J|A|C|S
ARTICLES
Published on Web 01/27/2007

C—H Activation Reactions of Ruthenium N-Heterocyclic Carbene Complexes: Application in a Catalytic Tandem Reaction Involving C—C Bond Formation from Alcohols

Suzanne Burling,[†] Belinda M. Paine,[†] Devendrababu Nama,[‡] Victoria S. Brown,[†] Mary F. Mahon,[†] Timothy J. Prior,[§] Paul S. Pregosin,[‡] Michael K. Whittlesey,*[,†] and Jonathan M. J. Williams*[,†]

Contribution from the Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K., Laboratory of Inorganic Chemistry, ETHZ, Honggerberg, CH-8093 Zurich, Switzerland, and Station 16.2 SMX, CLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.

Received August 9, 2006; E-mail: m.k.whittlesey@bath.ac.uk (M.K.W.); j.m.j.williams@bath.ac.uk (J.M.J.W.)

Abstract: A series of ruthenium hydride N-alkyl heterocyclic carbene complexes has been investigated as catalysts for a tandem oxidation/Wittig/reduction reaction to give C—C bonds from alcohols. The C—H-activated carbene complex Ru(I^{i}Pr$_2$Me$_2$)′(PPh$_3$)$_2$(CO)H (**9**) proves to be the most active precursor catalyzing the reaction of PhCH$_2$OH and Ph$_3$P=CHCN in 3 h at 70 °C. These results provide (a) a rare case in which N-alkyl carbenes afford higher catalytic activity than their N-aryl counterparts and (b) a novel example of the importance of NHC C—H activation in a catalytic cycle.

Introduction

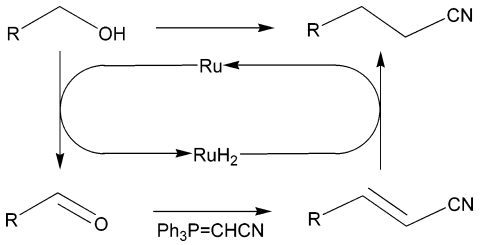
Ruthenium-catalyzed organic transformations have benefited significantly from the enormous current interest in using N-heterocyclic carbenes (NHCs) as ligands in organometallic chemistry.[1] The often facile substitution of tertiary phosphines by NHCs has afforded a wide range of both coordinatively saturated and unsaturated Ru complexes that have subsequently shown activity for C=C and/or C=O hydrogenation;[2] C=C isomerization;[3] and, most successfully of all, ring-opening and ring-closing metathesis reactions.[4,5] NHCs have a number of features that make them appealing for catalytic applications,[6] and of particular importance is the decreased lability and higher thermal stability in comparison to PR_3, features that help to stabilize longer-lived and more active catalytically relevant species.[7] In addition, the shape of NHCs and the position of the N-bound substituents relative to the metal allow for larger variations of both steric bulk and σ-donor ability to be introduced compared to phosphine ligands,[8] allowing catalytic activity to be more finely tuned.[9]

A subset of Ru—NHC-catalyzed reactions involves one-pot, coupled transformations. Such domino or tandem reactions (recently defined by Fogg as those in which "all catalytic

[†] University of Bath.
[‡] ETHZ.
[§] Daresbury Laboratory.

(1) Nolan, S. P. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH: Weinheim, Germany, 2006.
(2) (a) Dharmasena, U. L.; Foucault, H. M.; dos Santos, E. N.; Fogg, D. E.; Nolan, S. P. *Organometallics* **2005**, *24*, 1056. (b) Chiu, P. L.; Lee, H. M. *Organometallics* **2005**, *24*, 1692. (c) Baratta, W.; Schütz, J.; Herdtweck, E.; Herrmann, W. A.; Rigo, P. *J. Organomet. Chem.* **2005**, *690*, 5570. (d) Csabai, P.; Joó, F. *Organometallics* **2004**, *23*, 5640. (e) Poyatos, M.; Mata, J. A.; Falomir, E.; Crabtree, R. H.; Peris, E. *Organometallics* **2003**, *22*, 1110. (f) Dinger, M. B.; Mol, J. C. *Eur. J. Inorg. Chem.* **2003**, 2827. (g) Danopoulos, A. A.; Winston, S.; Motherwell, W. B. *Chem. Commun.* **2002**, 1376. (h) Lee, H. M.; Smith, D. C.; He, Z. J.; Stevens, E. D.; Yi, C. S.; Nolan, S. P. *Organometallics* **2001**, *20*, 794.
(3) (a) Terada, Y.; Arisawa, M.; Nishida, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 4063. (b) Çetinkaya, B.; Demir, S.; Özdemir, I.; Toupet, L.; Sémeril, D.; Bruneau, C.; Dixneuf, P. H. *Chem. Eur. J.* **2003**, *9*, 2323.
(4) (a) Funk, T. W.; Berlin, J. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 1840. (b) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117. (c) Louie, J.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2004**, *40*, 247. (d) Hoveyda, A. H.; Gillingham, D. G.; Van Veldhuizen, J. J.; Kataoka, O.; Garber, S. B.; Kingsbury, J. S.; Harrity, J. P. A. *Org. Biomol. Chem.* **2004**, *2*, 8. (e) Choi, T.-L.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1743. (f) Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003. (g) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035. (h) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18 (i) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012. (j) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168. (k) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674. (l) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2416. (m) Ackermann, L.; Fürstner, A.; Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787. (n) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. (o) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247. (p) Schanz, H.-J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5187. (q) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490.
(5) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543.
(6) (a) Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437. (b) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815. (c) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239. (d) Viciu, M. S.; Navarro, O.; Germaneau, R. F.; Kelly, R. A., III; Sommer, W. J.; Marion, N.; Stevens, E. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2004**, *23*, 1629. (e) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (f) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69.
(7) (a) Lee, H. M.; Jiang, T.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 1255. (b) Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3492. (c) Hillier, A. C.; Lee, H. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 4246. (d) Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053. (e) Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *585*, 348. (f) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5375. (g) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 2371. For examples in which NHCs are substituted by phosphines, see: (h) Simms, R. W.; Drewitt, M. J.; Baird, M. C. *Organometallics* **2002**, *21*, 2958. (i) Titcomb, L. R.; Caddick, S.; Cloke, F. G. N.; Wilson, D. J.; McKerrecher, D. *Chem. Commun.* **2001**, 1388.

Scheme 1

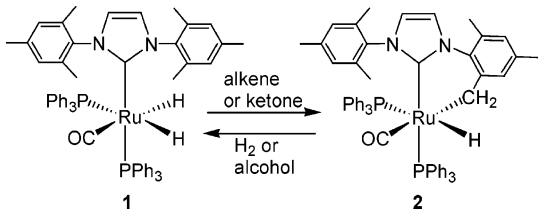


species—whether masked or apparent—[are] present at the outset")[10] offer a powerful synthetic methodology for converting relatively simple substrates into more complex organic products.[11] A number of elegant examples have been reported recently that combine a metathesis step with subsequent hydrogenation[10,12] and isomerization[3,13,14] reactions. In the majority of these cases, and in contrast to catalytic reactions involving only a single process,[14,15] the organometallic chemistry is only poorly understood, as the major focus has been on determining the scope of reactive substrates. Thus, in the case of the tandem ring-closing metathesis (RCM)−isomerization reaction, reference has been made to the involvement of a "hydride-containing species" in mediating the second step, but the exact structure of this compound remains to be established.[12,16]

We have recently reported that the N-aryl-substituted NHC dihydride complex Ru(IMes)$(PPh_3)_2(CO)H_2$ [**1**, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] catalyzes a tandem oxidation/reduction reaction in conjunction with a Wittig reaction (Scheme 1) that allows for the formation of C—C bonds from alcohols.[17]

The ruthenium mediates dehydrogenation of an alcohol to form an aldehyde and hydrogenation of the intermediate alkene to afford the final saturated hydrocarbon product. Key to the hydrogen-transfer chemistry of **1** appears to be the reversible C—H bond activation of the coordinated IMes ligand, which affords the metallated product Ru(IMes)′$(PPh_3)_2(CO)H$ (**2**) (a C—H-activated carbene ligand is henceforth denoted as NHC′) in the presence of an alkene or ketone as a hydrogen acceptor (Scheme 2).[18]

Scheme 2



The reversibility of the C—H cleavage might simply prevent complex **2** from being a dead-end species and hence aid the retention of the ruthenium within the catalytic cycle or alternatively facilitate formation of a coordinatively unsaturated and catalytically active ruthenium fragment. Either way, the use of **1** for the Wittig reaction of benzyl alcohol resulted in a significant lowering of both reaction temperature (from 150 to 80 °C) and time (from 72 to 24 h) in comparison to earlier work employing an iridium-based complex.[19]

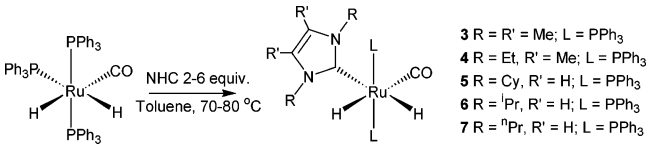
In light of the enhancement brought about by **1**, we have now conducted an extensive investigation of a wide selection of ruthenium NHC complexes containing different N-substituted ligands. We reasoned that any oxidative addition process (i.e., C—H activation of the carbene) should be enhanced by more electron-donating ligands and have therefore focused on N-alkyl substituents. Contrary to a number of reports suggesting that N-alkyl groups result in lower reactivity than their N-aryl counterparts,[20,21] we report a case in which the most electron-rich of ligands employed, the isopropyl-substituted carbene $I^iPr_2Me_2$ (1,3-bis-isopropyl-4,5-dimethylimidazol-2-ylidene)[22] affords a complex that catalyzes the tandem Wittig reaction at lower temperature and in significantly shorter time than the IMes complex **1**. Although stoichiometric bond activation of NHCs has been described in a number of cases,[23] our work provides the first example of carbene C—H activation being applied to a catalytic reaction[24] with the unique ability of $I^iPr_2Me_2$ to undergo direct (and reversible) C—H cleavage yielding the most active catalyst precursor for C—C bond formation.

