Stable Dicarbonylcarbene Complexes of Bis(oxazolinyl)pyridine Ruthenium and Osmium

Hisao Nishiyama,* Katsuyuki Aoki, Hirofumi Itoh, Taichiro Iwamura, Naoya Sakata, Osamu Kurihara, and Yukihiro Motoyama
School of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441

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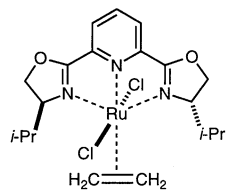
The reaction of $RuCl_2$(pybox)(C_2H_4) [pybox = 2,6-bis(oxazolinyl)pyridine] **1** and $OsCl_2$(pybox)(propylene) **6** with dimethyl diazomalonate gave stable dicarbonylcarbene complexes **9** and **10** in 92% and 59% yields, respectively. The carbene moiety of **9** proved to be almost parallel in the Cl-Ru-Cl plane by 10-12° and perpendicular to the pybox plane by X-ray analysis. The transfer of the carbene moiety of **9** to styrene could be observed at 110 °C to give the corresponding cyclopropane **15** but in a low yield (11%) with asymmetric induction in 36% ee.

Transition metal carbene complexes have been extensively studied as fascinating organometallic species, which exhibit a variety of chemical reactivity and act as catalysts.[1] Especially, they are thought to be intermediates of catalytic cyclopropanation of olefins. In the series of our catalytic chemistry with bis(oxazolinyl)pyridine (pybox) as a chiral ligand and its ruthenium-ethylene complex **1**,[2] we have recently reported some carbene complexes of Ru-pybox system **2**-**4**.[3-5] High asymmetric induction was also confirmed by the stoichiometric carbene transfer of the chiral aryloxycarbonylcarbene complex **4**, derived from the corresponding diazoacetate.[5]



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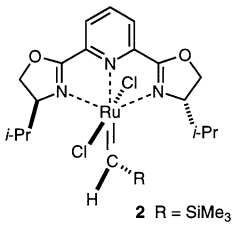
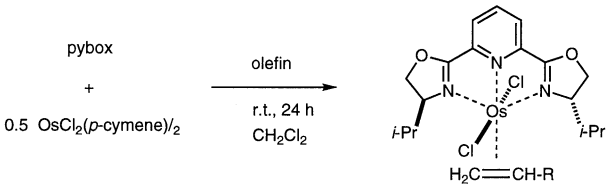


2 R = $SiMe_3$
3 R = CH=CPh_2
4 R = CO_2(2,6-di-*i*-PrPh)

We report here preparation of some new dicarbonylcarbene complexes of Ru-pybox and Os-pybox systems including X-ray analysis of one of the Ru-pybox carbene complexes. In terms of dicarbonyl diazo compounds, there are a few reports about some cyclopropanations,[6] μ-bridging carbene complexes,[7] and carbene complexes of metal-porphyrin derivatives.[8]

Starting olefin complexes of ruthenium- and osmium-pybox were prepared by reaction of pybox and the cymene complexes[2,9] under the corresponding olefin atmosphere (Scheme 1). The synthesis of $RuCl_2$(pybox)(ethylene) **1** has already been reported by us.[2] The osmium-ethylene complex **5** has a higher decomposition point 203-205 °C, compared to the ruthenium-ethylene complex **2** (dec. 102-105 °C). Although the ruthenium-pybox compiexes of propylene and styrene could not be isolated, the corresponding osmium-pybox complexes of propylene and styrene **6** and **7** were obtained as stable forms, respectively; **6**, dec. 117-120 °C; **7**, dec. 110-114 °C.[10] As the osmium-ethylene complex **5** is too stable to be applied as a reaction precursor, the propylene complex **6** was adopted.

