12) For examples of C−H activated five-membered N-mesityl carbene ligands, see: (a) Huang, J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2000**, *19*, 1194. (b) Reference 6a. (c) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546. (d) Abdur- Rashid, K.; Fedorkiw, T.; Lough, A. J.; Morris, R. H. *Organometallics* **2004**, *23*, 86. (e) Torres, O.; Martín, M.; Sola, E. *Organometallics* **2009**, *28*, 863.

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(14) Related H/D exchange in N-mesityl-substituted imidazol-2-ylidene complexes of Ru has been reported. (a) Giunta, D.; Hölscher, M.; Lehmann, C. W.; Mynott, R.; Wirtz, C.; Leitner, W. *Adv. Synth. Catal.* **2003**, *345*, 1139. (b) Lee, J. P.; Ke, Z.; Ramírez, M. A.; Gunnoe, T. B.; Cundari, T. R.; Boyle, P. D.; Petersen, J. L. *Organometallics* **2009**, *28*, 1758.

(15) Ru(6-Mes)(PPh_3)(CO)HCl proved to be soluble even in hexane, preventing isolation.

(16) The appearance of a singlet in the ^{31}P{^{1}H} NMR spectrum of **3a** is unexpected (cf. **3b**), given that the two phosphines should be rendered inequivalent by the activated isopropyl arm. We have observed the same thing previously, however, for the trans-phosphine isomer of Ru(I^{i}Pr$_2$Me$_2$)′(PPh_3)$_2$(CO)H (I^{i}Pr$_2$Me$_2$ = 1,3-bis(isopropyl)-4,5- dimethylimidazol-2-ylidene).[6e]

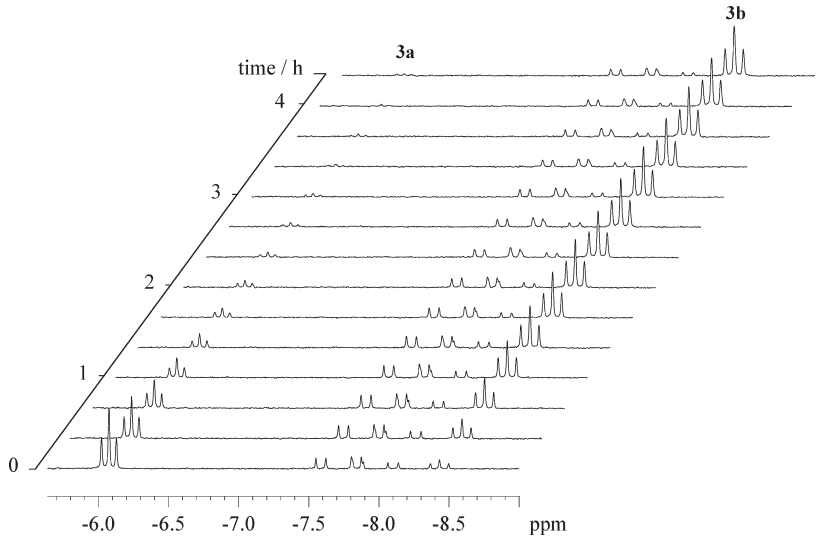
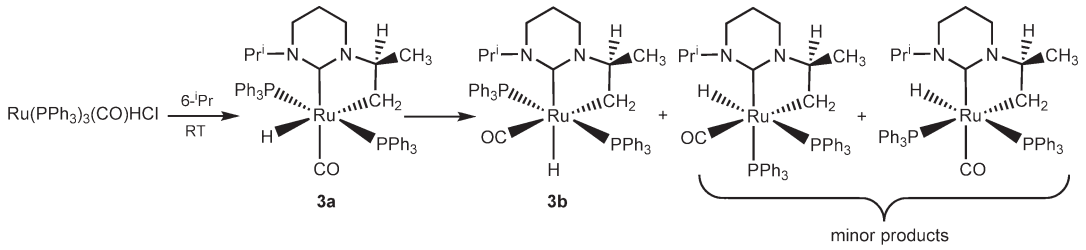


Figure 3. Time course plot of the hydride region of the ^{1}H NMR spectrum (400 MHz, C_6D_6) showing the isomerization of **3a** at 338 K.

