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Diastereotopic relationship between planar and central chiralities in the formation of $Ru(\eta^3-allyl)(CO)(PPh_3)(L-L')$ complexes

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Abstract

Hydride ruthenium complexes, RuHCl(CO)(PPh₃)₂(L-L') **3** (L-L' = bidentate ligand having nitrogen and oxygen) react with allenes to give Ru(η^3 -allyl)(CO)(PPh₃)(L-L') complexes **5** in good yields *via* hydrometalation reaction. The complexes **5** have planar chirality at the η^3 -allyl ligand and central chirality at the Ru metal, and consist of one pair of enantiomers. Ligand substitution reaction of Ru(η^3 -allyl)Cl(CO)(PPh₃)₂ complexes **6** with bidentate ligands (L-L') also afford the complexes **5** which have the same stereochemistry as those formed by the hydrometalation reaction. The planar chirality is controlled by the central chirality at the Ru metal in both the formations of the complexes **5**. The structure of **5a** (L-L' = N-N bidentate ligand) was determined by the X-ray crystal structure analysis.

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Keywords: n³-Allyl ruthenium complex; Hydrometalation; Ligand substitution; Diastereotopic relation; Planar and central chiralities

1. Introduction

Planar chiral organometallic complexes have attracted much attention due to their potential as effective asymmetric catalysts [1]. Among these planar chiral complexes, many η^3 -allyl transition metal complexes of iron [2], palladium [3] and molybdenum [4] have been demonstrated as excellent allylation reagents in asymmetric organic transformations. With respect to ruthenium complexes, only one planar chiral η^3 -allyl complex has been reported [5], although the corresponding planar chiral η^5 -cyclopentadienyl complexes have been widely investigated [6]. One of the useful methods to prepare the planar chiral η^3 -allyl complexes is asymmetric coordination of allylic reagents to metals which is induced by central chirality at the metals and also chirality of the auxiliary ligands. Asymmetric induction by a chiral center at the metal to the η^3 -allyl ligand is expected to be particularly effective because of the proximity between the metal and the η^3 -allyl ligand.

We have recently found that RuHCl(CO)(PPh₃)₃ reacted with allenes to give η^3 -allyl complexes Ru(η^3 -allyl)(CO)(Cl)(PPh₃)₂ which further undergoes the ligand substitution of the Cl and PPh₃ ligands with bidentate ligand (L–L') to afford $Ru(\eta^3-allyl)(CO)(PPh_3)(L-L')$ complexes. The complexes $Ru(\eta^3-allyl)(CO)(PPh_3)(L-$ L') have both planar chirality at the η^3 -allyl ligand and central chirality at the metal. Further, the complexes have also been prepared by hydrometalation reaction of $RuH(CO)(PPh_3)_2(L-L')$ with allenes. A remarkable correlation is observed for the chirality at the metal center and the η^3 -allyl ligand between these formation reactions of $Ru(\eta^3-allyl)(CO)(PPh_3)(L-L')$ complexes. In this communication, we report the formation and structure of the $Ru(\eta^3-allyl)(CO)(PPh_3)(L-L')$ complexes, and discuss diastereotopic relationship between the planar and central chiralities.

The reaction of RuHCl(CO)(PPh₃)₃ 1 with N–N bidentate ligand 2a in the presence of KOH gave hydride ruthenium complex 3a in 83% yield as air and moisture stable yellow solids (Scheme 1). The structure

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of **3a** was determined by the spectral charactaristics.¹ The complex **3b** was similarly prepared, while the complex **3c** was synthesized according to the literature procedure [7].

Hydrometalation of the complexes 3 with allenes 4 afforded η^3 -allyl ruthenium complexes 5¹ in good yields, which consisted of only one pair of enantiomers (R_{allyl} , S_{Ru})-5 and (S_{allyl} , R_{Ru})-5 among the four possible diastereomers (Scheme 2, Table 1). ¹H NMR signals of the allylic protons of 5 showed that the two enantiomers were formed. VT-¹H NMR observation of the complex



Fig. 1. Molecular structure of **5a**. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–C(2) 1.404(5), C(2)–C(3) 1.405(5), Ru–C(1) 2.277(3), Ru–C(2) 2.199(3), Ru–C(3) 2.209(4), Ru–C(4) 1.848(4), Ru–P 2.365(4), Ru–N(1) 2.137(3), Ru–N(2) 2.159(3), C(1)–C(2)–C(3) 122.4(4), N(1)–Ru–C(4) 175.6(1), N(1)–Ru–N(2) 77.1(1), N(2)–Ru–P 93.35(8).

5a revealed that no isomerization occurs between the diastereomers at 90 °C in C_6D_6 .

