Trimethylsilylcarbene and Bis(trimethylsilyl) Formaldehyde Azine Complexes of Chiral Bis(4-isopropyloxazolinyl)pyridine(dichloro)ruthenium(II)

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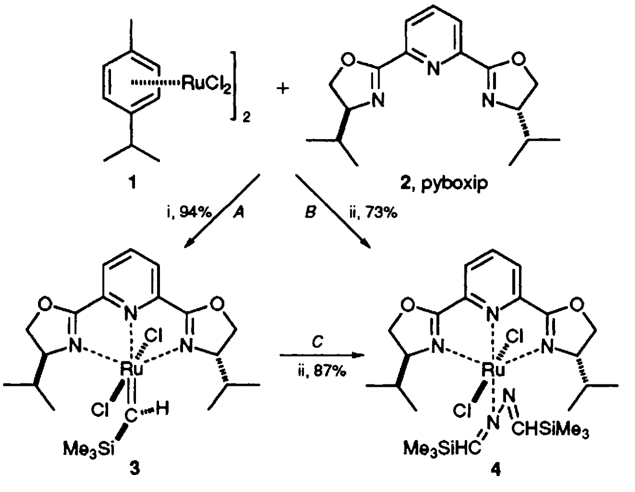
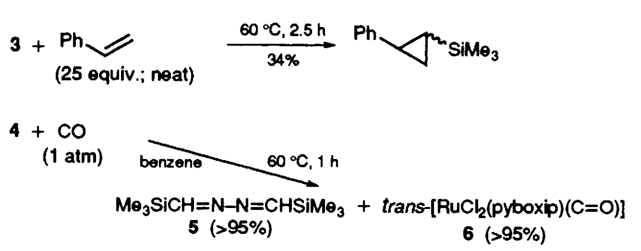
A mixture of [{Ru^{II}Cl$_2$(*p*-cymene)}$_2$] 1 and 2,6-bis(4-isopropyloxazolinyl)pyridine (pyboxip) 2 was treated with trimethylsilyldiazomethane to give the trimethylsilylcarbene complex *trans*-[Ru^{II}Cl$_2$(pyboxip)(=CHSiMe$_3$)] 3 at 0–15 °C in 94% yield and the azine complex *trans*-[Ru^{II}Cl$_2$(pyboxip)(Me$_3$SiCH=N–N=CHSiMe$_3$)] at 25–35 °C in 73% yield; the catalytic activity of 3 was examined for dimerization and asymmetric cyclopropanation with ethyl diazoacetate.

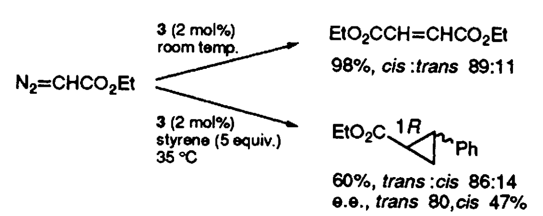
We have recently reported a highly efficient asymmetric cyclopropanation of olefins and diazoacetates with a chiral bis(oxazolinyl)pyridineruthenium(II) (Ru–pybox) catalyst.[1] Although we could not detect a metal–carbene species derived from diazoacetate as an intermediate in the catalytic cycle, we could isolate a carbene complex by using trimethylsilyldiazomethane. We report herein the new carbene complex and a new azine complex of a Ru–Pybox system, together with their catalytic activities.



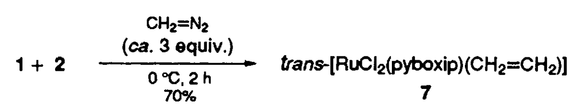
Scheme 1 *Reagents and conditions*: i, Me$_3$SiCH=N$_2$ (2.0 equiv.), 0–15 °C, 1 h; ii, Me$_3$SiCH=N$_2$ (3.0 equiv.), 25–35 °C, 2 h



Scheme 2



Scheme 3



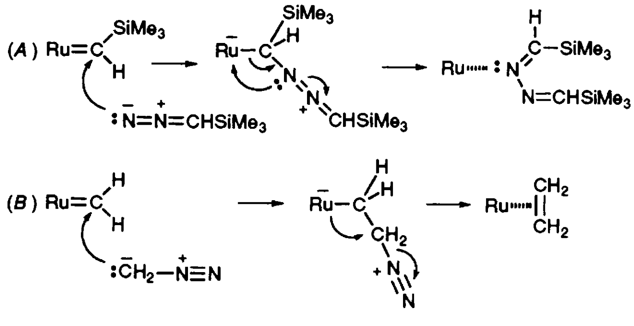
Scheme 4

Treatment of a mixture of [{RuCl$_2$(*p*-cymene)}] 1[2] and pyboxip 2[3] in dichloromethane at 0–15 °C for 1 h gave the trimethylsilylcarbene complex, *trans*-[RuCl$_2$(pyboxip)(=CHSiMe$_3$)] 3 in 94% yield as a dark brown solid (Scheme 1, *A*).† The trimethylsilylcarbene complex 3 is thermally and air stable in the solid state but decomposes gradually in solution. ^{1}H and ^{13}C NMR spectra of 3 exhibited characteristic signals for the metal–carbene moiety: Ru=CH–Si, δ_H 26.52 and δ_C 388.9. In spite of the unsymmetrical situation of the carbene moiety, the proton and carbon NMR signals of the pyboxip ligand in 3 are not affected and they show a pattern consistent with the C_2 symmetrical structure. At a higher temperature, 25–35 °C, an excess of trimethylsilyldiazomethane (3 equiv.) produced the new azine complex, *trans*-[RuCl$_2$(pyboxip)(Me$_3$SiCH=N–N=CHSiMe$_3$)] 4 in 73% yield (Scheme 1, *B*).‡ Treatment of the trimethylsilycarbene complex 3 with trimethylsilyldiazomethane at 25–35 °C also gave the azine complex 4 (Scheme 1, *C*). Interestingly, a large excess of trimethylsilyldiazomethane in 1,2-dichloroethane was catalytically dimerized to give the bis(trimethylsilyl) azine 5§ in 60–70% yield at 50 °C for 1 h with the *in situ* catalyst 1 + 2 (1 : 1; 5 mol%). Complexes 3 and 4 (5 mol%) were also active for this dimerization. Therefore, 3 and 4 are thought to be the intermediates in the catalytic cycle.