Results and Discussion

Synthesis and Characterization of Ru(NHC)$(PPh_3)_2(CO)H_2$ Complexes. The mono-NHC complexes Ru(NHC)$(PPh_3)_2(CO)H_2$ (NHC = IMe_4, **3**; IEt_2Me_2, **4**; ICy, **5**; I^iPr_2, **6**; I^nPr_2, **7**) were readily prepared upon heating $Ru(PPh_3)_3(CO)H_2$ with between 2 and 6 equiv of the appropriate NHC precursor (Scheme 3).[25] Under these conditions, **3**−**7** were formed as the major products, although the bis- and tris-substituted complexes $Ru(NHC)_2(PPh_3)(CO)H_2$ and $Ru(NHC)_3(CO)H_2$ were often

(8) (a) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485. (b) Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Petersen, J. L.; Cavallo, L.; Nolan, S. P. *Organometallics* **2003**, *22*, 4322. (c) Huang, J.; Jafarpour, L.; Hillier, A. C.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 2878.
(9) Jackstell, R.; Harkal, S.; Jiao, H.; Spannenberg, A.; Borgmann, C.; Röttger, D.; Nierlich, F.; Elliot, M.; Niven, S.; Cavell, K. J.; Navarro, O.; Viciu, M. S.; Nolan, S. P.; Beller, M. *Chem. Eur. J.* **2004**, *10*, 3891.
(10) Fogg, D. E.; dos Santos, E. N. *Coord. Chem. Rev.* **2004**, *248*, 2365. For a review of tandem reactions involving more than one metal species, see: Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001.
(11) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115.
(12) (a) Børsting, P.; Nielsen, P. *Chem. Commun.* **2002**, 2140. (b) Louie, J.; Bielawski, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 11312.
(13) Sutton, A. E.; Seigal, B. A.; Finnegan, D. F.; Snapper, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 13390.
(14) (a) Schmidt, B. *Eur. J. Org. Chem.* **2003**, 816. (b) Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H. J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204.
(15) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749.
(16) (a) Hong, S. H.; Sanders, D. P.; Lee, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 17160. (b) Hong, S. H.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 7414.
(17) Edwards, M. G.; Jazzar, R. F. R.; Paine, B. M.; Shermer, D. J.; Whittlesey, M. K.; Williams, J. M. J.; Edney, D. D. *Chem. Commun.* **2004**, 90.
(18) (a) Burling, S.; Whittlesey, M. K.; Williams, J. M. J. *Adv. Synth. Catal.* **2005**, *347*, 591. (b) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944.
(19) (a) Edwards, M. G.; Williams, J. M. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4740. (b) Black, P. J.; Cami-Kobeci, G.; Edwards, M. G.; Slatford, P. A.; Whittlesey, M. K.; Williams, J. M. J. *Org. Biomol. Chem.* **2006**, *4*, 116.
(20) (a) Mayr, M.; Wurst, K.; Ongania, K.-H.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 1256. (b) Simal, F.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Denk, K.; Kohl, F. J.; Weskamp, T.; Herrmann, W. A. *Chem. Eur. J.* **2002**, *8*, 3047.
(21) Of course, electronic influence might have to be offset against changes in steric properties. See, for example: (a) Fructos, M. R.; de Frémont, P.; Nolan, S. P.; Díaz-Requejo, M. M.; Pérez, P. J. *Organometallics* **2006**, *25*, 2237. (b) Ledoux, N.; Allaert, B.; Pattyn, S.; Mierde, H. V.; Vercaemst, C.; Verpoort, F. *Chem. Eur. J.* **2006**, *12*, 4654. Moreover, in a study of metathesis activity, Fürstner has noted that different NHC ligands prove optimal for different substrates: Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, R.; Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236.
(22) (a) Alder, R. W.; Allen, P. R.; Williams, S. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1267. (b) Magill, A. M.; Cavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717.

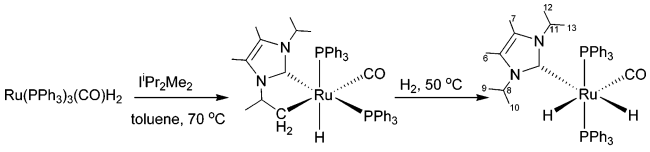
Scheme 3



detectable by NMR spectroscopy, with the relative amounts depending on the specific NHC and the number of equivalents being used. Complexes **3**−**7** could all be isolated as white crystalline, moderately air-sensitive solids using a workup procedure involving crystallization from benzene/ethanol.[26] The appearance of two hydride resonances (typically in the range from δ −5 to δ −10), both with a doublet of triplet multiplicities, and singlet $^{31}P\{^1H\}$ NMR signals is consistent with a stereochemistry having the NHC trans to hydride and trans phosphines (Scheme 3). This is distinct from the cis phosphine arrangement observed in the IMes complex **1**.[18b] IR spectroscopy gives ν_{CO} values within 2 cm^{-1} of each other for **3**−**7**.

The geometries of complexes **4**−**7** were confirmed by X-ray crystallography (the structures of **4**[23j] and **5**[27] have been reported previously; structural information is provided in the Supporting Information). In all cases, the Ru−C_{NHC} distances [2.140(4)−2.171(3) Å] are longer than in **1** [2.0956(17) Å], reflecting the change of trans ligand to hydride rather than phosphine. The P−Ru−P angles are all compressed below the ideal 180° angle and range from 155.549(19)° in **6** to 164.32(4)° in **4**.

Scheme 4



Direct C−H Activation of I^{i}Pr$_2$Me$_2$. A more intriguing reaction was observed upon heating $Ru(PPh_3)_3(CO)H_2$ with 4 equiv of I^{i}Pr$_2$Me$_2$. This procedure failed to give the expected dihydride complex $Ru(I^iPr_2Me_2)(PPh_3)_2(CO)H_2$ (**8**), but afforded instead $Ru(I^iPr_2Me_2)'(PPh_3)_2(CO)H$ (**9**) resulting from C−H activation of an isopropyl methyl group in the NHC ligand (Scheme 4). This complex contrasts starkly with all of our previous examples of carbene activation[18b,23j,o] in having no obvious hydrogen acceptor present during preparation. Multinuclear NMR spectroscopy revealed a doublet-of-doublets pattern for the hydride signal with cis (J_{HP} = 28.0 Hz) and trans (J_{HP} = 104.8 Hz) phosphorus couplings, two doublets (J_{PP} = 16.7 Hz) in the $^{31}P\{^1H\}$ spectrum, and a high-frequency carbene signal (with doublet-of-doublets multiplicity) in the $^{13}C\{^1H\}$ NMR spectrum (δ 187.8, J_{CP} = 10.1 Hz, J_{CP} = 82.7 Hz). These data are consistent with a structure containing cis phosphines. This stereochemistry, along with the formation of the five-membered ruthenacycle, was confirmed by X-ray crystallography as shown in Figure 1. Complex **9** is formed as a single diastereomer where the methyl group on the activated arm is oriented syn with respect to the hydride and anti with respect to the phosphine, presumably for steric reasons. The Ru-metallated carbon distance of 2.2100(16) Å is the same as that seen in the C−H-activated ethyl carbene complex $Ru(IEt_2Me_2)'(PPh_3)_2(CO)H$ (**10**) [2.2107(17) Å].[23j]

Bubbling hydrogen through a benzene solution of 9 at 50 °C for 2 h led to complete conversion to **8** (Scheme 4), which displayed hydride and phosphine NMR resonances similar to those of complexes **3**−**7**. Additional NMR studies on **8** showed that the two isopropyl groups are inequivalent in solution at ambient temperature, suggesting that the plane defined by the

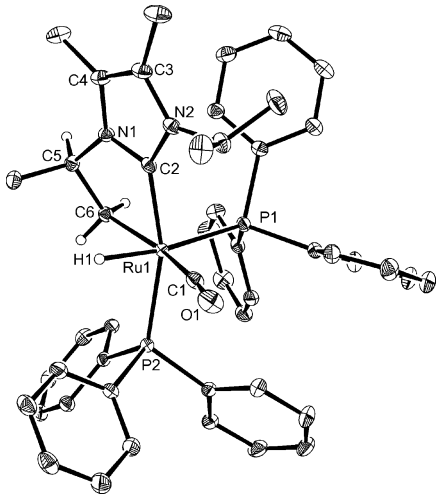


Figure 1. Molecular structure of **9**. Thermal ellipsoids are represented at 30% probability. The majority of hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Ru(1)−C(2), 2.0594(16); Ru(1)−C(6), 2.2100(16); Ru(1)−P(1), 2.4357(4); Ru(1)−P(2), 2.3445(4); C(5)−C(6)−Ru(1), 110.5(1); P(1)−Ru(1)−P(2), 102.152(15).

