DOI: 10.1002/ejic.201000677

Triple Alkyl C–H Bond Activation Mediated by Ruthenium(II): Preparation of Isopropenyl-Substituted Carbene Complexes

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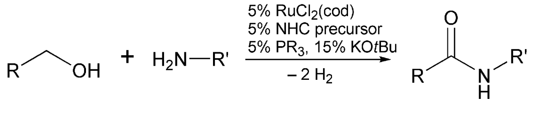
Keywords: Ruthenium / N-Heterocyclic carbene / NHC / Nitrogen heterocycles / C–H activation

The reaction of $[RuCl_2(cod)]_x$ (cod = 1,5-cyclooctadiene), 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (IPr), tricyclohexylphosphane (PCy_3) and KO*t*Bu in a 1:1:2:1 ratio affords the new alkenyl carbene complex $[RuCl(IPr'')(PCy_3)_2]$ (**1**) in 24 % isolated yield. Triphenylphosphane complex $[RuCl(IPr'')(PPh_3)_2]$ (**2**) was isolated together with the single C–H activated complex $[RuCl(IPr')(PPh_3)_2]$ (**3**). Complexes **1** and **2** feature a metalated isopropenyl substituent on the IPr'' ligand, which results from the triple C–H activation of an isopropyl group. A stepwise mechanism for the formation of complexes **1** and **2** is proposed.

Introduction

N-Heterocyclic carbenes (NHCs) are widely used as ligands in transition metal complexes due to their relatively facile preparation, the easy modification of the sterics and their beneficial donor properties.[1] First described by Lappert and co-workers as early as 1977,[2] NHC ruthenium complexes nowadays play a pivotal role as catalysts, e.g. for olefin metathesis.[3] Furthermore, the propensity of ruthenium to activate ligand C–H, C–C and C–N bonds is noteworthy.[4,5] Metal-ligand cooperativity of C–H activated ruthenium carbene complexes has recently been demonstrated for the ruthenium catalyzed tandem oxidation/Wittig/reduction of alcohols.[6]

Our investigation was stimulated by a recent report of a ruthenium-catalyzed synthesis of organic amides from primary alcohols and amines which used a mixture of $[RuCl_2(cod)]_x$ (cod = 1,5-cyclooctadiene), an imidazolium salt, a tertiary phosphane and potassium *tert*-butoxide as catalyst (Scheme 1).[7] This system allows for tuning and optimization, however, the nature of the complexes present in the catalytically active mixture is difficult to ascertain. Therefore, we decided to investigate the $[RuCl_2(cod)]_x$/NHC/phosphane reaction system more closely with the aim of identifying well-defined compounds. Here, we present initial results which show that, under certain conditions, triple C–H activation of the NHC results in the formation of isopropenyl-substituted carbene complexes.



Scheme 1. Dehydrogenative amide synthesis catalyzed by ruthenium complexes.

Results and Discussion

As the combination of the isopropyl-substituted NHC 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (IPr) and tricyclohexylphosphane (PCy_3) gives particularly active catalysts for the dehydrogenative amide synthesis,[7] we initially concentrated on this ligand combination. In a first experiment, we heated a toluene solution of $[RuCl_2(cod)]_x$ with IPr, PCy_3 and KO*t*Bu (1:1:1:2 ratio) at 100 °C. After 20 min, the ^{31}P NMR spectra of the reaction mixture showed a complicated product mixture (Figure S1 of the Supporting Information).[8] A signal at $\delta = 10.0$ ppm probably originates from free PCy_3, but a host of other unidentified signals was present. Using two equivalents of phosphane and one equivalent of both the carbene and the base (Scheme 1a), we obtained a red solution which, according to ^{31}P NMR spectroscopy, contained one major product (singlet at $\delta = 31.9$ ppm). After recrystallization from dichloromethane, we isolated the new isopropenyl-substituted carbene complex $[RuCl(IPr'')(PCy_3)_2]$ (**1**) as deep red crystals in moderate yield (24%). This complex provides a remarkable example for the ruthenium-mediated multiple C–H bond activation of a pendant ligand alkyl group.

Complex **1** was initially characterized by multinuclear NMR spectroscopy and elemental analysis. In deuterated dichloromethane, the isopropenyl substituent on the carbene gives rise to a low-field ^1H NMR singlet at δ =

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000677.