The coordination of trimethylsilylcarbene in 3 and the azine in 4 was also unambiguously confirmed as follows: (*i*) carbene transfer from 3 to styrene was observed at 60 °C in 34% yield (Scheme 2). (*ii*) Under carbon monoxide atmosphere at 60 °C, 4 released the free azine 5 in 100% yield, together with the corresponding carbonyl complex 6[1] (Scheme 2).

Ruthenium and osmium porphyrin systems have been well investigated for formation of carbene complexes and for their catalytic activity for dimerization of diazoacetates and cyclopropanation.[4] We also examined the catalytic activity of the carbene in complex 3. Ethyl diazoacetate was dimerized with 3 (2 mol%) in high yield (98%) with a high *cis*-selectivity (89 : 11; Scheme 3). In the presence of styrene, complex 3 was highly active for cyclopropanation with ethyl diazoacetate to give phenylcyclopropanecarboxylates in 60% yield, with a *trans* : *cis* ratio of 86 : 14 and an enantioselectivity of 80 and 47%, respectively (Scheme 3).[1]

Use of diazomethane in place of trimethylsilyldiazomethane in attempts to synthesise the corresponding carbene complex led only to the ethylene complex 7[1] in 70% yield (Scheme 4).



Scheme 5

The contrast between the formation of the azine-complex **4** with trimethylsilyldiazomethane and the ethylene complex **7** with diazomethane could be explained as being due to steric hindrance of both silyl groups on the carbene complex **3** and trimethylsilyldiazomethane or the low cationic nature of the silycarbene moiety (Scheme 5, path *A*). Diazomethane reacts with the intermediate carbene complex giving the alkene as in the above dimerization of diazoacetate (path *B*).

Received, 1st March 1994; Com. 4/01254B

Footnotes

† Synthesis of *trans*-[RuCl$_2$(pyboxip)(=CHSiMe$_3$)] **3**. To a mixture of [{Ru^{II}Cl$_2$(*p*-cymene)}$_2$] **1** (200 mg, 0.33 mmol) and 2,6-bis(4-isopropyloxazolinyl)pyridine **2** (197 mg, 0.66 mg mmol) in dichloromethane (15 ml) was added a solution of trimethylsilyldiazomethane in hexane (1.32 mmol, *ca.* 0.6 mol dm^{-3}) at −20 °C. The temperature was gradually raised to 15 °C, and the mixture stirred for 1 h and concentrated. The residue was washed with hexane to give **3** (346 mg, 94%) as a dark brown solid. decomp. 102 °C, ^{1}H NMR (270 MHz, CDCl$_3$, Me$_4$Si) δ 0.48 (s, 9 H, SiCH$_3$), 0.60 (d, *J* 7.3 Hz, 6 H), 0.79 (d, *J* 7.3 Hz, 6 H), 1.24 (br, 2 H), 3.73 (m, 2 H, NCH), 4.66 (t, *J* 7.9 Hz ×2, 2 H, OCH), 4.84 (t, *J* 7.9 Hz ×2, 2 H, OCH), 7.96 (d, *J* 7.9 Hz, 2 H), 8.06 (d, *J* 7.9 Hz, 1 H), 26.52 (s, 1 H, Ru–CH). ^{13}C NMR (67.8 MHz, C$_6$D$_6$) δ 0.99, 14.97, 18.82, 28.24, 71.50, 72.12, 121.6, 137.0, 139.5, 161.2, 388.9 (Ru–C).

‡ *Spectroscopic data* for **4** (violet solid, decomp. 145 °C): ^{1}H NMR (270 MHz, CDCl$_3$, Me$_4$Si) δ 0.27 (s, 9H, Si-CH$_3$), 0.30 (s, 9 H, Si-CH$_3$), 0.82 (d, *J* 7.3 Hz, 6 H), 0.94 (d, *J* 7.3 Hz, 6 H), 2.40 (m, 2 H), 4.17 (m, 2 H), 4.65–4.85 (m, 4 H), 7.48 (t, *J* 7.3 Hz, 1 H), 7.56 (d, *J* 7.3 Hz, 2 H), 7.85 (s, 1 H, azine), 8.89 (s, 1 H, azine). ^{13}C NMR (67.8 MHz, C$_6$D$_6$) δ −0.72, −0.97, 15.69, 19.46, 29.88, 70.13, 71.11, 121.6, 127.9, 151.3, 165.7, 171.2 (azine), 176.9 (azine).

§ *Spectroscopic data* for **6** (pale yellow oil): ^{1}H NMR (270 MHz, CDCl$_3$, Me$_4$Si) δ 0.17 (s, 1.08 H), 0.18 (s, 7.92 H), 7.91 (s, 1.76 H), 8.09 (s, 0.24 H) (isomer ratio 88 : 12); IR (film) ν/cm^{-1} 1240, 829, 725; *m*/*z* 201 (M + 1, 30%), 186 (35), 173 (100).

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