Scheme 3



When a sample of $Ru(PPh_3)_3(CO)HCl$ with 1.5 equiv of 6-^{i}Pr was prepared and analyzed immediately by NMR spectroscopy, only a mixture of the starting precursor and the activated complex **3a** was seen, with no signals arising from the unactivated hydride chloride species Ru(6-^{i}Pr)-$(PPh_3)_2(CO)HCl$.

Over a period of 72 h in C_6D_6 at room temperature, the triplet hydride signal for **3a** at δ −6.07 decreased in intensity and three new isomers were formed. Two of these, at δ −7.71 and −7.97, exhibited doublet of doublet multiplicities with cis (ca. 30 Hz) and trans (ca. 70 Hz) J_{HP} couplings, consistent with the minor products shown in Scheme 3. The major hydride-containing species appeared as a triplet at δ −8.43 and is assigned to **3b**, the trans-phosphine isomer in which the relative positions of the hydride and CO ligands have changed. The geometry proposed for **3b** is supported not only by the appearance of a strong NOE correlation between Ru−H and the methylene protons of the metalated arm but more conclusively by the appearance of a large, trans-$^2J_{HC}$ doublet splitting of 16 Hz that was observed between Ru−*H* and Ru−C_{NHC} in the phase-sensitive ^{1}H−^{13}C HMQC spectrum. Smaller cis-couplings of 6 and 3 Hz were found between *H*−Ru−*C*O and *H*−Ru−*C*H$_2$ respectively in the *J*-resolved ^{1}H−^{13}C HMBC spectrum.

A stacked ^{1}H NMR plot showing the depletion of **3a** over a 4 h period at 338 K is shown in Figure 3. The depletion of **3a** was monitored by ^{1}H NMR spectroscopy over the temperature range 303−343 K to afford an Eyring plot, from which $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of 98.2 ± 4.6 kJ mol^{-1} and 15.5 ± 14.5 J mol^{-1} K^{-1} were determined.[17] The near-zero value for the entropy of activation suggests that **3a** does not isomerize via ligand dissociation, a conclusion further supported by the fact that the addition of a large excess (ca. 17 equiv) of PPh_3 had no effect on the rate of disappearance of **3a** (measured at 328 K).

Treatment of the hydride fluoride precursor $Ru(PPh_3)_3$-(CO)HF with 2−6 equiv of 6-^{i}Pr resulted in the formation of a mixture of **3a** and **3b**, along with several other unidentifiable Ru-hydride complexes over the course of 1 h at room temperature. A ^{19}F NMR spectrum of the reaction mixture showed no Ru−F resonances, indicating that, as in the analogous reaction with $Ru(PPh_3)_3(CO)HCl$, the initially formed substitution products Ru(6-^{i}Pr)$(PPh_3)_2(CO)HX$ must be susceptible to very facile C−H cleavage.

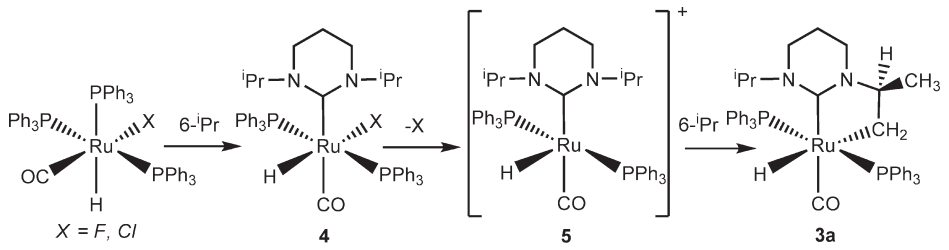
No reaction between 6-^{i}Pr and $Ru(PPh_3)_3(CO)H_2$ was apparent after 24 h at room temperature, although under more forcing conditions (343 K, 48 h), complete conversion to **3b** was observed, presumably as a result of the isomerization of the first formed **3a**. Exposure of **3b** to 1 atm of D_2 at room temperature gave a clear Ru−D signal and deuterium incorporation into both the methyl and methine groups of the 6-^{i}Pr ligand. Thus, as for 6-Mes in **2**, activation of 6-^{i}Pr is reversible.

