Note

Synthesis, characterization, and catalytic application of a new chiral P,N-indene ligand derived from (R)-BINOL

Dominik Wechsler [a], Gabriele Schatte [b], Mark Stradiotto [a,*]

[a] Department of Chemistry, Dalhousie University, Halifax, NS, Canada B3H 4J3
[b] Saskatchewan Structural Sciences Centre, University of Saskatchewan, Saskatoon, SK, Canada S7N 5C9

ABSTRACT

Lithiation of 2-dimethylaminoindene followed by quenching with $[(R)$-$(1,1'$-binaphthalene-2,2'-diyl)]chlorophosphite and treatment with triethylamine afforded the crystallographically characterized enantiopure P,N-indene **3** in 71% isolated yield. In the course of rhodium coordination chemistry studies involving **3**, the formation of the isolable complex $[(\kappa^2$-P,N-**3**$)(\kappa^1$-P,N-**3**$)RhCl]$ (**7**) (81%) was observed, thereby confirming the propensity of this new ligand to form $L_nRh(\mathbf{3})_2$ complexes. Such coordination chemistry behavior may contribute in part to the generally poor catalytic performance exhibited by mixtures of **3** and rhodium precursor complexes in the asymmetric hydrogenation and hydrosilylation studies described herein.

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1. Introduction

Chiral platinum-group metal complexes are widely employed as catalysts in the synthesis of chiral, non-racemic molecules on both bench-top and industrial scales [1]. Notwithstanding the utility of enantiopure (often C_2-symmetric) P,P- and N,N-ligands in promoting such metal-mediated asymmetric transformations, related heterobidentate C_1-symmetric P,N-ligands that combine soft (P) and hard (N) donor fragments have in some cases been shown offer inroads to reactivity that cannot be accessed by use of homobidentate ligand systems [2]. Indeed, the successful application of heterobidentate chelates including the phosphinooxazoline (PHOX) family of ligands [3] has prompted the development of alternative classes of chiral P,N-ligands for use in promoting new and/or challenging metal-mediated asymmetric substrate transformations [2].

In this context we have demonstrated that P,N-substituted indenes including 1-P^iPr_2-2-NMe_2-indene (**1**; Scheme 1) can be employed in the synthesis of neutral, cationic, and formally zwitterionic κ^2-P,N platinum-group metal complexes that are of use as catalysts in the reduction of unsaturated substrates [4]. In seeking to advance this research, we became interested in developing chiral variants of **1**; given the well-established utility of enantiopure 1,1'-bi-2-naphthol (BINOL)-derived ligands including MonoPhos [5] in platinum-group metal catalysis, we identified chi-

ral P,N-substituted indenes prepared from (R)-BINOL (i.e. **2**, or alternatively the vinylic isomer **3**) as attractive targets of inquiry [6]. Herein we report on the synthesis and characterization of the new chiral indene ligand **3**, our efforts to develop the rhodium coordination chemistry of this ligand, and the application of **3** in rhodium-mediated asymmetric alkene hydrogenation and ketone hydrosilylation.
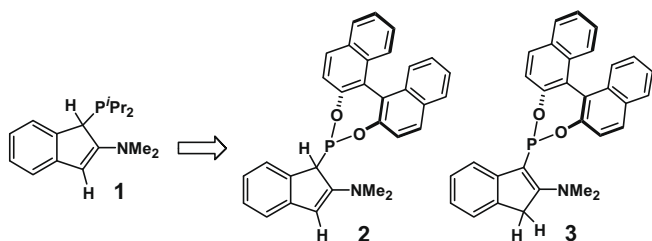
2. Experimental

2.1. General considerations

All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. 2-Dimethylaminoindene **4** [7] and $[(R)$-$(1,1'$-binaphthalene-2,2'-diyl)]chlorophosphite [8] were prepared by use of literature procedures and were dried in vacuo for 24 h prior to use. Otherwise, the purification and handling of reagents, as well as the rhodium-catalyzed alkene hydrogenation and ketone hydrosilylation experiments, were carried out by using published protocols [9]. ^1H, ^{13}C, and ^{31}P NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^1H and ^{13}C) or 85% H_3PO_4 in D_2O (for ^{31}P). ^1H and ^{13}C NMR chemical shift assignments are made on the basis of data obtained from ^{13}C DEPT, ^1H–^1H COSY,

* Corresponding author. Tel.: +1 902 494 7190; fax: +1 902 494 1310.
   E-mail address: mark.stradiotto@dal.ca (M. Stradiotto).