(23) There has been a recent review of C−H activation in NHC complexes: Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247. For other examples, see: (a) Corberán, R.; Sanaú, M.; Peris, E. *Organometallics* **2006**, *25*, 4002. (b) Hanasaka, F.; Tanabe, Y.; Fujita, K.;Yamaguchi, R. *Organometallics* **2006**, *25*, 826. (c) Ferrence, G. M.; Arduengo, A. J., III; Jockisch, A.; Kim, H.-J.; McDonald, R.; Takats, J. *J. Alloys Compd.* **2006**, *418*, 184. (d) Cariou, R.; Fischmeister, C.; Toupet, L.; Dixneuf, P. H. *Organometallics* **2006**, *25*, 2126. (e) Burling, S.; Mahon, M. F.; Powell, R. E.; Whittlesey, M. K.; Williams, J. M. J. *J. Am. Chem. Soc.* **2006**, *128*, 13702. (f) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516. (g) Scott, N. M.; Pons, V.; Stevens, E. D.; Heinekey, D. M.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 2512. (h) Cabeza, J. A.; del Rio, I.; Sanchez-Vega, M. G. *Chem. Commun.* **2005**, 3956. (i) Baratta, W.; Schütz, J.; Herdtweck, E.; Herrmann, W. A.; Rigo, P. *J. Organomet. Chem.* **2005**, *690*, 5570. (j) Burling, S.; Mahon, M. F.; Paine, B. M.; Whittlesey, M. K.; Williams, J. M. J. *Organometallics* **2004**, *23*, 4537. (k) Abdur-Rashid, K.; Fedorkiw, T.; Lough, A. J.; Morris, R. H. *Organometallics* **2004**, *23*, 86. (l) Dorta, R.; Stevens, E. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5054. (m) Caddick, S.; Cloke, F. G. N.; Hitchcock, P. B.; de K. Lewis, A. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5824. (n) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Deng, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546. (o) Chilvers, M. J.; Jazzar, R. F. R.; Mahon, M. F.; Whittlesey, M. K. *Adv. Synth. Catal.* **2003**, *345*, 1111. (p) Giunta, D.; Hölscher, M.; Lehmann, C. W.; Mynott, R.; Wirtz, C.; Leitner, W. *Adv. Synth. Catal.* **2003**, *345*, 1139. (q) Danopoulos, A. A.; Winston, S.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2002**, 3090. (r) Prinz, M.; Grosche, M.; Herdtweck, E.; Herrmann, W. A. *Organometallics* **2000**, *19*, 1692. (s) Huang, J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2000**, *19*, 1194. (t) Doyle, M. J.; Lappert, M. F.; Pye, P. L.; Terreros, P. *J. Chem. Soc., Dalton. Trans.* **1984**, 2355. (u) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 196.

(24) Competitive intramolecular C−H activation and catalytic, intermolecular H/D exchange has very recently been described: Corberán, R.; Sanaú, M.; Peris, E. *J. Am. Chem. Soc.* **2006**, *128*, 3974.

(25) Typically, heating at 70 °C in toluene for 16−20 h was sufficient to consume $Ru(PPh_3)_3(CO)H_2$, although the reaction with IMe_4 required 3 days at 80 °C to give complete conversion into a mixture of **4**, $Ru(IMe_4)_2(PPh_3)(CO)H_2$, and $Ru(IMe_4)_3(CO)H_2$.

(26) The *n*-propyl complex $Ru(I^nPr)(PPh_3)_2(CO)H_2$ (**7**) was found to exist as a mixture of isomers in solution. Whereas the major isomer contained the same NHC-*trans*-hydride/P-*trans*-P geometry as in **3**−**6**, it was accompanied by varying amounts of the *trans*-dihydride/*trans*-phosphine complex (^1H δ −5.02, triplet, J_{PH} = 20.3 Hz; $^{31}P\{^1H\}$ δ 62.8, singlet) and lesser amounts of a third isomer, containing inequivalent PPh_3 ligands with a cis disposition. Complete isomerization to the major isomer occurs upon standing for 16 h at room temperature.

(27) Burling, S.; Kociok-Köhn, G.; Mahon, M. F.; Whittlesey, M. K.; Williams, J. M. J. *Organometallics* **2005**, *24*, 5868.

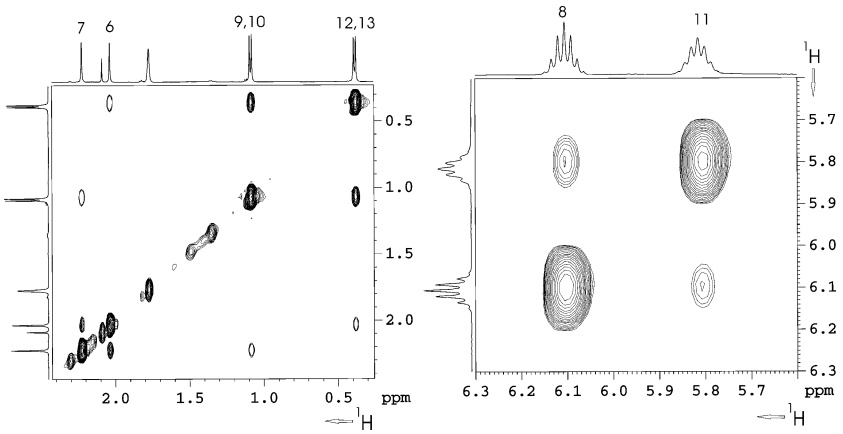


Figure 2. Sections of the phase-sensitive ^{1}H−^{1}H NOESY spectrum for complex **8** in THF solution. The left section shows the exchange from methyl resonances (top right), and the right section shows the exchange between two methine signals. Numbering assignments are shown in Scheme 4.

three atoms N−C−N does not eclipse the P−Ru−P axis, but rather lies rotated at some angle away from the two phosphine ligands. Sections of the phase-sensitive 2-D NOESY exchange spectrum for this complex are shown in Figure 2 and reveal that the two isopropyl groups do exchange with one another (i.e., there is rotation about the Ru−C_{NHC} bond) but that the exchange is not rapid.[28] The appearance of a single ν_{CO} band in the IR spectrum of **8** at 1917 cm^{-1} is in agreement with I^{i}Pr$_2$Me$_2$ being the most electron donating of the NHCs employed in this study.

Alkene-Induced C−H Bond Activation Reactions in Ru(NHC)(PPh$_3$)$_2$(CO)H$_2$. None of the NHC ligands employed other than I^{i}Pr$_2$Me$_2$ showed any direct C−H activation. This lack of reactivity is intriguing in the case of Ru(I^{i}Pr$_2$)(PPh$_3$)$_2$(CO)H$_2$ (**6**), where the only difference in the ligand is replacement of the two backbone methyl groups by hydrogen atoms. Complex **6** does undergo reversible C−H activation (to give **11**, the structure of which was verified by X-ray diffraction, as shown in Figure 3), but only upon heating in the presence of H$_2$C=CHSiMe$_3$. We assume that the backbone methyl groups of the I^{i}Pr$_2$Me$_2$ ligand restrict the conformation of the isopropyl group by allylic strain, favoring the conformation required for C−H insertion to occur. Both **11** and the activated N-ethyl complex **10** (which is formed upon heating **4** with alkene) contain a trans phosphine arrangement indicated by the triplet hydride signals (e.g., for **11**, at δ −7.20 with J_{HP} = 24.7 Hz) seen in the ^{1}H NMR spectra. Whereas in the case of **10** the ^{31}P{^{1}H} NMR spectrum displayed only a singlet resonance, the spectrum for **11** showed an AB pattern (J_{PP} = 294.0 Hz) due to the inequivalence of the phosphine groups because of the activation of the isopropyl methyl group.

Extension of the length of the N-substituent from ethyl to *n*-propyl suppresses the C−H cleavage chemistry. Thus, even after being heated with H$_2$C=CHSiMe$_3$ at 50 °C for 16 h, Ru(I^{n}Pr$_2$)(PPh$_3$)$_2$(CO)H$_2$ (**7**) is left unchanged. This lack of reactivity is presumably due not only to the inability of the *n*-propyl methyl group to orient itself close enough to the metal for activation, but also to the strain that would be inherent in any six-membered ruthenacycle product. Ring strain must account for the lack of C−H cleavage at the N−Me groups[23c,h] upon heating of **3** in the presence of excess H$_2$C=CHSiMe$_3$ at 50 °C, although **3** does react by cyclometallation of one of the PPh$_3$ ligands to give **12** (Scheme 5), indicated by a characteristic low-frequency signal in the ^{31}P{^{1}H} NMR spectrum (δ −21.8, J_{PP} = 20.6 Hz).[29] This cyclometallation proves to be reversible in the presence of either 1 atm H$_2$ or with a primary or secondary alcohol at 50 °C to regenerate **3** cleanly.

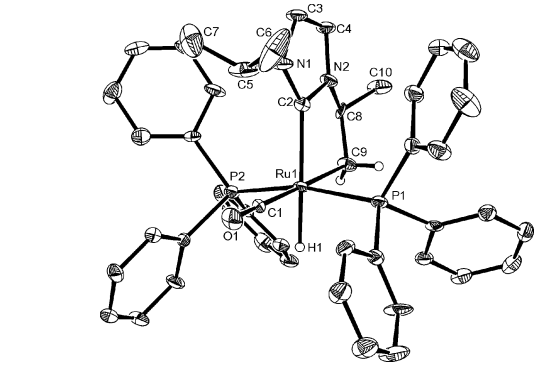
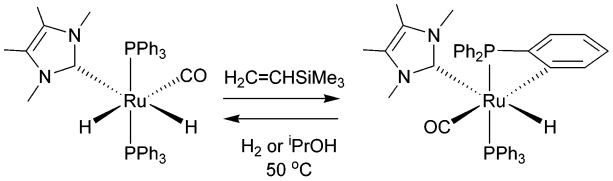
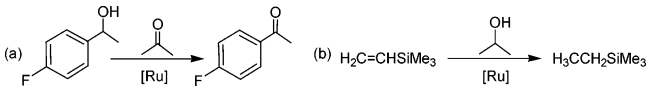


Figure 3. Molecular structure of **11**. Thermal ellipsoids are represented at 30% probability. The majority of hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Ru(1)−C(2), 2.095(8); Ru(1)−C(9), 2.203(10); Ru(1)−P(1), 2.340(3); Ru(1)−P(2), 2.339(3); C(8)−C(9)−Ru(1), 112.8(1); P(1)−Ru(1)−P(2), 166.35(8).