Conclusions

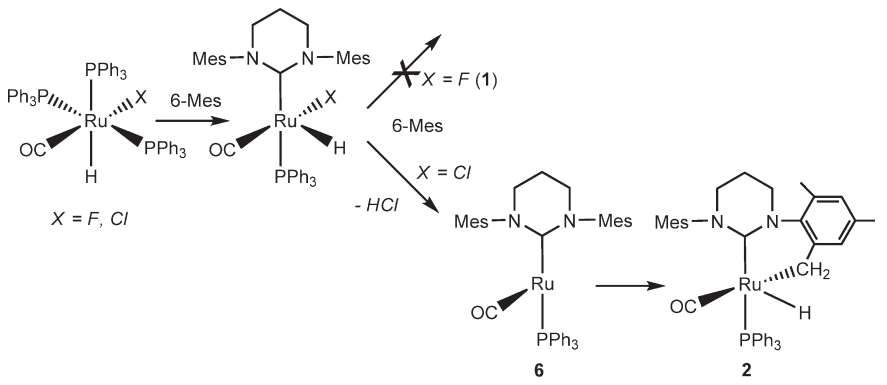
C−H activation of both 6-Mes and 6-^{i}Pr has been shown to occur with the hydride chloride complex $Ru(PPh_3)_3$-(CO)HCl, whereas the hydride fluoride species $Ru(PPh_3)_3$-(CO)HF activates only 6-^{i}Pr directly and yields the isolable 16-electron hydride fluoride substitution product

(17) See Supporting Information for experimental values and Eyring plot.

Scheme 4



Scheme 5



Ru(6-Mes)(PPh_3)(CO)HF with 6-Mes. Addition of Et_3SiH to Ru(6-Mes)(PPh_3)(CO)HF affords Ru(6-Mes)′(PPh_3)(CO)H, presumably via the undetectable dihydride intermediate Ru(6-Mes)(PPh_3)(CO)H_2. While C−H activation of five-membered N-heterocyclic carbenes is a well-established reaction for a wide range of M-NHC complexes,[12,18] our results provide the first examples of metal-induced C−H cleavage in ring-expanded NHCs.

A possible pathway to explain the activation of 6-^{i}Pr by both Ru(PPh_3)$_3$(CO)HF and Ru(PPh_3)$_3$(CO)HCl is shown in Scheme 4. Initial substitution of phosphine by 6-^{i}Pr followed by isomerization would afford the six-coordinate trans hydride-halide species **4**. Support for such an isomerization step is provided by the isolation of the trans-(H,Cl) product Ru(IEt_2Me_2)(PPh_3)$_2$(CO)HCl upon reaction of Ru(PPh_3)$_3$(CO)HCl with IEt_2Me_2 (1,3-diethyl-4,5-dimethylimidazol-2-ylidene).[6d] The combination of a sterically crowded metal center and a trans labilizing hydride ligand could facilitate loss of fluoride and chloride from **4** to yield the five-coordinate cationic species **5**, which in the presence of excess 6-^{i}Pr could undergo C−H activation to form **3a**. We recently reported activation of the analogous cationic species [Ru($I^iPr_2Me_2$)′(PPh_3)$_2$(CO)H]$^+$ ($I^iPr_2Me_2$ = 1,3-bis(isopropyl)-4,5-dimethylimidazol-2-ylidene) by NHC-induced deprotonation of the N-^{i}Pr substituent.[19] The stereochemistry of **3a** with hydride trans to the activated NHC arm excludes an alternative mechanism involving carbene-induced formal reductive elimination of HX from **4** (involving a cis-H,X isomer) and intramolecular C−H oxidative addition in the resulting Ru(0) fragment Ru(6-^{i}Pr)(PPh_3)$_2$(CO).[20]

The greater steric bulk of the 6-Mes ligand favors the formation of the five-coordinate species Ru(6-Mes)(PPh_3)(CO)HX (Scheme 5), which we have shown react differently for X = F and X = Cl. While **1** (X = F) is inert to C−H activation, Ru(6-Mes)(PPh_3)(CO)HCl affords the C−H activated product **2** in the presence of excess 6-Mes at elevated temperature. We propose that 6-Mes induces dehydrochlorination of Ru(6-Mes)(PPh_3)(CO)HCl to afford the highly reactive three-coordinate intermediate **6**, which then undergoes intramolecular activation of a mesityl methyl C−H bond.[20] The unwillingness of **1** to undergo dehydrofluorination may simply reflect the greater strength of the Ru−F bond compared to the Ru−Cl bond.[21]

As a final point, it is worth noting that unlike Ru(6-Mes)(PPh_3)(CO)HCl, neither Ru(IMes)(PPh_3)(CO)HCl nor Ru(SIMes)(PPh_3)(CO)HCl undergoes C−H activation.[22] This suggests that metal complexes that simply bind

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five-membered carbenes may show different reactivity toward their six- (and seven-) membered counterparts.