7.45 ppm. The $^{13}C\{^1H\}$ NMR spectrum showed resonances for the sp^2-hybridized isopropenyl C atoms at δ = 130.4 and 151.3 ppm, shifted downfield compared to signals at δ = 120.7 and 123.5 ppm that arise from the alkene carbons in the NHC backbone. A singlet detected at δ = 29.6 ppm in the ^{31}P NMR spectrum is in the typical range of tricyclohexylphosphane complexes of ruthenium(II).[9]

Compound **1** is only the second structurally characterized alkenyl carbene complex of ruthenium reported to date.[10] A single-crystal X-ray study of **1** (Figure 1) confirmed the presence of a metalated isopropenyl substituent on the triple C–H-activated carbene IPr′′.[11] The compound crystallizes in the orthorhombic space group *Cmca*. Each molecule resides on a crystallographic mirror plane. The ruthenium atom shows a distorted square-pyramidal coordination by the bidentate IPr′′ ligand, one chlorine, and the two phosphanes. The Ru–C distances [Ru1–C1 1.9999(17), Ru1–C5 1.9979(18)] are typical for sp^2 hybridized carbon atoms bound to ruthenium(II).[4,10,12,13] The C4–C5 bond length of 1.341(2) Å indicates a double bond. The isopropenyl hydrogen atom H5, which was refined freely, is located exactly in the Ru1–C4–C5 plane. A noteworthy feature of the structure is the comparably short Ru1–C38 distance of 2.941(3) Å, which may indicate a weak β agostic interaction of one cyclohexyl group with the metal. Agostic bonds in related ruthenium(II) phosphane and NHC complexes range from 2.64 to 2.95 Å.[4m,14,15] Since ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** at room temperature (see above) indicate that all six cyclohexyl moieties are equivalent on the NMR timescale, it seems unlikely that the agostic interaction persists in solution.

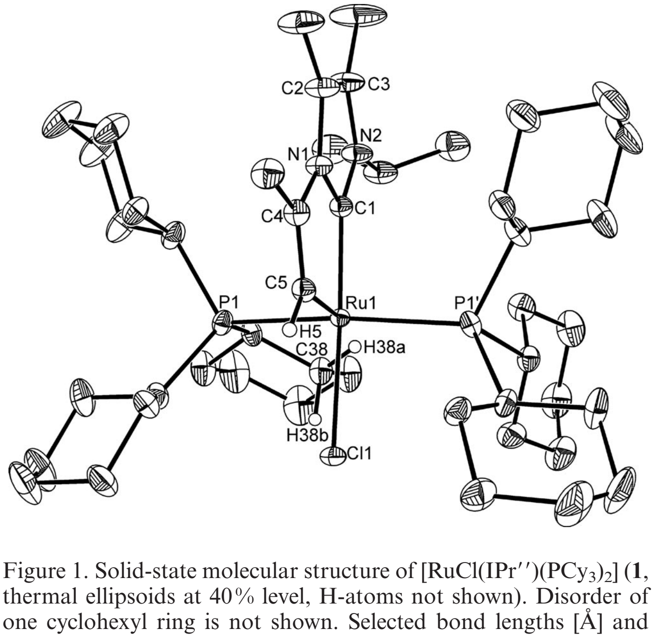


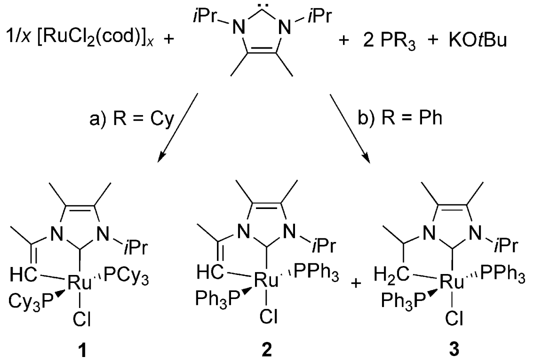
Figure 1. Solid-state molecular structure of $[RuCl(IPr'')(PCy_3)_2]$ (**1**, thermal ellipsoids at 40% level, H-atoms not shown). Disorder of one cyclohexyl ring is not shown. Selected bond lengths [Å] and angles [°]: Ru1–C1 1.9999(17), Ru1–C5 1.9979(18), Ru1–P1 2.3700(3), Ru1–Cl1 2.4723(4), C2–C3 1.343(3), C4–C5 1.341(2), C4–C6 1.495(3), C4–N1 1.433(2), Cl1–Ru1–C5 95.58(5), C1–Ru1–C5 77.34(7), Cl1–Ru1–P1 88.316(9), C1–Ru1–P1 92.328(10), P1–Ru1–P1′ 168.803(17), C1–Ru1–Cl1 172.92(5), C5–C4–N1 111.56(15), Ru1–C5–C4 119.86(13).

