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Cycloruthenated tertiary amines and ethylene: further insight to the Ru-mediated olefin–aryl coupling reaction

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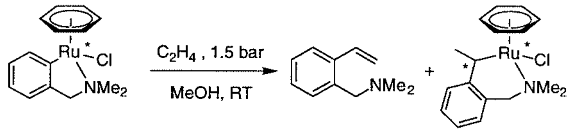
The reaction between cycloruthenated *N*,*N*-dimethylbenzylamine and ethylene under very mild conditions afforded 2-vinyl-*N*,*N*-dimethylbenzylamine and an organometallic Ru derivative resulting from the overall insertion of one carbon atom in the Ru–C bond of the starting material.

The insertion of an olefin in a transition metal–carbon σ-bond is a classical reaction in organometallic chemistry. With palladium, this process is followed by β-hydrogen elimination and is widely known as the Heck reaction.[1] Recently, functionalisation reactions of aryl C–H bonds with terminal olefins catalysed by ruthenium hydride complexes were reported.[2,3] In these reactions the products are alkyl substituted compounds resulting from the 'formal' insertion of the olefinic double bond into a C–H bond. We now report that air stable cycloruthenated *N*,*N*-dimethylbenzylamine derivatives react at low pressure (1.5 atm) and room temperature (RT) with ethylene to afford vinylbenzylamines, as in the Heck reaction, and an organometallic compound resulting from the insertion of ethylene into the Ru–C bond.

In a typical experiment, an orange suspension of (η^6-C_6H_6)Ru($C_6H_4CH_2NMe_2$)Cl **1a** in methanol was stirred at room temperature under 1.5 bar of ethylene over 1.5 h [eqn. (1)]. 2-Vinyl-*N*,*N*-dimethylbenzylamine **2a**‡ and the new organoruthenium compound **3a**‡ were isolated. The ^1H and ^{13}C NMR spectra and combustion analyses of **3a** are consistent with the structure depicted in eqn. (1).



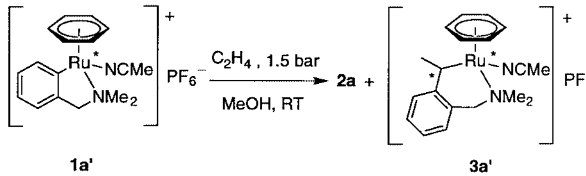
(1)

1a
Racemic

2a
81%

3a
19%
($R_{Ru}R_{C'}$): 50%
($S_{Ru}S_{C'}$): 50%

We found that it was possible to influence the ratio of **2a** to **3a** by removing the chloride ligand of the starting material. Thus, the yellow cationic derivative **1a′**[4c] led to a much higher yield of the red organometallic species **3a′** when it was treated with ethylene [eqn. (2)].



(2)

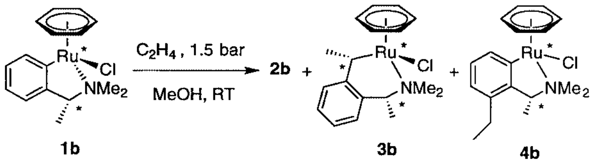
1a'

13%

3a'
87%

These reactions led to the formation of a chiral C atom σ-bonded to Ru, the Ru atom being itself a stereogenic center.[4] Interestingly, only one enantiomeric pair was observed by ^1H NMR in both cases, indicating that these reactions occur with a high level of diastereoselectivity. The stereochemistry of **3a** has been investigated by a ^1H NOE experiment. The η^6-benzene ring was found to interact strongly with one of the *N*-methyl and with the *C*-methyl which also interacts with the proton of the aryl ligand. The proton on the carbon α to Ru (C′) interacts neither with the latter nor with the η^6-benzene ring. Consequently, **3a** displays a boat conformation, with the C-methyl and the η^6-benzene ring in the equatorial and the axial positions respectively. The absolute configuration of the enantiomers are thus ($R_{Ru}R_{C'}$) and ($S_{Ru}S_{C'}$).

In order to confirm the chiral control of the reaction, the optically active complex (η^6-C_6H_6)Ru(C_6H_4-2-(*R*)-CH(Me)NMe_2)Cl **1b** (de = 90%)[4] was treated with ethylene under the same conditions. Surprisingly in addition to **2b** and **3b**,‡ the respective analogues of **2a** and **3a**, a third product **4b**‡ was observed in trace amounts [eqn. (3)]. Its structure is that of a new cyclometallated benzylamine derivative displaying an ethyl substituent in position 3.