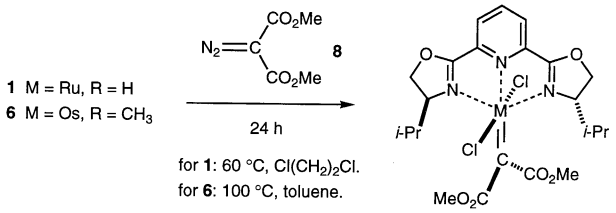
The reactions of ruthenium-ethylene complex **1** and osmium-



5 R = H (96%)
6 R = CH_3 (70%)
7 R = Ph (71%)

Scheme 1.

propylene complex **6** with dimethyl diazomalonate **8**[11] were carried out at 60 °C in dichloroethane and at 100 °C in toluene to produce new stable bis(methoxycarbonyl)carbene complexes **9** in 92% and **10** in 59%, respectively (Scheme 2).[12] The complexes could be purified by silica-gel column chromatography at 0-20 °C. The characteristic carbene-carbon signals of their ^{13}C NMR appeared at δ 296.1 ppm for **9** and δ 234.0 ppm for **10**,



9 M = Ru (92%)
10 M = Os (59%)

Scheme 2.

respectively; cf. δ 388.9 ppm for **2**[3] and δ 301.8 ppm for **4**[5].

A single crystal X-ray analysis of **9** was successfully carried out to show that the length of the Ru-C bond is 1.88 Å indicating a metal-carbon double bond (Figure 1).[13] The carbene carbon atom C(18) has sp^2 configuration; i.e., the geometry around C(18) is almost planar with ca. 114-124° of the three angles, Ru(1)-C(18)-C(19), Ru(1)-C(18)-C(21), and C(19)-C(18)-C(21). It is quite interesting that the dihedral angle of the carbene plane C(19)-C(18)-C(21) and the Cl-Ru-Cl plane is ca. 10-12°. This configuration can imply as follows: (1) the sp^2 electron pair of the singlet dicarbonyl carbene moiety ligates to the vacant orbital of the $RuCl_2$-pybox fragment. (2) the electrons of the ruthenium filled d-orbital in the plane of pybox make backdonation to the vacant p-orbital of the coordinated carbene carbon atom C(18). Furthermore, the two carbonyl planes O-C=O are almost perpendicular to the C(19)-C(18)-C(20) plane. Thus, the two ester groups and the two isopropyl groups completely surround the inner carbene carbon atom C(18).

Non-chiral Ru-ethylene complex **11** with non-substituted bis(oxazolinyl)pyridine readily reacted at 60~80 °C with the diazomalonate **8** but to give a very complicated mixture. The expected carbene complex could not be obtained. The bulky isopropyl substituents on pybox ligand may be necessary to stabilize its carbene complex.

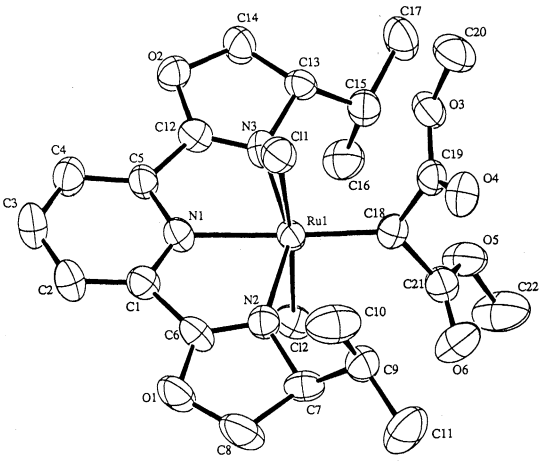
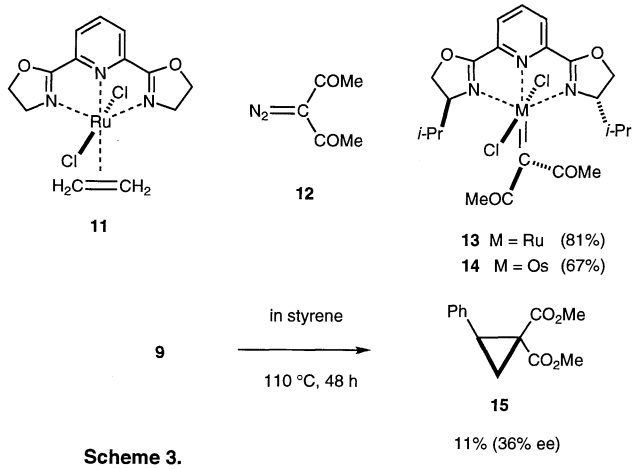


Figure 1. Molecular structure of $RuCl_2(pybox)[=C(CO_2Me)_2]$ **9**.

Similarly, the reaction of the olefin complexes **1** and **6** with diazoacetylacetone **12** was carried out to give the corresponding stable diacetylcarbene complexes **13** (50 °C, 2 h, 81%) and **14** (100 °C, 21 h, 67%).[14]



Scheme 3.