Although unusual, the formation of alkenyl-substituted carbene ligands from alkyl carbenes is not limited to complex **1**. Triphenylphosphane complex $[RuCl(IPr'')(PPh_3)_2]$ (**2**), which displays the same the triple C–H activated IPr′′ ligand as **1**, is formed by heating a toluene solution of $[RuCl_2(cod)]_x$, PPh_3, IPr and KO*t*Bu (1:2:1:1 ratio, Scheme 1b).[8] After 4 h at 100 °C, a mixture of **2** with the known single C–H activated carbene complex $[RuCl(IPr')(PPh_3)_2]$ (**3**)[15] had formed. Longer heating resulted in the partial decomposition of **2**, which is thermally less stable than **1**. Similar to our results, Whittlesey et al. recently reported that the complexes $[RuHCl(L)(PiPr_3)_2]$ [L = IPr and 1,3-diethyl-4,5-dimethylimidazol-2-ylidene (IEt)] slowly convert into alkenyl carbene complexes $[RuCl(L'')(PiPr_3)_2]$ when stored under an ethene atmosphere.[15] The identity of the latter was established by multinuclear NMR spectroscopy.

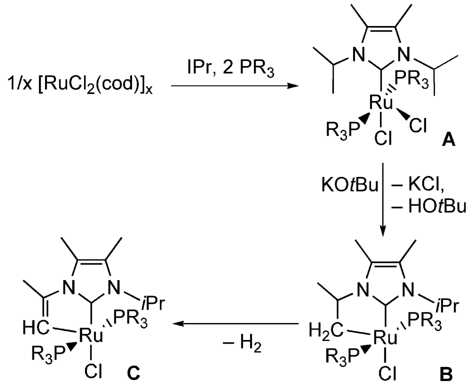
Complexes **2** and **3** could not be separated by fractional crystallization because of their very similar solubilities, but the molecular structure of **2**, which crystallizes in the triclinic space group $P\bar{1}$, was determined by X-ray crystallography (Figure S2 of the Supporting Information).[8] The structures of **1** and **2** are overall quite similar. In particular, the Ru–C distances are almost identical in both complexes. Notable differences are observed in the Ru–P and Ru–Cl bond lengths, which are longer in **1** [Ru1–P1 2.3700(3) Å; Ru1–Cl1 2.4723(4) Å] than in **2** [Ru1–P1,P2 2.3295(6), 2.3376(6) Å; Ru1–Cl1 2.4431(6) Å]. While **1** displays a square pyramidal geometry (see above), the coordination environment of the ruthenium center in **2** is distorted toward a trigonal bipyramid. This is apparent in the much more obtuse Cl1–Ru1–C5 angle of 121.11(8)° in **2** compared to only 95.58(5)° in **1**. The structural differences between **1** and **2** are probably a consequence of the absence of an agostic interaction in **2**, and the larger steric demand of the bulky tricyclohexylphosphane compared to triphenylphosphane.

The formation of alkenyl-substituted carbene complexes very likely proceeds stepwise according to Scheme 2. First, NHC complex **A** is formed from $[RuCl_2(cod)]_x$, the free carbene ligand IPr and two equivalents of phosphane. Related complexes are well documented.[15] Second, base-induced C–H activation leads to the formation of complex **B**, which displays a deprotonated isopropyl substituent. Such single C–H activations have frequently been encountered.[4] Indeed, our investigations showed that single C–H activated complex **3** can be isolated in 51% yield from $[RuCl_2(PPh_3)_3]$, IPr and potassium *tert*-butoxide.[8] In the last step, the triple C–H activated product **C** is formed by elimination of dihydrogen (Scheme 3). In support of this mechanistic proposal, ^1H and $^{31}P\{^1H\}$ NMR monitoring of a toluene solution of complex **3** showed 27% conversion to alkenyl carbene complex **2** after heating the solution to 100 °C for 4 h. Complex **2** gives rise to a $^{31}P\{^1H\}$ NMR singlet at δ = 41.1 ppm in deuterated dichloromethane. Minor amounts of the known hydride-containing species *trans*-$[RuHCl(IPr)(PPh_3)_2]$ (singlet at δ = 47.1 ppm) and *cis*-$[RuHCl(IPr)(PPh_3)_2]$ (broad signals at δ = 49.1 and

