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A Ruthenium Olefin Metathesis Catalyst with a Four-Membered N-Heterocyclic Carbene Ligand

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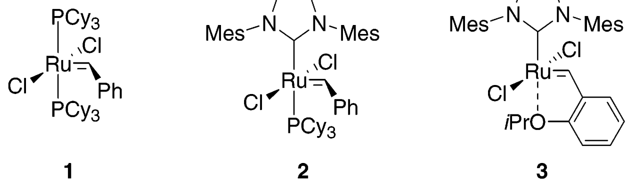
*Summary: The first ruthenium olefin metathesis catalyst bearing a four-membered N-heterocyclic carbene (**5**) was synthesized and characterized by NMR spectroscopy and X-ray crystallography. The synthesis of a (carbene)-carbonylrhodium complex (**6**) was also reported, allowing the study of the electronic properties of this new carbene ligand. The complex **5** was screened toward different olefin metathesis reactions, and it showed a slow reactivity.*

Olefin metathesis reactions are useful tools for the formation of C−C bonds in organic synthesis.[1] In the past decade, numerous well-defined metathesis catalysts have been prepared and studied;[2] of these, the Ru-based complex **1**[3] shows the highest level of functional group and environmental tolerance (Chart 1). Dramatic improvements in activity were observed with complexes **2**[4] and **3**,[5] using a five-membered N-heterocyclic carbene (NHC) as ligand, due to their better σ-donor ability compared to that of a phosphine.[6] Since then, numerous five-membered NHC ligands with different substituents have been studied.[7] Additional investigations of diaminocarbenes have shown that a slight change in their framework can generate different steric and electronic properties.[8] Therefore, we set out to study the impact of architectural modifications of the NHC ligand on the activity of the Ru-based catalyst. Our group recently reported the first six-membered NHC Ru-based catalyst,[9] which was found to have a lower activity for olefin metathesis compared to **2**, due to increased steric hindrance. Here, we report the preparation of the first Ru complex (**5**) featuring a four-membered N-heterocyclic carbene ligand and its olefin metathesis activity.

Chart 1. Olefin Metathesis Catalysts



Complex **5** was prepared in 30% isolated yield by reacting the carbene generated in situ, by deprotonation of the iminium salt **4**[10] with KHMDS, with (PPh$_3$)Cl$_2$Ru=CH-*o*-O-*i*-PrC$_6$H$_5$[11] at 60 °C overnight (Scheme 1). Complex **5** was isolated as an air-stable brown solid and characterized via NMR spectroscopy. Although the benzylidene protons Hα in **3** and **5** appear in the same region (δ(Hα_3) 16.56 ppm, δ(Hα_5) 16.69 ppm) the carbene carbon Cα is more shielded in **5** (δ(Cα_5) 287.2 ppm) than in **3** (δ(Cα_3) 296.8 ppm).[5] For the four-membered NHC ligand, the ^{13}C signal for C$_{\text{carbene}}$ (δ(C$_{\text{NCN}}$) 237.5 ppm) is more downfield than in the case of complex **3** (δ(C$_{\text{NCN}}$) 211.1 ppm).

Single crystals of catalyst **5** suitable for X-ray analysis were obtained by cooling a dichloromethane−pentane solution at −20 °C (Figure 1).[12a] The aryl groups on the four-membered NHC ligand in **5** are nonsymmetric (C1−N1−C2 = 135.3° and C1−N2−C14 = 127.0°); they bend less toward the chloride−benzylidene plane than in complex **3** (C1−N(1,2)−C$_{\text{mesityl}}$ = 127°).[5] The N−C1 bond lengths are longer (C1−N = 1.386−1.401 Å) than in **3** (C−N$_{\text{complex 3}}$ = 1.351−1.350 Å), and the geometry around the nitrogen atoms is not strictly planar (sums of the bond angles for the two nitrogen atoms on complex **5**: 357.2 and 347.8°). These crystallographic