(3)

1b
(R_CS_{Ru}):95%
(R_CR_{Ru}): 5%

75%

3b
20%
($R_CS_{Ru}S_{C'}$)

4b
< 5%

For complexes **3b** and **4b**, one diastereoisomer only was observed by ^1H NMR indicating that these compounds are the result of highly diastereoselective processes. Unfortunately owing to its instability, **3b** could not be isolated as a pure solid. Nevertheless its stereochemistry was investigated through a ^1H ROESY experiment of the crude reaction mixture. The methyl substituent of the carbon atom σ-bonded to Ru (C′) interacts with the proton of the aryl ligand and with the η^6-C_6H_6 ring whereas the corresponding proton interacts with none of these. These results indicate an equatorial position for the methyl group and axial position for the η^6-benzene ring as in **3a**. The methyl group α to N interacts equally with both *N*-methyls and with the proton of the aryl ligand but not with the η^6-benzene indicating an equatorial position as well. Moreover, the absence of any interaction between the η^6-benzene ring and the benzylic proton attached to N, together with the deshielding of the latter signal, indicate that this proton should be close to the chlorine atom as in the starting material **1b**. Consequently, **3b** should display a boat conformation with the protons α to Ru and N on bridgehead positions and its absolute configuration should therefore be ($R_CS_{Ru}S_{C'}$).

When **3b** was left in solution it isomerised slowly into **4b** together with decomposition but no conversion into **2b** was detected. Thus **2b** and **3b** are independent products which, however, are likely to come from the same intermediate (see below). The important instability of **3b** as compared to that of **3a** might be due to steric congestion around the Ru atom. The

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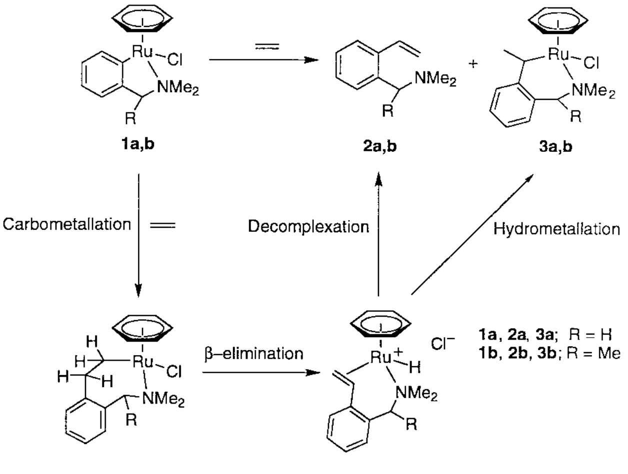
rearrangement process **3b** → **4b** remains unclear yet. Running the reaction in CD_3OD did not result in deuterium incorporation in the new ethyl group. Moreover, when a sample of the crude reaction mixture was left in an aprotic solvent such as $CDCl_3$ this demetallation–remetallation process also occured. These observations tend to indicate that **4b** may be formed through an intramolecular rearrangement as demonstrated by Steenwinkel *et al.* for a related ruthenocyclic molecule.[5]

To the best of our knowledge the only precedent of a Ru-mediated functionalization of a C–H bond to afford a vinyl derivative such as **2a**,**b** was reported by Murai and coworkers[6] when reacting aromatic imines or imidates with mono-substituted olefins in the presence of catalytic amounts of $Ru_3(CO)_{12}$. It is generally assumed that this type of product is formed by β-H elimination from a carbometallation intermediate. Consequently the formation of **2a**,**b** and **3a**,**b** can be rationalised according to the reaction path depicted in Scheme 1. The first step involves the insertion of ethylene into the C–Ru bond followed by a β-H elimination leading to an olefin–hydride complex.[7] This leads on one hand to the metal free substituted olefin **2a**,**b** as in the Heck reaction and on the other hand to the one carbon-atom insertion complex **3a**,**b** by anti-Markovnikov hydrometallation of the olefinic unit (Scheme 1).



Scheme 1

Studies are currently under way to determine the conditions that would allow us to direct the reaction toward the exclusive formation of one of these products.