The molecular structure of **5a** is unambiguously determined by X-ray crystal structure analysis, as illustrated in Fig. 1. ² Complex **5a** has a trigonal bipyramidal structure where the anionic nitrogen and carbonyl ligands are located at the apical position, whereas PPh₃, imine nitrogen and η^3 -allyl ligands are at the equatorial positions. The phenyl group on the η^3 -allyl ligand is situated *away* from PPh₃ ligand. It should be noted that **5a** possesses both planar and central chiralities.

A plausible mechanism for the formation of **5** is shown in Scheme 3. Hydrometalation of **4** with the hydride complex **3** affords σ -allyl complex **7** which is then converted to **5** via face-selective π -complexation. Path B is disfavored probably owing to the steric replusion between the η^3 -allyl and PPh₃ ligands. In fact, the complex (R_{allyl} , S_{Ru})-**5** and its enantiomer were produced with no formation of diastereomer (S_{allyl} , S_{Ru})-**5** or (R_{allyl} , R_{Ru})-**5**.

Ligand substitution reaction of $Ru(\eta^3-allyl)(CO)(Cl)$ (PPh₃)₂ complex **6** with bidentate ligand **2** was carried out (Scheme 4, Table 2).

Complex **6a** was synthesized from hydrometalation of the complex **1** with phenylallene **4a** in 90% yield [8].

Selected data. For 3a: m.p. 203-205 °C (dec.), IR (KBr) 1997 (Ru-H), 1908 (CO), 1561 (C=N) cm⁻¹, ¹H NMR (270 MHz, CDCl₃) δ 7.38-7.08 (m, 32H, N=CH, pyrrole and Ar), 6.78-6.71 (m, 5H, Ar), 6.53 (d, 1H, $J_{\rm HH} = 3.6$ Hz, pyrrole), 6.12 (d, 1H, $J_{\rm HH} = 3.6$ Hz, pyrrole), -10.83 (t, 1H, $J_{PH} = 19.6$ Hz, Ru–H), ${}^{31}P{}^{1}H$ NMR (200 MHz, CDCl₃) δ 45.4 (s) ppm. For 5a: m.p. 199-202 °C (dec.), IR (NaCl) 1932 (CO), 1567 (C=N) cm⁻¹, ¹H NMR (270 MHz, C₆D₆) δ 7.64-6.81 (m, 25H, N=CH and Ar), 6.40-6.38 (m, 1H, Ar), 6.14 (br s, 1H, Ar), 6.14–6.11 (m, 2H, Ar), 5.81–5.70 (m, 1H, =CH), 3.40 (dd, 1H, $J_{\text{PH}} = 6.6, J_{\text{HH}} = 11.9 \text{ Hz}, = \text{CH}$), 2.98 (d, 1H, $J_{\text{HH}} = 6.9 \text{ Hz}, = \text{CH}$), 1.83 (d, 1H, $J_{\text{HH}} = 11.5 \text{ Hz}$, =CH), ³¹P{¹H} NMR (200 MHz, CDCl₃) δ 44.6 (s) ppm; for 5e: m.p. 172–174 °C (dec.), IR (NaCl) 1929 (CO), 1584, 1516, 1434, 1399 cm⁻¹, ¹H NMR (270 MHz, C_6D_6) δ 7.39–6.48 (m, 20H, Ar), 5.34 (m, 1H, =CH), 4.49 (s, 1H, acac-H), 3.24 (dd, 1H, $J_{\text{PH}} = 7.0, J_{\text{HH}} = 11.9 \text{ Hz}, = \text{CH}), 2.30 \text{ (d, 1H, } J = 7.0 \text{ Hz}, = \text{CH}), 1.44$ (d, 1H, J = 11.2 Hz, =CH), 1.08 (s, 3H, CH₃), 0.89 (s, 3H, CH₃) ppm, Anal. found (calcd) for C₃₃H₃₁O₃PRu · 0.5H₂O: C, 64.14 (64.28); H, 5.20 (5.23). For 9: m.p. 143-145 °C (dec.), IR (KBr) 1985 (Ru-H), 1908 (CO), 1577 (N=C) cm⁻¹, ¹H NMR (270 MHz, CDCl₃) δ 7.45– 7.24 (m, 30H, Ar and N=CH), 7.12-6.99 (m, 3H, Ar), 6.68 (m, 1H, pyrrole), 6.59 (m, 1H, pyrrole), 6.38 (m, 1H, pyrrole), 5.95-5.90 (m, 3H, Ar), 3.59 (q, 1H, $J_{HH} = 6.6$ Hz, CHMePh), 1.12 (d, 3H, $J_{HH} = 6.6$ Hz, CH₃), -11.12 (t, 1H, J_{PH} = 18.0 Hz, Ru-H) ppm. For 10: m.p. 118-122 °C, IR (NaCl) 1923 (CO), 1580 (N=C) cm⁻¹, ¹H NMR of allyl and pheylethyl groups (270 MHz, $CDCl_3$), major product: δ 5.73– 5.62 (m, 1H, CH=), 4.27 (q, 1H, $J_{\rm HH}$ = 6.6 Hz, CHMePh), 2.89 (d, 1H, $J_{\rm HH} = 7.6$ Hz, CH=), 2.81 (dd, 1H, $J_{\rm HH} = 6.3$, $J_{\rm PH} = 12.2$ Hz, CH=), 1.53–1.50 (m, 1H, CH=), 0.82 (d, 3H, $J_{\rm HH} = 6.6$ Hz, CH₃), minor product: δ 5.73–5.62 (m, 1H, CH=), 4.16 (q, 1H, $J_{\rm HH} = 7.3$ Hz, CHMePh), 3.09 (d, 1H, $J_{HH} = 7.3$ Hz, CH=), 2.66 (dd, 1H, $J_{HH} = 6.3$, $J_{\rm PH} = 11.9$ Hz, CH=), 1.50–1.45 (m, 1H, CH=), 0.70 (d, 3H, $J_{\rm HH} = 7.3$ Hz, CH₃) ppm.