Scheme 5



Scheme 6



Transfer Hydrogenation of Alcohols and Alkenes. Both the oxidation of the alcohol and the reduction of the alkene shown in Scheme 1 require metal-mediated hydrogen transfer to an appropriate acceptor. To probe the catalytic activity of complexes **3**−**9** in comparison to that of **1**,[17,18] these two steps were studied separately (Scheme 6).

(28) Restricted rotation about both the Ru−C_{IMes} and N−$C_{mesityl}$ bonds in **1** was also investigated. See the Supporting Information for full details.

(29) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

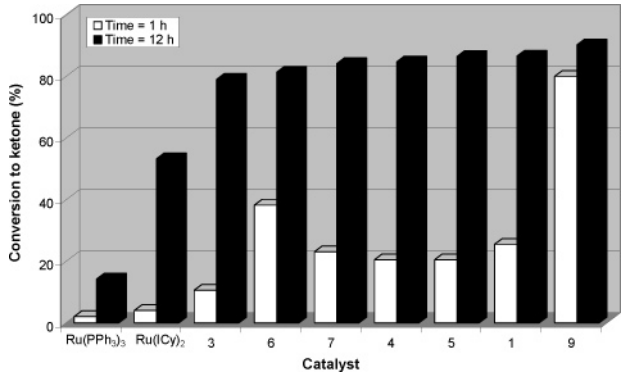


Figure 4. Ruthenium-catalyzed oxidation of 4-fluoro-α-methylbenzyl alcohol with acetone after 1- and 12-h reaction times (2 mol % Ru, C_6D_6, 50 °C). Percentage conversions (averages of at least two runs) are based on ^{1}H NMR integrals of product ketones [$Ru(PPh_3)_3$═$Ru(PPh_3)_3(CO)H_2$, $Ru(ICy)_2$═$Ru(ICy)_2(PPh_3)(CO)H_2$].

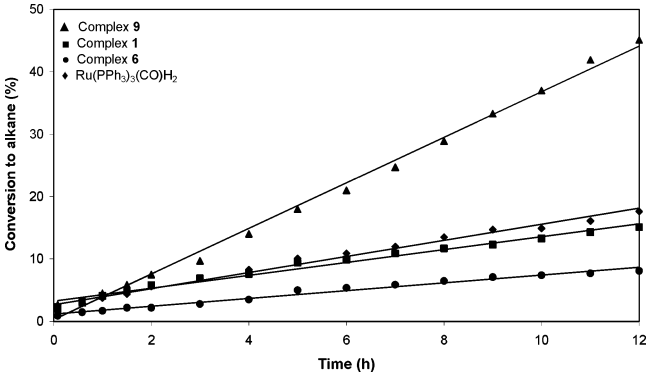


Figure 5. Reduction of trimethylvinylsilane with ^{i}PrOH catalyzed by $Ru(PPh_3)_3(CO)H_2$ and Ru—NHC complexes **1**, **6**, and **9** (2 mol % Ru, C_6D_6, 50 °C, 12 h). Percentage conversions (averages of at least two runs) are based on integration of the ^{1}H NMR signals for $CH_3CH_2SiMe_3$.

The oxidation of 4-fluoro-α-methylbenzyl alcohol with acetone (2 mol % Ru, 50 °C) was chosen because of the favorable oxidation potential of the alcohol[30] and was followed by ^{1}H NMR spectroscopy at 50 °C. The conversions into ketone found with each of the ruthenium complexes are shown in Figure 4. The data clearly indicate that the presence of an NHC ligand enhances conversion compared to $Ru(PPh_3)_3(CO)H_2$, although incorporation of a second NHC into the metal coordination sphere [illustrated in Figure 4 by $Ru(ICy)_2(PPh_3)(CO)H_2$] resulted in noticeably poorer catalytic activity.[31] Inspection of both the $^{31}P\{^1H\}$ NMR spectra and the high-frequency region of the ^{1}H spectra at the end of the reactions with **3**−**7** showed the absence of any new species, indicating good catalyst stability and longevity. The only exception to this was for the IMes species **1**, where resonances for $Ru(PPh_3)_3(CO)H_2$ were detected. Although **1** is the only example in which the carbene is trans to phosphine, it is unclear whether this is related to the relatively facile dissociation of NHC.

After a reaction time of 12 h, the dihydride complexes **3**−**7**, along with the C—H-activated species **9**, led to similar conversions into product. When the oxidation reactions were run for just 1 h, a dramatic difference was seen in catalytic activity, with **9** affording over twice as much ketone as any other complex. Two other trends stand out: the effect of removing the backbone methyl groups from the ligand (in complex **6**) is clearly detrimental to activity (only 38% conversion in the same time), whereas complexes that are not susceptible to C—H activation (i.e., **5** and **7**) show poor activity.

The ruthenium-catalyzed transfer hydrogenation of H_2C═$CHSiMe_3$ with ^{i}PrOH was next examined with the same group of complexes. The data in Figure 5 show that, under the same time/temperature conditions as used for alcohol oxidation, alkene reduction is considerably slower, with a maximum conversion of ca. 50% found after 12 h. Significantly, the C—H-activated complex **9** showed the most activity.[32]

Tandem Wittig Reaction. In line with the activity seen for the individual steps, the most active catalyst precursor for the overall Wittig reaction of $PhCH_2OH$ with the cyano ylide Ph_3P═

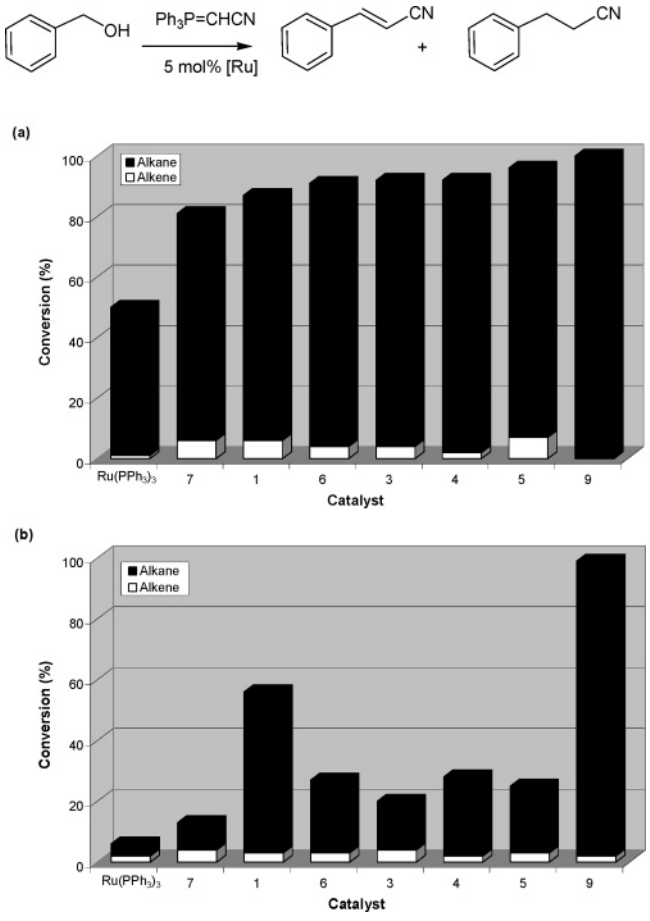


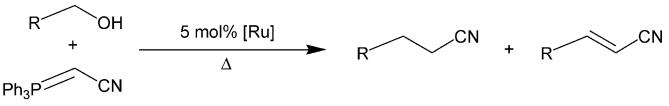
Figure 6. Activities of various ruthenium complexes (5 mol % Ru, C_6D_6) for the indirect Wittig reaction of benzyl alcohol and Ph_3P═CHCN over (a) 24 h at 80 °C and (b) 3 h at 70 °C. Percentage conversions (averages of at least two runs) are based on integration of the ^{1}H NMR signals for $PhCH_2CH_2CN$ and PhCH═CHCN [$Ru(PPh_3)_3$═$Ru(PPh_3)_3(CO)H_2$].