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Notes and references

‡ *Selected data* (J/Hz): **2a**: δ_H(200 MHz, $CDCl_3$) 7.55 (m, 1H, C_6H_4), 7.26 (m, 3H, C_6H_4), 7.17 (dd, 1H, $C\mathit{H}{=}CH_2$, ^3J 17.5, ^3J 11.0), 5.68 (dd, 1H, $CH{=}C\mathit{H}_EH_Z$, ^3J 17.5, ^2J 1.4), 5.30 (dd, 1H, $CH{=}CH_E\mathit{H}_Z$, ^3J 11.0, ^2J 1.4), 3.44 (s, 2H, CH_2N), 2.24 (s, 6H, NMe_2). **2b**: δ_H(200 MHz, $CDCl_3$) 7.44 (m, 2H, C_6H_4), 7.24 (m, 2H, C_6H_4), 7.23 (dd, 1H, $C\mathit{H}{=}CH_2$, ^3J 17.4, ^3J 11.0), 5.57 (dd, 1H, $CH{=}C\mathit{H}_EH_Z$, ^3J 17.4, ^2J 1.6), 5.29 (dd, 1H, $CH{=}CH_E\mathit{H}_Z$, ^3J 11.0, ^2J 1.6), 3.53 (q, 1H, $C\mathit{H}CH_3$, ^3J 6.6), 2.21 (s, 6H, NMe_2), 1.31 (d, 3H, $CHC\mathit{H}_3$). **3a**: Anal. Calc. (found) for $C_{17}H_{22}NClRu{\cdot}0.25CH_2Cl_2$: C, 52.04 (52.27); H, 5.70 (5.72); N, 3.52 (3.66)%. δ_H(300 MHz, $CDCl_3$) 7.58 (d, 1H, C_6H_4, ^3J 7.7), 7.33 (m, 2H, C_6H_4), 6.88 (d, 1H, C_6H_4, ^3J 4.0), 4.90 (s, 6H, C_6H_6), 3.53 (q, 1H, $C\mathit{H}CH_3$, ^3J 7.1), 3.39 and 2.29 (AB, 2H, CH_2N, ^2J 11.4), 3.24 and 2.28 (2s, 6H, NMe_2), 2.14 (d, 3H, $CHC\mathit{H}_3$). δ_C(75 MHz, $CDCl_3$) 153.8, 133.3, 129.4, 129.0, 121.6 and 120.4 (C_6H_4), 83.0 (C_6H_6), 64.7 (CH_2N), 56.5 and 56.3 (NMe), 36.8 (CHRu), 24.5 ($CH\mathit{C}H_3$). **3a′**: δ_H(200 MHz, CD_3CN) 7.62 (d, 1H, C_6H_4, ^3J 7.4), 7.34 (m, 2H, C_6H_4), 6.99 (d, 1H, C_6H_4, ^3J 6.6), 5.14 (s, 6H, C_6H_6), 3.24 and 2.63 (AB, 2H, CH_2N, ^2J 11.8), 3.09 (q, 1H, $C\mathit{H}CH_3$, ^3J 7.4), 3.01 and 2.38 (2s, 6H, NMe_2), 2.14 (s, 3H, CH_3CN), 2.08 (d, 3H, $CHC\mathit{H}_3$). **3b**: δ_H(500 MHz, CD_2Cl_2) 7.57 (d, 1H, C_6H_4, ^3J 7.7), 7.29 (t, 1H, C_6H_4), 7.02 (d, 1H, C_6H_4). 6.90 (t, 1H, C_6H_4), 4.88 (s, 6H, C_6H_6), 3.57 (2q, 2H, $C\mathit{H}CH_3Ru$ and $C\mathit{H}CH_3N$), 3.32 and 2.07 (2s, 6H, NMe_2), 2.11 (d, 3H, $CHC\mathit{H}_3Ru$, ^3J 7.1), 1.29 (d, 3H, $CHC\mathit{H}_3N$, ^3J 6.9). **4b**: δ_H(500 MHz, CD_2Cl_2) 7.51 (d, 1H, C_6H_3, ^3J 7.4), 6.94 (t, 1H, C_6H_3). 6.68 (d, 1H, C_6H_3), 5.32 (s, 6H, C_6H_6), 3.45 (q, 1H, $C\mathit{H}CH_3$, ^3J 6.6), 3.10 and 2.33 (2s, 6H, NMe_2), 2.44 (q, 2H, $C\mathit{H}_2CH_3$, ^3J 7.6), 1.16 (d, 3H, $CHC\mathit{H}_3$), 1.14 (t, 3H, $CH_2C\mathit{H}_3$).

1 R. F. Heck, *Org. React. (New York)*, 1982, **27**, 345.
2 S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda and N. Chatani, *Nature*, 1993, **366**, 529; F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani and S. Murai, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 62.
3 Y. Guari, S. Sabo-Etienne and B. Chaudret, *J. Am. Chem. Soc.*, 1998, **120**, 4228.
4 (*a*) H. C. L. Abbenhuis, M. Pfeffer, J. P. Sutter, A. de Cian, J. Fischer, H. Li Ji and J. H. Nelson, *Organometallics*, 1993, **12**, 4464; (*b*) S. Attar, J. H. Nelson, J. Fischer, A. de Cian, J. P. Sutter and M. Pfeffer, *Organometallics*, 1995, **14**, 4559; (*c*) S. Fernandez, M. Pfeffer, V. Ritleng and C. Sirlin, *Organometallics*, 1999, **18**, 2390.
5 P. Steenwinkel, S. L. James, R. A. Gossage, D. M. Grove, H. Kooijman, W. J. J. Smeets, A. L. Spek and G. van Koten, *Organometallics*, 1998, **17**, 4680.
6 F. Kakiuchi, M. Yamauchi, N. Chatani and S. Murai, *Chem. Lett.*, 1996, 111; F. Kakiuchi, T. Sato, M. Yamauchi, N. Chatani and S. Murai, *Chem. Lett.*, 1999, 19.
7 For a leading reference concerning olefin–hydride complexes, see: J. W. Faller and K. J. Chase, *Organometallics*, 1995, **14**, 1592.

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