² Crystallographic data for **5a**: C₃₉H₃₃ON₂RuP, *F.W.* = 677.75, triclinic, *P*-1(# 2), *a* = 9.5995(4) Å, *b* = 10.5294(4) Å, *c* = 16.0483(9) Å, *α* = 80.340(2)°, *β* = 83.113(2)°, *γ* = 83.313(1)°, *V* = 1589.7(1) 3, *Z* = 2, *D*_{calc} = 1.416 g/cm³. The intensity data were collected at 23 °C on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. The 14,249 independent reflections were measured over a 2*θ* range of 6.0–55.0°. All non-hydrogen atoms were refined anisotropically. Full matrix least-squares refinement using 6260 reflections converged to final agreement factors $R_1[I > 3\sigma(I)] =$ 0.040, $wR_2[I > 3\sigma(I)] = 0.089$ with GOF = 1.02. The structure was solved by direct methods using SIR92 and refined by full-matrix least squares on *F*. Drawings were generated using ORTEP-III (Burnett & Jhonson, 1996).

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Run	Complex 3	Allene 4	R	Temp/°C	Complex 5	Yield (%) ^a
1	3a	4a	Ph	65	5a	93
2	3a	4b	Tolyl	65	5b	80
3	3a	4c	p - t BuC ₆ H ₄	65	5c	52
4	3b	4a	Ph	40	5d	61
5	3c	4 a	Ph	40	5e	73

 Table 1

 Hydrometalation of the complexes 3 with allenes 4

^a Isolated yield.



Table 2Ligand substitution of the complexes 6 with ligands 2

Run	Complex 6	R	Ligand 2	Complex 5	Yield (%) ^a
1	6a	Ph	2a	5a	67
2	6b	Tolyl	2a	5b	90
3	6a	Ph	2b	5d	54
4	6a	Ph	2c	5e	52

^a Isolated yield.



Scheme 3.



The reaction of the complex **6a** with N–N bidentate ligand **2a** in the presence of K₂CO₃ in DMF at 100 °C gave the complex **5a** in 67% yield. The configuration of the complex was same as that of the complex obtained from the above hydrometalation reaction. The reaction proceeded *via* selective ligand substitution which is probably controlled by the planar chirality of the η^3 allyl ligand to give a pair of enantiomers. Reaction of the complex **6a** with the bidentate ligands **2b** and acetylacetone **2c** also provided the corresponding η^3 -allyl ruthenium complexes **5d** (54%) and **5e** (52%), respectively.

The above results indicate the distinct correlation of the central chirality at the metal with the planar chirality of the η^3 -allyl ligand in the formation of **5**. That is to say, central chirality S_{Ru} at the metal absolutely can control the chirality of η^3 -allyl ligand to R_{allyl} and vice versa.

If optically active bidentate ligand (L-L') is used, stereocontrolled chiral Ru center is expected to be produced. Chiral hydride complex 9 was prepared from complex 1 and optically active N-N bidentate ligand 8. Treatment of the complex 9 with phenylallene 4a in CHCl₃ at 50 °C resulted in the formation of a diastereomeric mixture of η^3 -allyl ruthenium complex **10** in 37% yield. ¹H NMR spectrum revealed the de of 16%. Now, it is not clear which the major product is. Therefore, it was found that the chirality of the auxiliary ligand is transfered to the planar chirality at the η^3 -allyl ligand through the central chirality at the Ru metal (see Scheme 5).

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