Configurationally stable metal-centered chirality: stereospecific and regioselective rhodaacylation of alkynes controlled by the third generation of the [Cp′-P]H ligand

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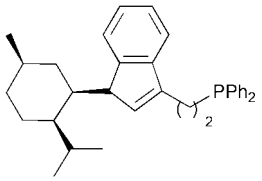
The rhodium cationic complex [[η⁵:η¹-{3-(NIM)Ind-P}$_{n=2}$]Rh(CO)Me]BF_4 (1) reacts with 1-phenylpropyne regioselectively and stereospecifically to afford the alkenyl complex [[η⁵:η¹-{3-(NIM)Ind-P}$_{n=2}$]Rh{η²-O=C(CH_3)-C(CH_3)=CPh}]BF_4 (2).

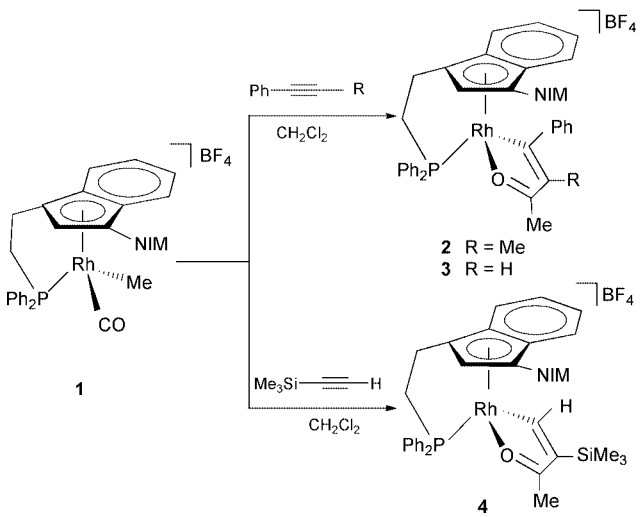
The design and synthesis of novel chiral transition-metal complexes having a stereogenic metal center provide an elegant and powerful method for stoichiometric or catalytic asymmetric transformations.[1–5] Nonetheless, chemistry using metal-centered chirality is much less developed than that using chiral auxiliaries or ligands.[6] In order to accomplish asymmetric reactions using metal-centered chirality, easy and convenient methods for the preparation of optically active complexes which are configurationally stable at the metal center should be supplied. Recently we have found that the third generation of



[{3-(NIM)Ind-P}$_{n=2}$] H

the [Cp′-P]H ligand, [{3-(NIM)Ind-P}$_{n=2}$]H was effective for controlling the central metal chirality in the oxidative addition of alkyl halide to the Rh carbonyl complex, compared to the first and the second generation of the [Cp′-P]H ligand.[7,8] Thus, oxidative addition using metal complexes with the third generation of the Cp′-P ligand could become a new preparation of an optically active complex having a metal-centered chirality. In order to use the chiral complex as an asymmetric catalyst, racemization or epimerization at the metal center must be prevented. Herein we show that the metal-centered chirality controlled by the {3-(NIM)Ind-P}$_{n=2}$ ligand[9] is configurationally stable, which causes the stereospecific and regioselective addition of alkynes to its cationic Rh complex.

The cationic rhodium complex, [[η⁵:η¹-{3-(NIM)Ind-P}$_{n=2}$]Rh(CO)Me]BF_4 (**1**), which was readily prepared from [η⁵:η¹-{3-(NIM)Ind-P}$_{n=2}$]RhI(COMe) and $AgBF_4$,[8] is a mixture of two diastereomers (major : minor = 96 : 4, 92% de).† Reaction of complex **1** with 1-phenylpropyne in CH_2Cl_2 at room temperature for 48 h afforded the alkenyl complex **2** in 79% isolated yield (Scheme 1).‡ From the ^1H or ^{31}P NMR of the reaction mixture, **2** was found to contain only two isomers (major : minor = 96 : 4). The structure of **2**-major was confirmed by the usual spectroscopic methods as well as X-ray crystallography (Fig. 1).§ The stereochemistry around the Rh is *S*, and the planar chirality is *R*. Complex **2** was produced through migratory insertion of CO into the Rh–Me bond in **1**[10] and the subsequent rhodaacylation of the alkyne,[11] followed by intramolecular coordination of the acyl oxygen to the Rh. Since four isomers from each diastereomer of **1**, based on the difference in the metal-centered chirality and the regiochemistry of the olefin, are possible, this transformation totally has the potential for the formation of the eight isomers. The results, however, indicated that only one isomer was produced from each diastereomer of **1**; the isomer ratio of **2** was the same as that of the starting complex **1**.† Thus, the metal-centered chirality did