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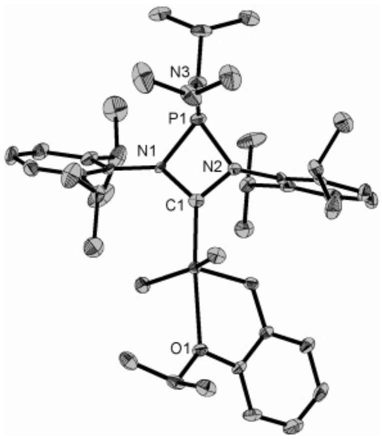
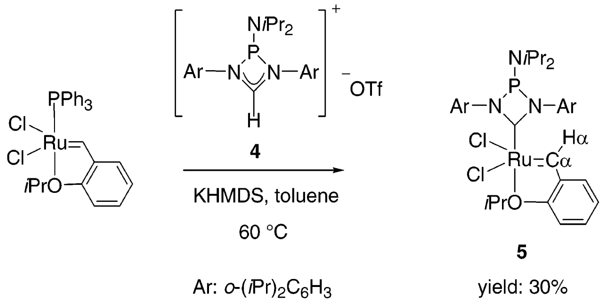


Figure 1. Thermal ellipsoid diagram of **5** (50% probability). Selected bond distances (Å) and angles (deg): Ru1−C1 = 1.921(4), Ru1−O1 = 2.360(3), Ru1−C32 = 1.832(4), C1−N1 = 1.386(4), C1−N2 = 1.401(5); C1−N2−C2 = 135.3(3), C1−N2−C14 = 127.0(3), Cl1−Ru1−Cl2 = 154.77(4).

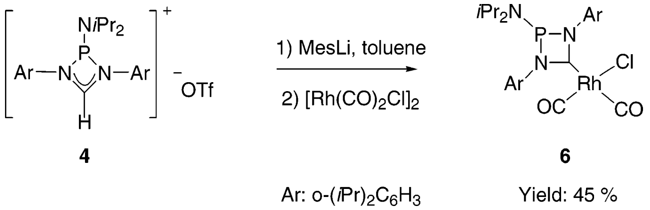
Scheme 1. Synthesis of Complex 5



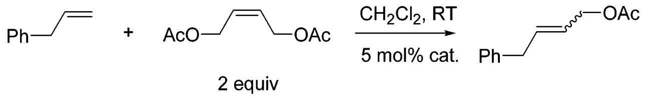
data signify diminished p_π overlap between the carbene carbon and the adjacent nitrogen atoms. Two additional notable features are: a shorter Ru1−C1 bond (1.921(4) Å vs 1.981(5) Å for **3**) and a longer Ru1−O1 bond (2.360(3) Å vs 2.261(3) Å for **3**).[13]

To study the electronic properties of the four-membered NHC, a carbene carbonyl complex was prepared for comparison of the stretching frequencies of its carbonyl ligands to related complexes.[8b,14] Thus, the rhodium complex **6** was obtained by first generating the carbene in situ and then reacting it with the chlorodicarbonylrhodium(I) dimer at ambient temperature (Scheme 2). In the product, the ^{13}C NMR signal for $C_{carbene}$ appears at 218.6 ppm as a doublet of doublets due to coupling with the rhodium and phosphorus atoms ($^1J_{CRh}$ = 60 Hz and $^2J_{CP}$ = 11 Hz). IR spectroscopy of **6** carried out in toluene reveals two CO-stretching vibrations of similar intensity at 2081 and 1994 cm^{-1}. The values of ν(CO) indicate that the four-membered NHC ligand is a slightly less effective σ-donor than the dihydroimidazol-2-ylidene analogue (in toluene, ν(CO) 2080 and 1988 cm^{-1}), presumably due to the more bent carbene angle.[15]

Scheme 2. Synthesis of Complex 6



Scheme 3. CM of Allylbenzene and *cis*-1,4-Diacetoxy-2-butene Using Catalysts 2, 3, and 5



The catalytic activity of the new complex **5** was first explored in the cross-metathesis (CM) of allylbenzene with *cis*-1,4-diacetoxy-2-butene (Scheme 3). The reaction was carried out in dichloromethane at ambient temperature. The conversion[16] afforded by **5** (73%) is comparable to those obtained with complexes **2** (79%) and **3** (72%). However, a longer reaction time was required for our system to reach this point (35 h vs <30 min for **2** and **3**).