Scheme 1.

^1H–^{13}C HSQC, and ^1H–^{13}C HMBC NMR experiments. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada.

2.2. Synthesis of 3

A vial containing a magnetic stir bar was charged with **4** (0.14 g, 0.88 mmol) and 4 mL of toluene. The solution was cooled to −35 °C followed by the addition of n-BuLi (1.6 M in hexanes, pre-cooled to −35 °C, 0.55 mL, 0.88 mmol). The mixture was stirred for 1 h at ambient temperature. Meanwhile, a second vial was charged with [(R)-(1,1′-binaphthalene-2,2′-diyl)]chlorophosphite (0.31 g, 0.88 mmol) and 3 mL toluene. The solution of [(R)-(1,1′-binaphtha-lene-2,2′-diyl)]chlorophosphite was added dropwise to the solution of the indenyl lithium salt, followed by 2 h of stirring. Triethylamine (0.49 mL, 3.5 mmol) was then added to the reaction mixture, and the mixture was stirred overnight, during which time a significant quantity of solid **3** (including crystals suitable for X-ray diffraction analysis) precipitated out of solution. The mixture was then concentrated to near dryness and washed with benzene (2 mL). The remaining solid was then dried in vacuo yielding **3** as an analytically pure white solid (0.30 g, 0.63 mmol, 71%). Anal. Calc. for $C_{31}H_{24}PNO_2$: C, 78.63; H, 5.11; N, 2.96. Found: C, 78.40; H, 4.95; N, 2.51%. ^1H NMR (CD_2Cl_2): δ 8.07 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C–H Naph.), 8.02 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C–H Naph.), 7.91 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C–H Naph.), 7.73 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C–H Naph.), 7.59 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C–H Naph.), 7.55–7.45 (m, 4H, C–Hs Naph.), 7.39–7.31 (m, 2H, C–Hs Naph.), 7.22 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C–H Naph.), 7.11 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C7–H), 6.59 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5–H or C6–H), 6.10 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4–H), 6.02 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C6–H or C5–H), 3.63 (s, 2H, CH_2), 3.38 (d, $^5J_{PH}$ = 3.5 Hz, 6H, NMe_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 170.9 (d, $^2J_{PC}$ = 27.7 Hz, C2), 152.6 (quat Naph.), 151.6 (quat Naph.), 146.3 (C3a or C7a), 133.9 (C7a or C3a), 133.1 (quat Naph.), 133.0 (quat Naph.), 131.5 (quat Naph.), 131.1 (quat Naph.), 130.6 (C–H Naph.), 130.1 (C–H Naph.), 128.4 (C–H Naph.), 128.4 (C–H Naph.), 128.2 (C–H Naph.), 126.8 (C–H Naph.), 126.5 (C–H Naph.), 126.1 (C–H Naph.), 125.9 (C–H Naph.), 125.5 (C6 or C5), 124.7 (C–H Naph.), 124.3 (C–H Naph.), 123.0 (quat), 122.2 (C–H Naph.), 121.8 (C7), 121.5 (C4), 120.3 (C5 or C6), 70.6 (quat), 45.5 (d, $^4J_{PC}$ = 23.0 Hz, NMe_2), 41.1 (d, $^3J_{PC}$ = 4.4 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 197.4.

2.3. Formation and characterization of 5

A vial containing a magnetic stir bar was charged with **4** (0.40 g, 0.25 mmol) and 2 mL of THF. The mixture was cooled to −35 °C, and magnetic stirring was initiated followed by the dropwise addition of n-BuLi (1.6 M in hexanes, pre-cooled to −35 °C, 0.16 mL, 0.25 mmol). Following the addition, the resulting mixture was stirred for 1 h. To the reaction mixture was then added $(Et_2N)_2PCl$ by using an Eppendorf pipette, followed by stirring for 3.5 h. ^{31}P NMR data obtained from an aliquot of the reaction mixture indicated the