Scheme 1

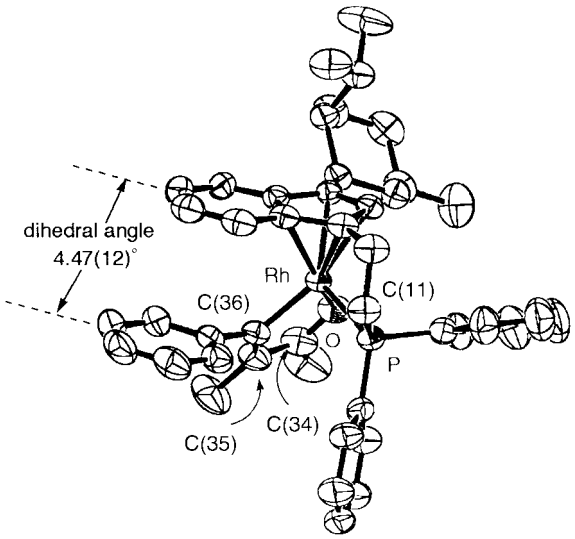


Fig. 1 ORTEP drawing of the X-ray crystal structure of the cationic part of **2**-major. Selected bond lengths (Å) and angles (°): Rh–O 2.0719(15), Rh–P 2.2690(6), Rh–C(36) 2.023(2), C(36)–C(35) 1.362(3), C(34)–C(35) 1.428(4), O–C(34) 1,258(3); Rh–O–C(34) 114.79(17), Rh–C(36)–C(35) 115.13(19), Rh–P–C(11) 105.86(12), O–C(34)–C(35) 118.5(2), C(36)–Rh–O 77.98(8), C(34)–C(35)–C(36) 113.5(2). The shortest interatomic distance between the indenyl group and the phenyl ring is 3.278(4) Å.

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not racemize or epimerize throughout these transformations and the regiochemistry of the olefinic part was completely controlled.

The mixed ligand complex containing both an indenyl and a tertiary phosphine ligand which are not connected by a spacer, $[Rh(\eta^5\text{-}C_9H_7)(PPh_3)(CO)Me]BF_4$, did not react with 1-phenylpropyne at room temperature. Although the cationic complex having the second generation Cp′-P ligand, $[[\eta^5:\eta^1\text{-}(Ind\text{-}P)_{n=2}]Rh(CO)Me]BF_4$, with 46% de (major : minor = 73 : 27) also reacted with 1-phenylpropyne under the same conditions, the corresponding alkenyl complexes comprised four diastereomers (69 : 24 : 5 : 1).† The third generation of the [Cp′-P]H ligand was much more effective for controlling the stereochemistry in this rhodaacylation.

Reaction of **1** (92% de) with phenyl acetylene in CH_2Cl_2 at room temperature for 12 h gave the corresponding alkenyl complex **3** with 92% de (Scheme 1).† The diastereomer excess of **3** was also almost the same as that of **1**. This reaction also proceeded stereospecifically. ^{1}H NMR of **3** showed a doublet with a small coupling constant (J = 1.4 Hz) at δ 6.21 for the olefinic proton and the HMQC spectrum showed that the proton was correlated to the β-olefinic carbon from Rh. Reaction of complex **1** (92% de) with trimethylsilylacetylene under the same conditions afforded the alkenyl complex **4** with 91% de (Scheme 1).†¶ This reaction also proceeded stereospecifically, but the opposite regioisomer to the product of the reaction with phenylacetylene was obtained. The structure of **4**-major was confirmed by the usual spectroscopic methods as well as X-ray crystallography. ^{1}H NMR revealed a doublet of doublets at δ 9.06 (J = 11.8 and 1.6 Hz) for the olefinic proton originating from the terminal acetylenic hydrogen. When trimethylsilylacetylene was used, the bulkier indenyl Rh moiety would attack the less hindered acetylenic terminal carbon selectively in the rhodaacylation process. In contrast, in the rhodaacylation of 1-phenylpropyne or phenylacetylene, the Rh–carbon bond was formed at the more hindered site.[12]

We are currently investigating application of the reaction to the stereoselective synthesis of general substituted olefins using a catalytic amount of a rhodium complex containing the Cp′-P ligand. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan, and General Sekiyu Research & Development Encouragement & Assistance Foundation.

Notes and references

† The isomer ratio was determined by ^{31}P NMR of the crude product obtained after removal of the solvents from the reaction mixture.