A similar trend is observed in the ring-closing metathesis (RCM) of diallyldiethyl malonate at 40 °C in dichloromethane.[4a,17] With **5**, the reaction reached completion within 20 min, whereas less than 10 min is necessary for complexes **2** and **3**.

Catalytic studies on the ring-opening polymerization (ROMP) of *cis*,*cis*-cycloocta-1,5-diene (COD) were also carried out (Table 1). Interestingly, with a monomer to catalyst ratio of 10 000:1, complex **5** afforded only oligomers at 25 °C after 24 h. However, at 55 °C polymer formation was observed for the neat species or in solution. According to this result, it appears that high temperatures are required for the complex **5** to promote the ROMP of COD.

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(12) (a) Crystal data for **5**: $C_{41}H_{60}N_3OPCl_2Ru$, M_r = 813.86, monoclinic, space group $P2_1/c$, a = 11.4195(10) Å, b = 10.9180(10) Å, c = 33.145(3) Å, β = 92.410(2)°, V = 4128.7(6) Å^3, Z = 4, μ(Mo Kα) = 0.710 73 Å, crystal size 0.22 × 0.10 × 0.07 mm^3, 34 715 reflections collected (9467 independent, R_{int} = 0.1018), 456 parameters, R1($I > 2\sigma(I)$) = 0.0554, wR2(all data) = 0.0959. (b) Crystal data for the analogue of **3**: $C_{37}H_{50}N_2OCl_2Ru$, M_r = 710.76, triclinic, space group $P\bar{1}$, a = 8.4906(13) Å, b = 19.887(3) Å, c = 22.986(3) Å, α = 111.210(2)°, β = 92.410(2)°, γ = 99.400(2)°, V = 3483.1(9) Å^3, Z = 4, μ(Mo Kα) = 0.710 73 Å, crystal size 0.32 × 0.11 × 0.04 mm^3, 30 040 reflections collected (15 113 independent, R_{int} = 0.0385), 775 parameters, R1($I > 2\sigma(I)$) = 0.0578, wR2(all data) = 0.1382. Data were collected at 100(2) K on a Bruker SMART 1000 diffractometer. The structures were solved by direct methods (SHELXS-97)[19] and refined using the least-squares method on F^2.[20] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 243404 (**5**) and 247037 (analogue of **3**).

(13) The X-ray structure analysis of the analogue of complex **3**,[21] featuring isopropyl goups at the ortho positions of each aryl substituent, was carried out for a better comparison (see the Supporting Information).[12b] Two different molecules are present in the unit cell; their Ru−O and Ru−$C_{carbene}$ bonds are in the same range as those in complex **3** (Ru−O = 2.229−2.248 Å and Ru−$C_{carbene}$ = 1.982−1.974 Å).

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(17) Conditions: 5 mol % catalyst, [diene] = 0.05 M, solvent CD_2Cl_2, T = 40 °C. Conversion is determined by ^{1}H NMR.

(18) In comparison with complex **2**, a smaller PDI was obtained when the reaction was run neat. This can be attributed to a slower gelling process (complex **2**, 30 min; complex **5**, 6 h) that favors better diffusion inside the sample.

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Table 1. ROMP of COD

catalyst	*T* (°C)	M:C[a]	concn (M)	M_n[b]	PDI[b]
2[4d]	25	10 000:1	neat	92 900	2.5
5	25	10 000:1	neat	oligomer	
5	55	10 000:1	neat	48 740	1.6[18]
2	55	1000:1	2	30 910	1.8
5	55	1000:1	2	27 530	1.9

[a] Initial monomer/catalyst ratio. [b] Determined by THF GPC, and results are reported relative to the poly(styrene) standards.

This report describes the synthesis of the first ruthenium complex bearing a four-membered NHC ligand, **5**, and compares its olefin metathesis activity to that of the imidazolylidene ruthenium catalysts **2** and **3**. Catalyst **5** appears to be slower than **2** or **3**. Further studies on the coordination properties of the four-membered NHC ligand are in progress in order to better understand this difference in activity.

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Supporting Information Available: Text giving detailed synthetic procedures for the compounds in this paper and tables and figures giving crystallographic data and additional views of the structures of **5** and the analogue of complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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