Experimental Section

All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques using dried and degassed solvents. Solvents were purified using an MBraun SPS solvent system (toluene, THF) or under a nitrogen atmosphere from sodium benzophenone ketyl (benzene, hexane) or Mg/I_2 (ethanol). C_6D_6 and d_8-THF were vacuum transferred from potassium. $Ru(PPh_3)_3(CO)HF$,[23] $Ru(PPh_3)_3(CO)HCl$,[24] $Ru(PPh_3)_3(CO)H_2$,[24] [6-MesH]BF_4,[5] and [6-^{i}PrH]BF_4[5] were prepared according to the literature. NMR spectra were recorded on Bruker Avance 400 and 500 MHz NMR spectrometers at 298 K and referenced as follows: C_6D_6 (^{1}H, δ 7.15; ^{13}C, δ 128.0), THF-d_8 (^{1}H: δ 3.58; ^{13}C, δ 67.6). ^{31}P{^{1}H} NMR chemical shifts were referenced externally to 85% H_3PO_4 (δ 0.0), while ^{19}F spectra were referenced to $CFCl_3$ (δ 0.0). IR spectra were recorded on a Nicolet Nexus FTIR spectrometer. Elemental analyses were performed by Elemental Microanalysis Ltd., Okehampton, Devon, UK. Mass spectrometry was undertaken using a micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik GmbH).

Ru(6-Mes)(PPh$_3$)(CO)HF (1). 1,3-Bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-1-ium tetrafluoroborate (261 mg, 0.64 mmol) and $KN(SiMe_3)_2$ (128 mg, 0.64 mmol) were suspended in dry benzene (50 mL) and stirred at ambient temperature for 10 min. The solution was filtered by cannula into a J. Young PTFE capped ampule containing $Ru(PPh_3)_3(CO)HF$ (300 mg, 0.32 mmol). The solution was heated at 343 K for 2 h, cooled to room temperature, and concentrated to half volume. Addition of hexane to the stirred solution afforded a yellow precipitate, which was isolated by cannula filtration. The solid was washed with hexane (2 × 20 mL) and dried in vacuo to give 200 mg of **1** as a yellow solid. Yield: 85%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.47 (m, 6H, PPh_3), 7.00 (m, 9H, PPh_3), 6.99 (s, 1H, 6-Mes), 6.82 (s, 1H, 6-Mes), 6.73 (s, 1H, 6-Mes), 6.71 (s, 1H, 6-Mes), 2.86 (m, 2H, NCH_2), 2.77 (s, 3H, *o*-/*p*-Me), 2.73 (m, 2H, NCH_2), 2.59 (s, 6H, *o*-/*p*-Me), 2.35 (s, 3H, *o*-/*p*-Me), 2.14 (s, 3H, *o*-/*p*-Me), 2.05 (s, 3H, *o*-/*p*-Me), 1.56 (m, 2H, $CH_2CH_2CH_2$), −22.83 (d, $^2J_{HP}$ = 27.4 Hz, 1H, Ru*H*). ^{31}P{^{1}H} NMR: δ 42.8 (d, $^2J_{PF}$ = 28.2 Hz). ^{19}F NMR: δ −238.9 (d, $^2J_{FP}$ = 28.2 Hz, Ru−F). ^{13}C{^{1}H} NMR: δ 211.8 (d, $^2J_{CP}$ = 101.6 Hz, Ru−*C*), 205.3 (dd, $^2J_{CP}$ = 77.1 Hz, $^2J_{CF}$ = 11.5 Hz, Ru−*C*O), 145.1 (s, PPh_3), 138.7 (s, 6-Mes), 138.2 (s, 6-Mes), 137.8 (s, 6-Mes), 137.6 (s, 6-Mes), 137.3 (s, 6-Mes), 136.5 (s, 6-Mes), 135.1 (d, $^2J_{CP}$ = 11.6 Hz, PPh_3), 130.7 (s, 6-Mes), 129.9 (s, 6-Mes), 129.8 (s, 6-Mes), 129.7 (s, 6-Mes), 129.3 (s, PPh_3), 128.1 (s, PPh_3), 46.5 (s, N*C*H_2), 45.7 (s, N*C*H_2), 21.4 (s, $CH_2CH_2CH_2$), 21.2 (s, *o*-/*p*-Me), 19.1 (s, *o*-/*p*-Me), 18.9 (s, *o*-/*p*-Me), 18.3 (s, *o*-/*p*-Me). IR (C_6D_6, cm^{-1}): 1894 (ν_{CO}). Anal. Calcd for $C_{41}H_{44}N_2OFPRu$: C, 67.21; H, 5.98; N, 3.98. Found: C, 67.29; H, 6.06; N, 3.83.