‡ *Preparation* of **2**: to a solution of **1** (20 mg, 0.028 mmol, 92% de) in CH_2Cl_2 (5 mL) was added 1-phenylpropyne (4 μL, 0.032 mmol) at room temperature. The reaction mixture was stirred for 48 h and then the solvent was removed *in vacuo* to give orange powders, which contained a diastereomeric mixture of **2**. The ratio was determined by ^{31}P NMR (major : minor = 94 : 6, 92% de). After washing with Et_2O (10 mL) and hexane (2 × 10 mL), recrystallization of the crude product from CH_2Cl_2 and Et_2O afforded **2** (18 mg, 0.022 mmol, 79%, major : minor = 94 : 6, 92% de) as analytically pure orange powders, mp 118–122 °C (dec.). δ_H ($CDCl_3$, major) 0.37 (d, J = 6.3 Hz, 3 H), 0.86 (d, J = 6.6 Hz, 3 H), 1.15 (d, J = 6.0 Hz, 3 H), 1.42 (d, J = 1.6 Hz, 3 H), 1.48–1.89 (m, 6 H), 1.92–2.10 (m, 2 H), 2.38 (d, J = 2.2 Hz, 3 H), 2.30–2.53 (m, 2 H), 2.69–2.98 (m, 2 H), 3.82–3.99 (m, 1 H), 4.05–4.23 (m, 1 H), 5.39 (s, 1 H), 6.15 (dd, J = 8.2, 1.1 Hz, 2 H), 6.29–6.38 (m, 1 H), 6.40–6.48 (m, 1 H), 6.83–6.93 (m, 1 H), 6.99–7.09 (m, 1 H), 7.16–7.41 (m, 8 H), 7.46–7.61 (m, 3 H) and 7.87–7.99 (m, 2 H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ 55.1 (d, $J_{P–Rh}$ = 179 Hz, major) and 62.0 (d, $J_{P–Rh}$ = 181 Hz, minor). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 232.2 (dd, J = 26, 12 Hz, *C*=C(Ph), major). IR (KBr, Nujol, cm^{-1}) 1544, 1261, 1058, 727, 694 and 522. MS (FAB) *m/z* 727 ($M^+ - BF_4$, cationic part of **2**). Anal. Found: C, 64.92; H, 6.10%. Calcd. for $C_{44}H_{49}BF_4OPRh$: C, 64.88; H, 6.06%.

§ *Crystal data* for $C_{44}H_{49}BF_4OPRh$ **2**-major: M = 814.52, triclinic, a = 10.0645(14), b = 10.9349(13), c = 9.9598(13) Å, α = 108.124(9), β = 106.426(10), γ = 84.967(11)°, U = 999.2(2) Å^3, T = 296 K, space group $P\bar{1}$ (No. 1), Z = 1, μ(Mo-Kα) = 0.519 mm^{-1}, 18387 reflections measured, 17568 unique (R_{int} = 0.0099) which were used in all calculations. $R1$(all) = 0.0416, $R1$(obsd) = 0.0316 (> 2σ(I)), $wR2$(all) = 0.0875, $wR2$(obsd) = 0.0826 (> 2σ(I)). CCDC 182/1600. See http://www.rsc.org/suppdata/cc/b0/b001735n/ for crystallographic files in .cif format.

¶ Spectroscopic data for **4**: mp 155–157 °C (dec.). δ_H ($CDCl_3$, major) 0.29 (d, J = 0.8 Hz, 9 H), 0.49 (d, J = 6.3 Hz, 3 H), 0.89 (d, J = 6.9 Hz, 3 H), 1.02–1.21 (m, 1 H), 1.11 (d, J = 6.0 Hz, 3 H), 1.51–1.73 (m, 2 H), 1.64–1.89 (m, 3 H), 1.93–2.23 (m, 3 H), 2.28 (s, 3 H), 2.37–2.65 (m, 1 H), 2.98–3.28 (m, 2 H), 3.45–3.68 (m, 1 H), 3.86–4.06 (m, 1 H), 5.58 (s, 1 H), 7.01–7.15 (m, 3 H), 7.31–7.42 (m, 4 H), 7.48–7.65 (m, 4 H), 7.67–7.78 (m, 3 H) and 9.06 (dd, J = 11.8, 1.6 Hz, 1 H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ 63.7 (d, $J_{P–Rh}$ = 184 Hz, major) and 64.0 (d, $J_{P–Rh}$ = 179 Hz, minor). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 232.8 (dd, J = 28, 15 Hz, *C*(H)=CSi(CH$_3$)$_3$, major). IR (KBr, Nujol, cm^{-1}) 3098, 3060, 1526, 1309, 1251, 1063, 845, 755, 709, 694 and 521. MS (FAB) *m/z* 709 ($M^+ - BF_4$, cationic part of **4**). Anal. Found: C, 60.45; H, 6.54%. Calcd. for $C_{40}H_{51}BF_4OPRhSi$: C, 60.31; H, 6.45%.

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12 Although DeShong *et al.* reported that regiochemistry in the insertion of an unsymmetrical alkyne into the Mn–carbon bond was controlled by the electronic character of the substituents of the alkyne,[13] we think that one of the reasons for the regioselectivity in the reaction of arylacetylenes could be the π–π stacking between the phenyl ring and the indenyl benzene ring. The presence of the π–π stacking could be also supported by the X-ray crystallographic analysis of **2**-major (Fig. 1).

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