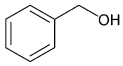
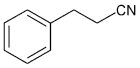
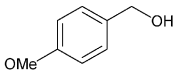
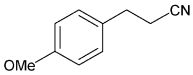
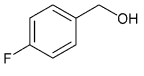
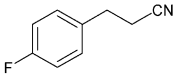
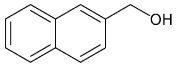
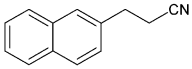
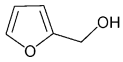
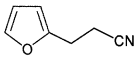
CHCN again proved to be complex **9** (Figure 6a). Whereas only small differences were seen among all of the ruthenium compounds over 24 h reaction times,[33] the true potential of **9** was apparent on shortening this time to 3 h, as well as lowering the temperature to 70 °C (Figure 6b).[34]

The high activity of $I^iPr_2Me_2$ was maintained when an in situ catalyst was prepared by simply mixing free carbene with Ru-

(30) Adkins, H.; Elofson, R. M.; Rossow, A. G.; Robinson, C. C. *J. Am. Chem. Soc.* **1949**, *71*, 3622.
(31) Bis-NHC complexes of the type $Ru(NHC)_2$(═CHPh)Cl_2 are less catalytically active for ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene than $Ru(NHC)(PCy_3)$(═CHPh)Cl_2: Herrmann, W. A.; Weskamp, T.; Böhm, V. P. W. *Adv. Organomet. Chem.* **2002**, *48*, 1.
(32) See the Supporting Information for tables of conversion data.
(33) No difference in reactivity was seen between **9** and the dihydride precursor **8**.

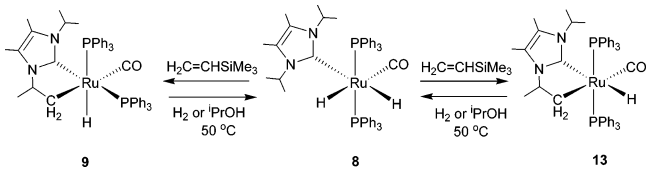
Table 1. Complex-**9**-Catalyzed Indirect Wittig Reaction[a] Utilizing Different Alcohols



Entry	Alcohol	Product	Conversion (%)	Alkene (%)	Alkane (%)
1			87	2	85
2			61	7	54
3			88	2	86
4			85	2	83
5			65	1	64

[a] Reaction conditions: 1 mL of toluene, 5 mol % **9**, 70 °C, 2 h. Conversions were determined by analysis of the ^{1}H NMR spectra and represent the averages of at least two runs.

Scheme 7



$(PPh_3)_3(CO)H_2$ in a 1:1 ratio (see the Supporting Information). As expected, increasing the loading of carbene to a 3:1 NHC/Ru ratio had a detrimental effect on catalyst activity, because of the formation of less active bis- (and tris-) $I^iPr_2Me_2$ complexes. The 1:1 combination of $Ru(PPh_3)_3(CO)H_2$ with IMes displayed much poorer activity than isolated **1**, reflecting the fact that replacement of PPh_3 by IMes is relatively slow.[35]

Influence of Alcohol Substrates on Wittig Chemistry. Various aryl alcohol substrates were reacted with $Ph_3P{=}CHCN$ in the presence of 5 mol % **9** at 70 °C for 2 h. As seen in Table 1, good conversion into the product alkanes was seen in most cases. Entries 2 and 5 involve relatively electron-rich aromatic groups, which would be expected to favor oxidation from alcohol to aldehyde (Scheme 1). Given that the poorest conversion into alkane is seen in these two cases, it seems probable that alkene reduction is therefore the rate-determining step in the overall sequence.

C−H Activation of $I^iPr_2Me_2$ Revisited. In light of the high catalytic activity shown by **9**, we now return to a discussion of its coordination chemistry. As noted above, addition of H_2 to **9** produces the dihydride complex **8**. This same transformation was also accomplished by stirring with ^{i}PrOH, indicating that the first step in the catalytic Wittig reaction presumably also involves conversion of **9** into **8** and oxidation of alcohol to aldehyde. Surprisingly, when a sample of **8** was reacted with excess $H_2C{=}CHSiMe_3$ at 50 °C, **9** was regenerated along with 1 equiv of an isomer with trans PPh_3 ligands, **13** (Scheme 7). This too could be converted back into **8** with either H_2 or ROH. Although we were unable to isolate **13** in pure form, ^{1}H NMR resonances at δ 1.61 and 1.00 and the corresponding $^{13}C\{^1H\}$ signal at δ 21.6 show the presence of a $Ru{-}CH_2$ group. Similarly, the appearance of a triplet resonance for the hydride (^{1}H NMR: δ −7.47) along with a phosphorus singlet agrees with the geometry shown in Scheme 7.

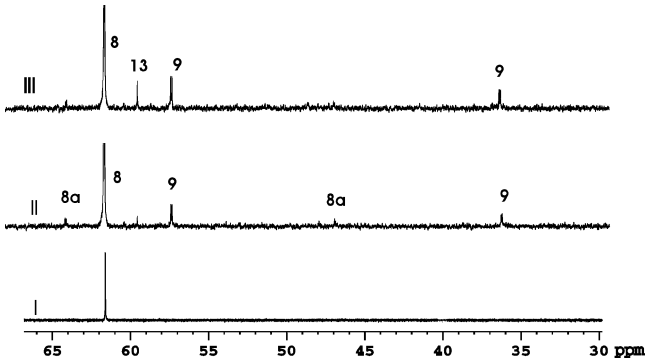


Figure 7. (I) $^{31}P\{^1H\}$ spectrum of complex **8** in THF solution. (II) Complex **8** and 1 equiv of $H_2C{=}CHSiMe_3$ after 3 h. (III) Complex **8** and an additional 10 equiv of $H_2C{=}CHSiMe_3$.

To probe the formation of the isomers **9** and **13** in more detail, a THF sample of **8** was treated with 1 equiv of $H_2C{=}CHSiMe_3$ at room temperature and monitored by $^{31}P\{^1H\}$ NMR spectroscopy. As shown in Figure 7, resonances for both **9** and **13** were apparent after 3 h, along with an additional species, which displayed two doublet resonances. These signals are assigned to the alternative *cis*-triphenylphosphine isomer **8a**. Good evidence for this assignment was provided by an exchange experiment involving the addition of 1 equiv of P(*p*-tolyl)$_3$ to a THF solution of **8**. The room-temperature spectrum recorded

(34) The Wittig reactions were typically performed with 2 equiv of $H_2C{=}CHSiMe_3$ added to promote the initial C−H activation. No reduction in conversion through to product alkanes was found when catalysis was performed with alkene excluded.

(35) This is clear from the 2-week reaction time that is typically needed for the synthesis of **1**.

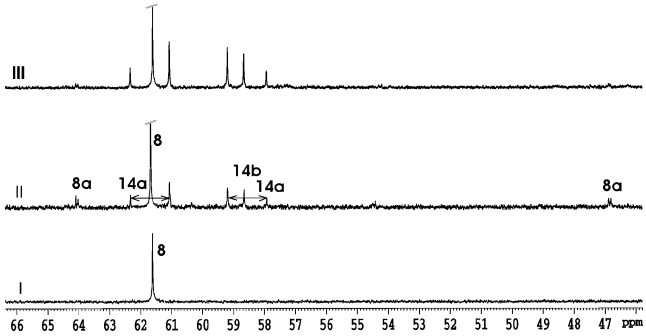
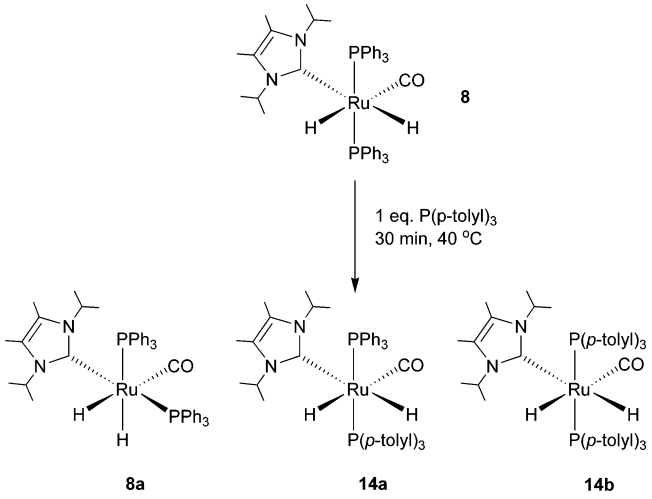
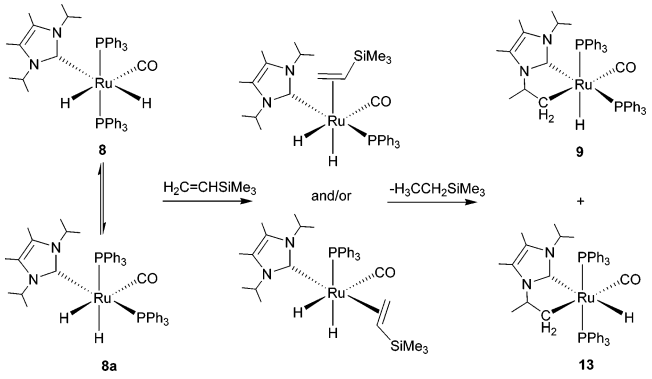


Figure 8. $^{31}P\{^1H\}$ NMR spectra of (I) **8** (THF-d_8, ambient temperature), (II) **8** and 1 equiv of P(*p*-tolyl)$_3$ at room temperature after being warmed for 30 min at 40 °C, and (III) after standing for 20 h at room temperature.

Scheme 8



Scheme 9



after 30 min of heating at 40 °C (Figure 8) displays signals for three new complexes, the mono and bis-P(*p*-tolyl)$_3$ complexes **14a** and **14b** along with **8a** (Scheme 8).[36] Over time, the concentration of **8a** diminishes as **14a** and **14b** become more prominent, indicating that **8a** cannot be a P(*p*-tolyl)$_3$-containing species.