73.7 ppm) were also detected as secondary by-products.[15] Partial decomposition at longer reaction times precluded the isolation of pure **2**.



Scheme 2. Synthesis of C–H activated complexes **1**–**3**.



Scheme 3. Stepwise formation of isopropenyl-substituted carbene complexes.

The C–H activation process appears to be reversible upon addition of H_2, but the carbene ligand is surprisingly labile. Thus, stirring a solution of **1** under a dihydrogen atmosphere resulted in a colorless precipitate, presumably the imidazolium salt [IPrH]Cl,[16] and the carbene-free complexes $[RuH_2(H_2)_2(PCy_3)_2]$ and [*trans*-$RuClH(H)_2(PCy_3)_2$], which were identified by ^1H and ^{31}P NMR spectroscopy and X-ray crystallography.[17,18]

No catalytic turnover could be observed when compound **1** was tested as catalyst for the dehydrogenative coupling of 2-phenyl ethanol and benzylamine. This suggests that alkenyl-substituted species such as **1** are not catalytically active, but might be catalyst deactivation products.

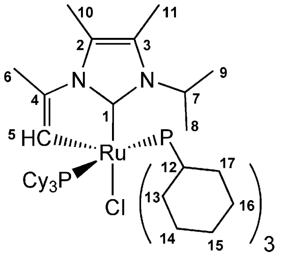
Conclusions

Alkenyl-substituted carbene complexes [RuCl(IPr′′)-$(PCy_3)_2$] (**1**) and [RuCl(IPr′′)$(PPh_3)_2$] (**2**) are accessible via a simple one-pot procedure from readily available starting materials. The synthesis of **1** and **2** highlights the fascinating ability of ruthenium to mediate the activation of up to three ligand alkyl C–H bonds. The presented approach is not confined to a specific phosphane spectator ligand although the nature of the phosphane (tricyclohexylphosphane vs. triphenylphosphane) appears to influence the thermal stability of the resulting complexes. On-going studies in our laboratory concern the reactivity of alkenyl carbene complexes and their potential to initiate catalytic transformations.

Experimental Section

General: All procedures were carried out under an inert atmosphere of purified argon and in dried solvents. $[RuCl_2(cod)]_x$, $[RuCl_2(PPh_3)_3]$ and IPr were prepared according to literature procedures.[19,20]

Synthesis of 1: $[RuCl_2(cod)]_x$ (0.820 g, 3 mmol), IPr (0.540 g, 3 mmol), PCy_3 (1.683 g, 6 mmol) and KO*t*Bu (0.336 g, 3 mmol) were suspended in toluene (100 mL) and heated to 100 °C for three hours. After cooling to room temperature the reaction mixture was filtered and the solvents evaporated to dryness. The precipitate was washed with *n*-hexane (2 × 10 mL), dried in vacuo and recrystallized from a minimum amount of dichloromethane at –80 °C; yield 0.640 g (24%); m.p. (argon, sealed capillary) 202 °C (dec.) ^1H NMR (400 MHz, CD_2Cl_2, connectivities were confirmed by COSY, HSQC and HMBC experiments): δ = 1.04 (m, 6 H, H14a), 1.16 (m, 12 H, H15a, H16a), 1.33 (m, 12 H, H13a, H17a), 1.55 (m, 6 H, H17a), 1.61 (s, 6 H, H8, H9), 1.62 (m, 6 H, H15b), 1.71 (m, 12 H, H14b, H16b), 1.72 (m, 6 H, H13b), 1.96 (m, 6 H, H12), 2.25 (s, 3 H, H10), 2.28 (s, 3 H, H6), 2.30 (s, 3 H, H11), 5.25 (m, 1 H, H7), 7.45 (br. s, 1 H, H5) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, connectivities were confirmed by HSQC and HMBC spectra): δ = 10.4 (s, C10), 11.0 (s, C11), 19.8 (s, C6), 24.2 (s, C8, C9), 27.2 (s, C15) 28.6 (t, $J_{C,P}$ = 4 Hz, C14), 28.7 (t, $J_{C,P}$ = 5 Hz, C16), 30.7 (s, C17), 30.8 (s, C13), 37.0 (t, $J_{C,P}$ = 7 Hz, C12), 50.9 (s, C7), 120.7 (s, C3), 123.5 (s, C2), 130.4 (s, C4), 151.3 (s, C5), 193.3 (s, C1) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 29.6 (s) ppm. $C_{47}H_{83}ClN_2P_2Ru$ (874.61): calcd. C 64.5, H 9.6, N 3.2; found C 63.6, H 9.4, N 3.3.