Although the dicarbonylcarbene complexes are fairly stable, we examined a possibility of the carbene transfer reaction from **9** to styrene in order to compare the reactivity to the monocarbonyl carbene complexes such as **4** (**4**: 60 °C in styrene, 2 h, 82% yield of the cyclopropane product).[5] The reaction of **9** did not proceed below 60 °C, but the desired cyclopropane **15** yielded only in 11% at refluxing temperature of toluene, accompanied with the asymmetric induction only in 36% (Scheme 3). The carbene transfer reaction from **13** and **14** to styrene was not successful.

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10 **5**: purple solid, ^1H NMR (270 MHz, $CDCl_3$, TMS): δ 0.80 (d, J = 6.8 Hz, 6H), 1.04 (d, J = 6.8 Hz, 6H), 2.56 (m, 2H), 4.40-4.60 (m, 6H), 4.85 (m, 2H), 4.99 (m, 2H), 7.11 (t, J = 7.3 Hz, 1H), 7.38 (d, J = 7.3 Hz, 2H). EA, CHN for **5**-**7**. **6** and **7** were single stereoisomers in terms of prochiral face recognition of propylene and styrene, respectively, even in solutions on the basis of NMR. The coordinated olefins of **5**, **6**, and **7** do not dissociate. The coordination of the *si*-face of styrene on **6** was confirmed by single-crystal X-ray analysis, which will be reported in near future.

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12 A solution of **1** (200 mg, 0.40 mmol) and **8** (70 mg, 0.48 mmol) in $Cl(CH_2)_2Cl$ (20 mL) was heated at 60 °C for 4 h; tlc: Rf =0.36 (EtOAc:MeOH = 20:1). After concentration, the mixture was charged into SiO_2 column at 0 °C with CH_2Cl_2:MeOH (30:1) as eluent. The dark purple band was collected to give purple solids of **9** (222 mg, 0.37 mmol) in 92%: dec. 185-190 °C; ^1H NMR (270 MHz, $CDCl_3$, TMS):δ 0.62 (d, J = 6.8 Hz, 6H), 0.92 (d, J = 6.8 Hz, 6H), 2.45 (m, 2H), 3.96 (s, 6H), 4.40 (m, 2H), 4.81 (t, J = 7.8 Hz, 2H), 4.95 (t, J = 7.8 Hz, 2H), 7.96 (d, J = 7.8 Hz, 2H), 8.18 (t, J =7.8 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS): 14.44, 19.17, 27.43, 51.32, 70.93, 72.31, 123.1, 139.28, 141.8, 160.9, 182.3, 296.1; EA, $C_{22}H_{29}N_3O_6Cl_2Ru$: Found C 43.67, H 4.88, N 7.03%; Calcd C 43.79, H 4.84, N 6.96%.

13 Crystal data of **9**: $C_{22}H_{29}N_3O_6Cl_2Ru$, orthorhombic, space group $P2_12_12_1$ (#19), a = 16.472(2), b = 17.220(3), c = 9.112(4) Å, V = 2581(1) $Å^3$, D_c = 1.551 gcm^{-3}, Z = 4, μ = 8.54 cm^{-1}. The intensity data ($2\theta < 50°$) were collected on a Rigaku AFC-7R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) and the structure was solved by heavy-atom Patterson methods (DIRDIF92PATTY). The final cycle of refinement was based on 3109 observed reflection ($I > 3\sigma(I)$) and 423 variable parameters and converged with R = 5.3% and R_W = 4.8%. The selected bond distances (Å) and angles (deg): Ru(1)-C(18) 1.880(7), C(18)-C(19) 1.499(9), C(18)-C(21) 1.49(10), N(2)-Ru(1)-N(3) 150.7(2), Ru(1)-C(18)-C(19) 121.5(5), Ru(1)-C(18)-C(21) 124.0(5), Cl(1)-Ru(1)-C(18)-C(19) -10.2(5), Cl(2)-Ru(1)-C(18)-C(21) -12.7(6).

14 **13**: dark brown solid, decomp. 191-193 °C; ^{13}C NMR, 331.6 ppm for Ru=*C*. **14**: red brown solid, decomp. 265-268 °C; ^{13}C NMR, 271.0 ppm for Os=*C*.