This depletion of **8a**, which occurs over longer time at room temperature, suggests that dissociative phosphine exchange into the complex can take place without warming. Hence, the mechanism shown in Scheme 9 is proposed to explain the formation of **9** and **13** upon reaction of **8** with $H_2C{=}CHSiMe_3$, with dissociation of PPh_3 allowing interconversion of **8** and **8a**. Alkene complexation is followed by insertion and reductive elimination of $CH_3CH_2SiMe_3$[37] to give an unobserved Ru(0) species that then readily adds the proximate isopropyl C—H bond to afford both **9** and **13**.[38]

When similar phosphine exchange experiments were performed on **9**, incorporation of P(*p*-tolyl)$_3$ occurred at room temperature to give a mixture containing starting material and the three new products **15a**—**c** (Scheme 10). The $^{31}P\{^1H\}$ spectrum (Figure 9), together with the $^{31}P\{^1H\}-^1H$ correlation spectrum (Figure 10), indicates that each of these new species contains cis phosphine ligands and that the eight ^{31}P signals correlate to the four ^1H hydride absorptions for each of the complexes. The structures of the products are consistent with phosphine exchange both trans to the carbene and trans to one of the two hydrides. As for **8a**, complex **9** is clearly able to react by facile phosphine dissociation. This is likely to be relevant to the observed catalytic activity, with reaction occurring via five-coordinate Ru(II) rather than after reduction to Ru(0).

Conclusions

A series of N-alkyl-substituted heterocyclic carbene ruthenium hydride complexes has been studied as catalyst precursors for C—C bond formation from alcohol substrates. In contrast to $Ru(PPh_3)_3(CO)H_2$, all of the mono-NHC complexes of the type $Ru(NHC)(PPh_3)_2(CO)H_2$ give better conversions into C—C coupled product. Most significantly, the C—H-activated isopropyl derivative $Ru(I^iPr_2Me_2)'(PPh_3)_2(CO)H$ (**9**) displays the highest activity, allowing the reaction temperature to be lowered and the reaction time to be dramatically shortened. Whereas bond activation in NHCs is now well established in stoichiometric chemistry, our results suggest that carbene C—H activation should find applications in catalytic processes.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Solvents were purified either using an MBraun SPS solvent system (toluene, THF, diethyl ether, dichloromethane) or under a nitrogen atmosphere from sodium benzophenone ketyl (benzene, hexane) or Mg/I_2 (ethanol). Deuterated solvents (Aldrich) were vacuum transferred from potassium (C_6D_6, THF-d_8) or calcium hydride ($CDCl_3$, CD_2Cl_2). Hydrogen (BOC, 99.99%) was used as received. $I^iPr_2Me_2$ and IMe_4 were prepared via the literature method.[39] I^iPr_2 and I^nPr_2 were synthesized by methods adapted from the literature; spectroscopic data are provided in the Supporting Information.[40,41] The following complexes were prepared via methods reported in the literature: $Ru(PPh_3)_3(CO)H_2$,[42] **1**,[18b] **4**,[23j] **5**, and $Ru(ICy)_2(PPh_3)(CO)H_2$.[27] (Triphenylphosphoranylidene)acetonitrile was prepared by adaptation of literature methods.[43]

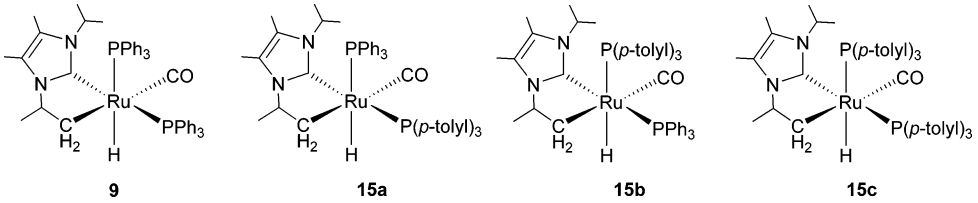
(36) No exchange was observed without warming.

(37) We have identified this compound, in the THF solution used for the reaction, via $^{29}Si-^1H$ correlation NMR.

(38) Our results cannot establish whether phosphine loss occurs only from one position within the coordination sphere.

(39) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.
(40) Herrmann, W. A.; Kocher, C.; Goossen, L. J.; Artus, G. R. J. *Chem. Eur. J.* **1996**, *2*, 1627.
(41) Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523. A slightly different route to I^iPr_2 is reported in: Niehues, M.; Kehr, G.; Erker, G.; Wibbeling, B.; Fröhlich, R.; Blacque, O.; Berke, H. *J. Organomet. Chem.* **2002**, *663*, 192.
(42) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.
(43) (a) Kiddle, J. J. *Tetrahedron Lett.* **2000**, *41*, 1339. (b) Wilt, J. W.; Ho, A. J. *J. Org. Chem.* **1971**, *36*, 2026.

Scheme 10



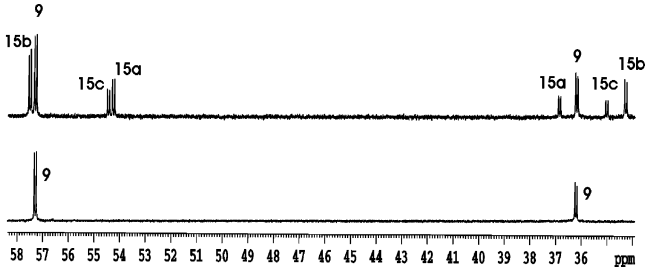


Figure 9. $^{31}P\{^1H\}$ NMR spectra (THF-d_8) showing formation of phosphine exchange products **15a**−**c** upon addition of 1 equiv of P(*p*-tolyl)$_3$ to complex **9**.

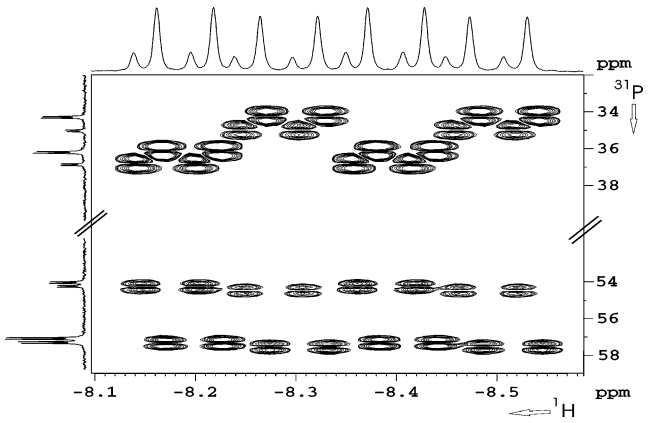


Figure 10. Section of the $^{31}P\{^1H\}-^1H$ COSY (THF-d_8) following reaction of **9** with 1 equiv of P(*p*-tolyl)$_3$.

NMR spectra were recorded on Bruker Avance 300 (Bath), 400 (Bath/ETHZ), and 500 (ETHZ) MHz NMR spectrometers, at 298 K unless otherwise stated, and referenced as follows: benzene (^1H, δ 7.15; $^{13}C\{^1H\}$, δ 128.0), chloroform (δ 7.15, δ 77.0), THF (δ 3.58), and dichloromethane (δ 5.32, δ 53.73). $^{31}P\{^1H\}$ NMR chemical shifts were referenced externally to 85% H_3PO_4 (δ 0.0). 2D experiments [^1H COSY, ^1H-X (X = ^{13}C, ^{31}P) HMQC/HMBC, NOESY] were performed using standard Bruker pulse sequences. IR spectra were recorded on a Nicolet Nexus FTIR spectrometer as C_6D_6 solutions. Elemental analyses were performed either at the University of Bath or by Elemental Microanalysis Ltd., Okehampton, Devon, U.K.

Ru(IMe$_4$)(PPh$_3$)$_2$(CO)H$_2$ (3). Toluene (30 mL) was added to IMe$_4$ (0.6 g, 4.9 mmol) and Ru(PPh$_3$)$_3$(CO)H$_2$ (1.5 g, 1.6 mmol). The mixture was heated at 80 °C with stirring for 3 days. The resulting solution was reduced in vacuo to precipitate a yellow solid. The mixture was filtered under argon, and the filtrate was taken to dryness in vacuo. The resulting residue was washed with EtOH (2 × 10 mL) to afford **3** as a white solid. Yield: 0.65 g (51%); Anal. Found (calcd) for $C_{44}H_{44}N_2OP_2Ru$: C, 67.71 (67.77); H, 5.79 (5.69); N, 3.59 (3.62). ^1H NMR (C_6D_6, 400 MHz): δ 7.98−7.94 (m, 12H, PPh$_3$), 7.04−6.95 (m, 18H, PPh$_3$), 3.10 (s, 3H, C*H*$_3$), 2.69 (s, 3H, C*H*$_3$), 1.37 (s, 3H, C*H*$_3$), 1.17 (s, 3H, C*H*$_3$), −5.92 (dt, J_{HP} = 26.9 Hz, J_{HH} = 5.5 Hz, 1H, Ru−*H*), −9.03 (dt, J_{HP} = 23.1 Hz, J_{HH} = 5.5 Hz, 1H, Ru−*H*). $^{31}P\{^1H\}$ NMR: δ 65.0 (s, *P*Ph$_3$). $^{13}C\{^1H\}$ NMR: δ 210.2 (t, J_{CP} = 9.6 Hz, Ru−*C*O), 194.1 (t, J_{CP} = 9.6 Hz, Ru−C_{IMe4}), 142.0 (vt, $|J_{CP} + J_{CP}|$ = 20.0 Hz, PPh$_3$), 134.9 (vt, $|J_{CP} + J_{CP}|$ = 6.4 Hz, PPh$_3$), 128.6 (s, PPh$_3$), 128.2 (vt, $|J_{CP} + J_{CP}|$ = 4.8 Hz, PPh$_3$), 123.8 (s, im *C*), 123.7 (s, im *C*), 37.2 (s, *C*H$_3$), 37.0 (s, *C*H$_3$), 10.4 (s, *C*H$_3$), 10.3 (s, *C*H$_3$). IR (cm^{-1}): 1922 (ν_{CO}).