Ru(6-Mes)′(PPh$_3$)(CO)H (2). Triethylsilane (165 mL, 1.0 mmol) was added to a C_6H_6 solution (20 mL) of **1** in an ampule fitted with a J. Young PTFE valve and heated at 343 K for 12 h. Upon cooling, the solvent was reduced in volume to 5 mL and hexane added to precipitate **2** as a yellow solid. This was isolated by cannula filtration, washed with hexane (2 × 10 mL), and dried under vacuum. Yield: 110 mg (70%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.28 (m, 6H, PPh_3), 6.99 (m, 9H, PPh_3), 6.90 (s, 1H, 6-Mes), 6.82 (s, 1H, 6-Mes), 6.78 (s, 1H, 6-Mes), 6.00 (s, 1H, 6-Mes), 2.76 (m, 1H, NCH_2), 2.74 (m, 1H, NCH_2), 2.68 (m, 1H, NCH_2), 2.46 (s, 6H, *o*-/*p*-Me), 2.41 (s, 3H, *o*-/*p*-Me), 2.21 (s, 3H, *o*-/*p*-Me), 2.12 (m, 1H, NCH_2), 1.99 (s, 3H, *o*-/*p*-Me), 1.99 (m, 1H, Ru−CH_2), 1.91 (m, 1H, Ru−CH_2), 1.36 (m, 2H, $CH_2CH_2CH_2$), −15.05 (d, $^2J_{HP}$ = 27.3 Hz, 1H, Ru*H*). ^{31}P{^{1}H} NMR: δ 52.9 (s). ^{13}C{^{1}H} NMR: δ 211.0 (d, $^2J_{CP}$ = 86.5 Hz, Ru−*C*), 206.8 (d, $^2J_{CP}$ = 13.6 Hz, Ru−*C*O), 143.2, 139.4, 139.1, 136.9, 136.7, 136.5, 135.5, 133.5 (s, 6-Mes *C*), 129.6, 129.4, 128.6, 124.6 (s, 6-Mes *C*H), 47.2 (d, $^4J_{CP}$ = 3.0 Hz, N*C*H_2), 45.2 (d, $^4J_{CP}$ = 3.0 Hz, N*C*H_2), 30.1 (d, $^2J_{CP}$ = 5.5 Hz, Ru−*C*H_2), 22.4 (s, $CH_2CH_2CH_2$), 21.3 (s, *o*-/*p*-Me), 21.1 (s, *o*-/*p*-Me), 19.3 (s, *o*-/*p*-Me), 18.8 (s, *o*-/*p*-Me), 18.2 (s, *o*-/*p*-*Me*). IR (C_6D_6, cm^{-1}): 1902 (ν_{CO}). ESI-TOF MS: $[M + THF + H]^+$ m/z = 785.2319 (theoretical 785.2317).