Supporting Information (see also the footnote on the first page of this article): NMR spectrum of the reaction mixture of $[RuCl_2(cod)]_x$ with IPr, PCy_3 and KO*t*Bu (1:1:1:2), crystallographic details, graphical representation of the molecular structure of **2**, synthesis and characterization data for complexes **2** and **3**.

Acknowledgments

We thank Dr. Sven Schneider (TU Munich) for valuable discussions, cand.-chem. Silke Frömel and Dr. Alexander Hepp for experimental assistance and discussions, and Prof. Dr. Werner Uhl for his generous support. Funding from the Fonds der Chemischen Industrie (Liebig fellowship to R. W.) and the Deutsche Forschungsgemeinschaft (DFG) (SFB858) is gratefully acknowledged.

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[11] Crystal data for **1**: $C_{47}H_{83}N_2P_2ClRu$, $M = 874.61$, crystal dimensions $0.50 \times 0.30 \times 0.10$ mm, orthorhombic (*Cmca*), $a = 24.0122(10)$ Å, $b = 20.0786(8)$ Å, $c = 20.0760(8)$ Å, $V = 9679.3(7)$ Å^3, $Z = 8$, $\rho_{\text{calcd.}} = 1.200$ g cm^{-3}, $\mu = 0.477$ mm^{-1}, Mo-K_α radiation ($\lambda = 0.71073$ Å), $T = 153(2)$ K, reflections measured 57206, unique 7563 ($R_{\text{int}} = 0.037$), 341 parameters, 3 restrains, final R indices $R_1 = 0.0268$, $wR_2 = 0.0667$, largest difference peak/hole 0.704 e Å^{-3}/–0.513 e Å^{-3}. Crystal data for **2**: $C_{53}H_{59}N_2O_{1.5}P_2ClRu$, $M = 946.48$, triclinic ($P\bar{1}$), $a = 10.3786(4)$ Å, $b = 12.3627(5)$ Å, $c = 19.2233(8)$ Å, $\alpha = 74.3160(10)°$, $\beta = 77.5630(10)°$, $\gamma = 87.2540(10)°$, $V = 2318.80(16)$ Å^3, $Z = 2$, $\rho_{\text{calcd.}} = 1.356$ g cm^{-3}, $\mu = 0.506$ mm^{-1}, Mo-K_α radiation ($\lambda = 0.71073$ Å), reflections measured 26541, unique 12852, 516 parameters, 15 restrains, $R = 0.0423$, $wR_2 = 0.1325$, largest difference peak/hole 1.143 e Å^{-3}/–0.912 e Å^{-3}. CCDC-779282 (for **1**) and -779283 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] Search in the CSD database, version 5.30, November 2008, resulted in: Ru–C bond lengths of 181 complexes containing a RuCl(NHC) fragment range from 1.908 to 2.168 Å (average 2.047 Å); Ru–Cl distances range from 2.261 to 2.532 Å (average: 2.395 Å).

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[16] ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.62$ (d, $J_{\text{H-H}} = 8$ Hz, 12 H, NCH(CH_3)$_2$), 2.20 (s, 6 H, CCH_3), 4.47 (m, 2 H, NCH(CH_3)$_2$), 10.51 (br. s, 1 H, IPrH^+) ppm.

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Received: June 22, 2010
Published Online: August 26, 2010