Ru(I^{i}Pr)(PPh$_3$)$_2$(CO)H$_2$ (6). Toluene (30 mL) was added to I^{i}Pr (0.7 g, 4.4 mmol) and Ru(PPh$_3$)$_3$(CO)H$_2$ (1.0 g, 1.1 mmol). The mixture was stirred at 70 °C for 20 h. The solution was removed in vacuo, and EtOH (20 mL) was added. The resulting red solution was stirred overnight to afford an off-white precipitate. The mixture was filtered, and the solid was washed with hexane. Yield: 0.48 g (55%); Anal. Found (calcd) for $C_{46}H_{48}N_2OP_2Ru$: C, 68.17 (68.39); H, 6.09 (5.99); N, 3.39 (3.47). ^1H NMR (C_6D_6, 400 MHz): δ 7.87−7.73 (m, 12H, PPh$_3$), 7.11−6.94 (m, 18H, PPh$_3$), 6.47 (d, J_{HH} = 1.6 Hz, 1H, im C*H*), 6.30 (d, J_{HH} = 1.6 Hz, 1H, im C*H*), 5.56 (sept, J_{HH} = 6.6 Hz, 1H, C*H*), 5.31 (sept, J_{HH} = 6.6 Hz, 1H, C*H*), 0.96 (d, J_{HH} = 6.6 Hz, C*H*$_3$), 0.38 (d, J_{HH} = 6.6 Hz, 6H, C*H*$_3$), −5.89 (dt, J_{HP} = 26.9 Hz, J_{HH} = 6.0 Hz, 1H, Ru−*H*), −9.46 (dt, J_{HP} = 26.9 Hz, J_{HH} = 6.0 Hz, 1H, Ru−*H*). $^{31}P\{^1H\}$ NMR: δ 61.4 (s, *P*Ph$_3$). $^{13}C\{^1H\}$ NMR: δ 208.5 (t, J_{CP} = 9.2 Hz, Ru−*C*O), 194.7 (t, J_{CP} = 8.3 Hz, Ru−$C_{IiPr2Me2}$), 142.3 (vt, $|J_{CP} + J_{CP}|$ = 20.2 Hz, PPh$_3$), 135.0 (vt, $|J_{CP} + J_{CP}|$ = 6.4 Hz, *C*H, PPh$_3$), 129.2 (s, PPh$_3$), 128.4 (vt, $|J_{CP} + J_{CP}|$ = 4.6 Hz, PPh$_3$), 117.1 (s, im *C*), 116.8 (s, im *C*), 52.8 (s, *C*H), 52.5 (s, *C*H), 24.0 (s, *C*H$_3$), 22.9 (s, *C*H$_3$). IR (cm^{-1}): 1922 (ν_{CO}).

Ru(I^{n}Pr)(PPh$_3$)$_2$(CO)H$_2$ (7). A toluene solution (10 mL) of I^{n}Pr (0.23 g, 1.52 mmol) and Ru(PPh$_3$)$_3$(CO)H$_2$ (0.23 g, 0.25 mmol) was stirred at 70 °C for 16 h. The volatiles were removed in vacuo, and the residue was dissolved in ethanol (10 mL). The resulting red solution was stirred over 3 days to afford an off-white precipitate, which was filtered and washed with hexane (2 × 10 mL). The product was recrystallized by dissolving it in the minimum volume of benzene and layering with ethanol, affording **7** as pale yellow crystals. Yield: 66 mg (32%). Anal. Found (calcd) for $C_{46}H_{48}N_2OP_2Ru$: C, 68.38 (68.39); H, 5.98 (5.99); N, 3.53 (3.47). ^1H NMR (C_6D_6, 400 MHz): δ 7.89−7.85 (m, 12H, PPh$_3$), 7.08−6.98 (m, 18H, PPh$_3$), 6.15 (d, J_{HH} = 2.2 Hz, 1H, im C*H*), 5.96 (d, J_{HH} = 2.2 Hz, 1H, im C*H*), 3.59 (m, 2H, N−C*H*$_2$), 3.31 (m, 2H, N−C*H*$_2$), 1.45 (m, 2H, C*H*$_2$−CH$_3$), 0.84 (m, 2H, C*H*$_2$−CH$_3$), 0.67 (t, J_{HH} = 7.1 Hz, 3H, CH$_2$−C*H*$_3$), 0.45 (t, J_{HH} = 7.1 Hz, 3H, CH$_2$−C*H*$_3$), −6.02 (dt, J_{HP} = 26.3 Hz, J_{HH} = 6.0 Hz, 1H, Ru−*H*), −9.15 (dt, J_{HP} = 25.2 Hz, J_{HH} = 6.0 Hz, 1H, Ru−*H*). $^{31}P\{^1H\}$ NMR: δ 64.1 (s, *P*Ph$_3$). $^{13}C\{^1H\}$ NMR: δ 208.0 (t, J_{CP} = 9.2 Hz, Ru−*C*O), 194.7 (t, J_{CP} = 8.3 Hz, Ru−C_{InPr}), 140.9 (vt, $|J_{CP} + J_{CP}|$ = 20.2 Hz, PPh$_3$), 133.9 (vt, $|J_{CP} + J_{CP}|$ = 6.4 Hz, PPh$_3$), 128.1 (s, PPh$_3$), 127.3 (vt, $|J_{CP} + J_{CP}|$ = 3.7 Hz, PPh$_3$), 119.1 (s, im *C*H), 118.9 (s, im *C*H), 53.3 (s, *C*H$_2$), 53.0 (s, *C*H$_2$), 23.9 (s, *C*H$_2$), 22.8 (s, *C*H$_2$), 11.0 (s, *C*H$_3$), 10.9 (s, *C*H$_3$). IR (cm^{-1}): 1920 (ν_{CO}).

Ru(I^{i}Pr$_2$Me$_2$)(PPh$_3$)$_2$(CO)H$_2$ (8). Complex **9** (0.50 g, 0.6 mmol) was dissolved in the minimum amount of warm benzene (10−15 mL), and H_2 was bubbled through the solution for 2 h at 50 °C. The solution was cooled to room temperature to precipitate a white solid. The solvent was removed by filtration, and the white solid was further purified by washing with hexane. Yield: 0.47 g (93%). Anal. Found (calcd) for $C_{48}H_{52}N_2OP_2Ru$: C, 68.97 (69.00); H, 6.27 (6.07); N, 3.35 (3.03). ^1H NMR (C_6D_6, 400 MHz): δ 7.73−7.93 (m, 12H, PPh$_3$), 6.94−7.11 (m, 18H, PPh$_3$), 6.36 (sept, J_{HH} = 7.1 Hz, 1H, C*H*), 6.08 (sept, J_{HH} = 7.1 Hz, 1H, C*H*), 1.82 (s, 3H, C*H*$_3$), 1.70 (s, 3H, C*H*$_3$), 1.08 (d, J_{HH} = 7.1 Hz, 6H, C*H*$_3$), 0.48 (d, J_{HH} = 7.1 Hz, 6H, C*H*$_3$), −5.79 (dt, J_{HP} = 26.9 Hz, J_{HH} = 6.0 Hz, 1H, Ru−*H*), −9.98 (dt, J_{HP} = 26.9 Hz, J_{HH} = 6.0 Hz, 1H, Ru−*H*). $^{31}P\{^1H\}$ NMR: δ 61.3 (s, *P*Ph$_3$). $^{13}C\{^1H\}$ NMR: δ

208.2 (t, J_{CP} = 9.2 Hz, Ru—*C*O), 195.8 (t, J_{CP} = 8.3 Hz, Ru—$C_{IiPr2Me2}$), 142.6 (vt, $|J_{CP} + J_{CP}|$ = 19.3 Hz, PPh_3), 135.1 (vt, $|J_{CP} + J_{CP}|$ = 6.4 Hz, PPh_3), 129.2 (s, PPh_3), 128.3 (vt, $|J_{CP} + J_{CP}|$ = 4.6 Hz, PPh_3), 126.2 (s, im *C*), 125.9 (s, im *C*), 54.5 (s, *C*H), 54.3 (s, *C*H), 22.6 (s, *C*H_3), 21.4 (s, *C*H_3), 11.5 (s, *C*H_3). IR (cm^{-1}): 1917 (ν_{CO}).