Ru(6-^{i}Pr)′(PPh$_3$)$_2$(CO)H (3a). 1,3-Bis(isopropyl)-3,4,5,6-tetrahydropyrimidin-1-ium tetrafluoroborate (488 mg, 1.90 mmol) and $KN(SiMe_3)_2$ (380 mg, 1.90 mmol) were suspended in dry benzene (25 mL) and stirred at ambient temperature for 10 min. The solution was filtered by cannula into a J. Young PTFE capped ampule containing $Ru(PPh_3)_3(CO)HCl$ (302 mg, 0.32 mmol) and the solution stirred at ambient temperature for 20 min. The dark brown solution was filtered by cannula and the filtrate reduced to dryness. This was washed with hexane (3 × 5 mL), redissolved in THF, and layered with hexane to give a yellow precipitate of **3a**, which was filtered and dried in vacuo to give 59 mg of yellow solid (yield 22%). ^{1}H NMR (THF-d_8, 500 MHz): δ 7.58 (m, 6H, PPh_3), 7.51 (m, 6H, PPh_3), 7.27 (m, 18H, PPh_3), 6.08 (sept, $^2J_{HH}$ = 6.7 Hz, 1H, C*H*Me$_2$), 2.90 (m, 1H, C*H*Me), 2.83 (m, 1H, NCH_2), 2.68 (m, 1H, NCH_2), 2.58 (m, 1H, NCH_2), 2.39 (m, 1H, NCH_2), 1.68 (m, 1H, $CH_2CH_2CH_2$), 1.50 (m, 1H, $CH_2CH_2CH_2$), 1.29 (m, 1H, Ru−CH_2), 0.93 (m, 1H, Ru−CH_2) 0.62 (d, J_{HH} = 6.3, 3H, NCH*Me*), 0.11 (d, $^2J_{HH}$ = 6.3 Hz, 3H, NCH*Me*$_2$), 0.01 (d, $^2J_{HH}$ = 6.7 Hz, 3H, NCH*Me*$_2$), −6.47 (t, $^2J_{HP}$ = 21.7 Hz, 1H, Ru*H*). ^{31}P{^{1}H} NMR: δ 55.5 (s). ^{13}C{^{1}H} NMR: δ 217.6 (t, $^2J_{CP}$ = 13.8 Hz, Ru−*C*), 211.6 (t, $^2J_{CP}$ = 18.1 Hz, Ru−*C*O), 70.8 (s, *C*HMe), 61.0 (s, *C*HMe$_2$), 45.8 (s, N*C*H_2), 38.0 (s, N*C*H_2), 26.5 (s, NCH*Me*), 21.6 (s, $CH_2CH_2CH_2$), 19.8 (s, NCH*Me*$_2$), 19.4 (s, NCH*Me*$_2$), 17.5

Table 1. Crystal Data and Structure Refinement for Compounds 1 and 2

	1	2
empirical formula	$C_{41}H_{44}FN_2OPRu$	$C_{42.50}H_{44.50}N_2OPRu$
fw	731.82	731.34
cryst syst	monoclinic	triclinic
space group	*C*2/*c*	*P*$\bar{1}$ (No. 2)
a/Å	38.8100(4)	9.8510(1)
b/Å	9.2900(1)	10.6390(1)
c/Å	20.1960(2)	20.5300(3)
α/deg	90	94.498(1)
β/deg	100.477(1)	95.050(1)
γ/deg	90	114.234(1)
U/Å^3	7160.17(13)	1938.81(4)
Z	8	2
D_c/g cm^{-3}	1.358	1.253
μ/mm^{-1}	0.522	0.478
F(000)	3040	761
cryst size/mm	0.20 × 0.12 × 0.07	0.45 × 0.30 × 0.25
θ min., max. for data collection	3.57, 27.49	3.53, 27.91
index ranges	$-50 \le h \le 50$; $-12 \le k \le 12$; $-26 \le l \le 26$	$-12 \le h \le 12$; $-14 \le k \le 13$; $-26 \le l \le 27$
reflns collected	68 511	30 697
indep reflns, R_{int}	8184, 0.0472	9215, 0.0381
reflns obsd ($>2\sigma$)	6877	7706
data completeness	0.997	0.994
absorp corr	multiscan	multiscan
max., min. transmn	0.946, 0.875	0.804, 0.770
data/restraints/params	8184/14/457	9215/7/454
goodness-of-fit on F^2	1.059	1.070
final R_1, wR_2 [$I > 2\sigma(I)$]	0.0296, 0.0675	0.0373, 0.0959
final R_1, wR_2 (all data)	0.0405, 0.0725	0.0506, 0.1024
largest diff peak, hole/e Å^{-3}	0.474, −0.754	1.229, −0.637

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(t, $^2J_{CP}$ = 7.5 Hz, Ru−CH_2). IR (C_6D_6, cm^{-1}): 1909 (ν_{CO}). The isomerization of **3a** in solution precluded characterization by elemental analysis, although analysis for **3b** is provided below.

Ru(6-^{i}Pr)′(PPh$_3$)$_2$(CO)H (3b). 1,3-Bis(isopropyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium tetrafluoroborate (563 mg, 2.20 mmol) and $KN(SiMe_3)_2$ (439 mg, 2.20 mmol) were suspended in dry benzene (15 mL) and stirred at ambient temperature for 10 min. The solution was filtered by cannula into a J. Young PTFE capped ampule containing $Ru(PPh_3)_3(CO)H_2$ (1.004 g, 1.09 mmol) and the solution heated with stirring at 343 K for 48 h. After cooling, the white suspension was filtered by cannula and the filtrate reduced to dryness. The resulting yellow residue was washed with hexane (3 × 5 mL), redissolved in C_6H_6, and layered with hexane to give **3b** as a cream precipitate. Yield: 330 mg, 33%. ^{1}H NMR (THF-d_8, 500 MHz): δ 7.74 (m, 6H, PPh_3), 7.50 (m, 6H, PPh_3), 7.23 (m, 18H, PPh_3), 5.14 (sept, $^2J_{HH}$ = 6.7 Hz, 1H, C*H*Me$_2$), 2.95 (m, 1H, NCH_2), 2.92 (m, 1H, NCH_2), 2.77 (m, 1H, C*H*Me), 2.57 (m, 1H, NCH_2), 2.49 (m, 1H, NCH_2), 1.78 (s, 1H, $CH_2CH_2CH_2$), 1.30 (s, 1H, $CH_2CH_2CH_2$), 0.69 (d, $^2J_{HH}$ = 6.7 Hz, 3H, NCH*Me*), 0.63 (d, $^2J_{HH}$ = 5.8 Hz, 3H, NCH*Me*$_2$), 0.48 (m, 1H, Ru−CH_2), 0.42 (d, $^2J_{HH}$ = 6.7 Hz, 3H, NCH*Me*$_2$), 0.38 (m, 1H, Ru−CH_2), −8.95 (t, $^2J_{HP}$ = 25.6 Hz, 1H, Ru*H*). ^{31}P{^{1}H} NMR: δ 57.5 (AB, $\Delta\nu$ = 449.8 Hz, J_{PP} = 288 Hz). ^{13}C{^{1}H} NMR: δ 222.7 (t, $^2J_{CP}$ = 7.5 Hz, Ru−*C*), 204.7 (dd, $^2J_{CP}$ = 13.0 Hz, $^2J_{CP}$ = 10.8 Hz, Ru−*C*O), 69.9 (s, *C*HMe), 60.0 (s, *C*HMe$_2$), 46.3 (s, N*C*H$_2$), 39.5 (s, N*C*H$_2$), 26.7 (s, NCH*Me*), 24.4 (t, $^2J_{CP}$ = 10.9 Hz, Ru−*C*H$_2$), 22.6 (s, $CH_2CH_2CH_2$), 21.0 (s, NCH*Me*$_2$), 19.9 (s, NCH*Me*$_2$). IR (C_6D_6, cm^{-1}): 1894 (ν_{CO}). Anal. Calcd for $C_{47}H_{50}N_2OP_2Ru$: C, 68.68; H, 6.13; N, 3.41. Found: C, 68.56; H, 6.18; N, 3.53.

X-ray Crystallography. Single crystals of compounds **1** and **2** were analyzed at 150 K, using Mo(Kα) radiation on a Nonius Kappa CCD diffractometer. Details of the data collections, solutions, and refinements are given in Table 1. The structures were solved using SHELXS-97[25] and refined using full-matrix least-squares in SHELXL-97.[25] Refinements were generally straightforward with the following exceptions and points of note. In **1**, the hydride ligand and carbonyl functionality were both disordered in a 65:35 ratio. The partial hydrides were readily located and refined at a distance of 1.6 Å from the ruthenium center. ADP similarity restraints were applied to the carbon and oxygen partial atoms in each of the disordered ligand fractions. The asymmetric unit in **2** contains one molecule of the activated carbene complex and a small region of disordered solvent. The latter best approximates a half molecule of benzene with half site-occupancy. In a similar vein to **1**, the hydride ligand in this complex was also located and refined at 1.6 Å from the metal center. The hydrogen atoms attached to the activated carbon (C12) were also located and, in this case, refined at a distance of 0.98 Å from the parent carbon. C4 exhibited 80:20 disorder, which was readily modeled. Hydrogen atoms attached to carbons C3 and C5 were included at full occupancy, based on the 80% fraction of C4. Distances in the solvent fragment were refined subject to restraints. The maximum residual electron density peaks are evident in this region, demonstrating the disorder alluded to herein.

Crystallographic data for compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 755195 and 755196. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: CIF files giving X-ray crystallographic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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