Ru(I^{i}Pr$_2$Me$_2$)′(PPh$_3$)$_2$(CO)H (9). Toluene (30 mL) was added to I^{i}Pr$_2$Me$_2$ (0.8 g, 4.4 mmol) and Ru(PPh$_3$)$_3$(CO)H$_2$ (1.0 g, 1.1 mmol) in an ampule under argon. The mixture was stirred at 70 °C for 20 h. The volatiles were removed in vacuo, and EtOH (20 mL) was added. The resulting red solution was stirred overnight to afford an off-white precipitate. The mixture was filtered, and the solid was washed with hexane (2 × 10 mL) to yield the C—H-activated product **9** as a white solid. Yield: 0.6 g (66%). Anal. Found (calcd) for $C_{48}H_{50}N_2OP_2Ru$: C, 68.57 (69.13); H, 6.40 (6.04); N, 3.25 (3.15). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.70−7.66 (m, 6H, PPh_3), 7.37−7.32 (m, 6H, PPh_3), 7.02−6.96 (m, 18H, PPh_3), 5.50 (sept, J_{HH} = 7.1 Hz, 1H, C*H*), 4.28 (m, 1H, C*H*), 1.99 (m, 1H, C*H*), 1.76 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.37 (d, J_{HH} = 7.1 Hz, 3H, CH_3), 1.28 (d, J_{HH} = 6.0 Hz, 3H, CH_3), 0.54 (d, J_{HH} = 7.1 Hz, 3H, CH_3), 0.49 (m, 1H, C*H*), −7.72 (dd, J_{HP} = 104.8 Hz, J_{HP} = 28.0 Hz, 1H, Ru—*H*). ^{31}P{^{1}H} NMR: δ 56.5 (d, J_{PP} = 16.7 Hz, *P*Ph_3), 35.8 (d, J_{PP} = 16.7 Hz, *P*Ph_3). ^{13}C{^{1}H} NMR: δ 207.4 (dd, J_{CP} = 5.5 Hz, J_{CP} = 13.8 Hz, Ru—*C*O), 187.8 (dd, J_{CP} = 10.1 Hz, J_{CP} = 82.7 Hz, Ru—$C_{IiPr2Me2}$), 140.3 (dd, J_{CP} = 34.9 Hz, J_{CP} = 1.8 Hz, PPh_3), 140.0 (dd, J_{CP} = 23.0 Hz, J_{CP} = 1.8 Hz, PPh_3), 135.5 (d, J_{CP} = 11.0 Hz, PPh_3), 134.8 (d, J_{CP} = 11.0 Hz, PPh_3), 129.4−129.0 (m, PPh_3), 128.4−128.1 (m, PPh_3), 124.0 (s, im *C*), 123.2 (s, im *C*), 59.1−58.8 (m, *C*H), 54.0 (s, *C*H), 24.5 (t, J_{CP} = 7.4 Hz, *C*H_2), 23.9 (s, *C*H_3), 22.4 (s, *C*H_3), 21.4 (s, *C*H_3), 11.3 (s, *C*H_3), 10.0 (s, CH_3). IR (cm^{-1}): 1884 (ν_{CO}).

Ru(I^{i}Pr$_2$)′(PPh$_3$)$_2$(CO)H (11). Trimethylvinylsilane (50 equiv) was added to **6** (15 mg) dissolved in C_6D_6 (0.6 mL). The sample was heated at 50 °C for 16 h. ^{31}P{^{1}H} NMR spectroscopy indicated complete conversion to the C—H-activated complex. The solvent was removed in vacuo, affording the title compound **11** as an orange solid in quantitative yield. Anal. Found (calcd) for $C_{46}H_{46}N_2OP_2Ru$: C, 68.36 (68.56); H, 5.79 (5.75); N, 3.46 (3.48). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.91−7.69 (m, 12H, PPh_3), 7.13−6.87 (m, 18H, PPh_3), 6.26 (d, J_{HH} = 1.6 Hz, 1H, im C*H*), 6.20 (d, J_{HH} = 1.6 Hz, 1H, im C*H*), 4.61 (sept, J_{HH} = 6.6 Hz, 1H, C*H*), 3.29−3.15 (m, 1H, C*H*), 1.37−1.22 (m, 1H, C*H*), 1.01−0.87 (m, 1H, C*H*), 0.77 (d, J_{HH} = 6.6 Hz, 3H, CH_3), 0.72 (d, J_{HH} = 6.6 Hz, 3H, CH_3), 0.64 (d, J_{HH} = 6.6 Hz, 3H, CH_3), −7.20 (t, J_{HP} = 24.7 Hz, 1H, Ru—*H*). ^{31}P{^{1}H} NMR: δ 61.5 (AB, $\Delta\nu$ = 382.5 Hz, J_{PP} = 294.9 Hz, *P*Ph_3). ^{13}C{^{1}H} NMR: δ 207.0 (t, J_{CP} = 12.9 Hz, Ru—*C*O), 195.8 (t, J_{CP} = 8.3 Hz, Ru—$C_{IiPr2Me2}$), 140.3 (dd, J_{CP} = 22.1 Hz, J_{CP} = 9.2 Hz, PPh_3), 140.0 (J_{CP} = 22.1 Hz, J_{CP} = 9.2 Hz, PPh_3), 135.1 (dd, J_{CP} = 20.2 Hz, J_{CP} = 2.8 Hz, PPh_3), 135.0 (dd, J_{CP} = 20.2 Hz, J_{CP} = 2.8 Hz, PPh_3), 129.2 (d, J_{CP} = 12.9 Hz, PPh_3), 128.5 (d, J_{CP} = 12.9 Hz, PPh_3), 118.0 (s, im *C*), 116.0 (s, im *C*), 60.9 (s, *C*H), 52.0 (s, *C*H), 25.4 (s, *C*H_3), 24.1 (t, J_{CP} = 11.0 Hz, *C*H_2), 24.0 (s, *C*H_3), 22.9 (s, *C*H_3).

General Procedure for Transfer Hydrogenation of Alkenes and Alcohols. The chosen alkene or alcohol (0.5 mmol) and ^{i}PrOH or acetone (5 equiv) were added to Ru(NHC)$_n$(PPh$_3$)$_{3-n}$(CO)H$_2$ (0.01 mmol) dissolved in C_6D_6 in a resealable NMR tube under argon. The reaction mixtures were heated at 50 °C in the probe of the NMR spectrometer, and ^{1}H spectra were recorded at regular intervals for 12 h. Conversion was determined by integration of the ^{1}H NMR spectra, and reported values represent the averages of at least two runs.

General Procedure for Indirect Wittig Reactions. The required ruthenium complex (5 mol %, 25 μmol) and (triphenylphosphoranylidene)acetonitrile (0.55 mmol, 1.1 equiv) were charged into a tube fitted with a resealable Young's PTFE tap. The tubes were placed in a carousel synthesizer (Fisher) and purged with argon. Toluene (1 mL) and the required alcohol (0.5 mmol) were added via syringe, and the tubes were sealed under argon. The reaction mixtures were heated (70 °C for 2, 3, or 20 h or 80 °C for 24 h) and then cooled to room temperature. Et_2O (5 mL) was added to each tube to quench the reaction, and the mixture was concentrated in vacuo to afford the crude product. Conversions were determined by analysis of the ^{1}H NMR spectra and represent the averages of at least two runs.

X-ray Crystallography. Single crystals of compounds **6**, **7**, **9**, and **11** were analyzed using a Nonius Kappa CCD diffractometer and Mo(Kα) radiation (λ = 0.71073 Å), and data for **11** were collected at Daresbury station 16.2 SMX (λ = 0.8460 Å). Details of the data collections, solutions, and refinements are provided in the Supporting Information. The structures were universally solved using SHELXS-97[44] and refined using full-matrix least-squares in SHELXL-97.[44] Multiscan absorption corrections were applied throughout, and convergence was uneventful, with the following exceptions and points of note:

The hydride hydrogen in **6** was located and refined at distance of 1.6 Å from the central metal. Disorder vexed the structure of **7**, which was also subject to racemic twinning. In particular, 70:30 disorder was evident for the positions of the central ruthenium, the carbonyl group, and the carbene-fragment atoms. Refinement was anisotropic with the exception of the minor carbene moiety. The minor carbonyl moiety (C1A and O1A) was refined subject to restraints on the ADPs therein, and the N1A—C3A and C3A—C4A distances were fixed in the final least-squares analysis. The hydride trans to the carbene in this structure was readily located and refined subject to being equidistant from Ru1 and Ru1A. The second hydride ligand could not be reliably located because of the disorder and, hence, was omitted from the refinement.

In **9**, the hydrogen atoms attached to C6 were located and refined at a distance of 0.89 Å from the parent carbon. The hydride (H1) was also located and subsequently treated in a manner similar to that for **6**. Modeling of the solid-state structure of complex **11** necessitated treatment of C8 as being disordered with C8A in a 55:45 ratio. As for the other structures in this study, the hydride hydrogen was located and refined at 1.6 Å from the central metal. The hydrogen atoms attached to C8 and C10 were also located and subsequently refined at 0.90 Å from the relevant parent atoms. Atom positions H10A, H10B, and H10C were refined subject to being equidistant from each other and 2.02 Å from C10. Successful convergence for **11** was achieved only after inclusion of a twin law to account for 20% twinning about the direct 100 direction.

The absolute structure parameters for 7 and **9** refined to 0.32(2) and 0.02(2), respectively. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 616616−616619 for compounds **6**, **7**, **11**, and **9** respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax, (+44) 1223 336033; e-mail, deposit@ccdc.cam.ac.uk].

Acknowledgment. M.K.W. and J.M.J.W. thank the EPSRC (SB) and University of Bath for financial support. P.S.P. thanks the Swiss National Science Foundation and the ETHZ for funding. We also thank Johnson Matthey plc for the loan of hydrated $RuCl_3$.

Supporting Information Available: Molecular structures of **4**−**7** (along with selected bond lengths/angles), crystal data and structure refinement and X-ray crystallographic files (in CIF format) for complexes **6**, **7**, **9**, and **11**. Synthesis and spectroscopic details for I^{n}Pr$_2$, I^{i}Pr$_2$, and ylides. Tables of full catalytic data for alcohol oxidation and Wittig reactions. Rate constants and Arrhenius plot associated with the variable-temperature proton measurements on **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA065790C

(44) Sheldrick, G. M. *Acta. Cryst.* **1990**, *467*−*473*, A46. Sheldrick, G. M. *SHELXL-97, a Computer Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997