clean conversion to **5**. The THF and other volatile materials were then removed in vacuo, and the residue was taken up in toluene. The solution was then filtered through Celite followed by removal of the toluene and other volatiles in vacuo and the solid was used without further purification. ^1H NMR (C_6D_6): δ 7.50 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C7–H), 7.27–7.20 (m, 2H, C4–H and C6–H), 7.03 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5–H), 5.54 (s, 1H, C3–H), 4.02 (d, $^2J_{PH}$ = 8.0 Hz, 1H, C1–H), 3.04–2.91 (m, 4H, 2 CH_2CH_3), 2.86–2.74 (m, 4H, 2 CH_2CH_3), 2.61 (s, 6H, NMe_2), 1.03 (m, 6H, 2 CH_2CH_3), 0.84 (m, 6H, 2 CH_2CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 160.0 (d, $^2J_{PC}$ = 6.7 Hz, C2), 146.8 (C7a), 138.8 (C3a), 126.1 (C6), 123.9 (d, $^3J_{PC}$ = 2.3 Hz, C7), 119.8 (C5), 117.7 (C4), 101.6 (C3), 53.0 (d, $^1J_{PC}$ = 42.6 Hz, C1), 43.4 (d, $^2J_{PC}$ = 19.2 Hz, 2 CH_2CH_3), 42.9 (d, $^2J_{PC}$ = 18.9 Hz, 2 CH_2CH_3), 41.9 (s, NMe_2), 14.7 (2 CH_2CH_3), 14.1 (2 CH_2CH_3); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 113.6.

2.4. Synthesis of 7

A vial containing a magnetic stir bar was charged with **3** (0.044 g, 0.094 mmol) and 3 mL of THF. To a separate vial, $[(COE)_2RhCl]_2$ (0.017 g, 0.024 mmol) and THF (2 mL) were added. The rhodium-containing solution was added to the THF slurry of **3** and magnetically stirred for 2 h. The solvent was then removed in vacuo, and the residue washed with pentane. Any residual solvent and other volatiles were removed in vacuo, leaving behind **7** as a light brown solid (0.041 g, 0.038 mmol, 81%). Anal. Calc. for $C_{62}H_{48}P_2N_2O_4RhCl$: C, 68.59; H, 4.46; N, 2.58. Found: C, 68.67; H, 4.46; N, 2.29%. ^1H NMR (C_6D_6): δ 9.52 (d, $^3J_{HH}$ = 7.4 Hz, 1H, aryl C–H), 8.61 (d, $^3J_{HH}$ = 8.7 Hz, 1H, aryl C–H), 7.89 (d, $^3J_{HH}$ = 8.8 Hz, 1H, aryl C–H), 7.80 (d, $^3J_{HH}$ = 8.1 Hz, 1H, aryl C–H), 7.63–7.69 (m, 2H, aryl C–Hs), 7.59 (t, $^3J_{HH}$ = 7.3 Hz, 1H, aryl C–H), 7.41–7.52 (m, 4H, aryl C–Hs), 7.25 (d, $^3J_{HH}$ = 8.7 Hz, 1H, aryl C–H), 7.13–7.17 (m, 1H, aryl C–H), 7.03–7.07 (m, 2H, aryl C–Hs), 6.98–7.02 (m, 2H, aryl C–Hs), 6.97 (d, $^3J_{HH}$ = 8.8 Hz, 1H, aryl C–H), 6.66–6.83 (m, 5H, aryl C–Hs), 6.51 (m, 1H, aryl C–H), 6.43 (m, 1H, aryl C–H), 6.11 (t, $^3J_{HH}$ = 7.4 Hz, 1H, aryl C–H), 6.06 (d, $^3J_{HH}$ = 6.0 Hz, 1H, aryl C–H), 5.67 (d, $^3J_{HH}$ = 8.9 Hz, 1H, aryl C–H), 5.42 (d, $^3J_{HH}$ = 8.9 Hz, 1H, aryl C–H), 5.23 (d, $^3J_{HH}$ = 7.8 Hz, 1H, aryl C–H), 5.21 (s, 1H, aryl C–H), 3.10 (s, 3H, bound NMe), 2.86 (s, 3H, bound NMe), 2.48–2.34 (m, 4H, CH_2), 1.98 (s, 6H, unbound NMe_2); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 176.4 (κ^2-P,N ligand C2), 156.8 (κ^1-P,N ligand C2), 156.7 (quat), 151.4 (quat), 151.3 (quat), 151.1 (quat), 150.7 (quat), 150.2 (quat), 149.8 (quat), 149.7 (quat), 148.0 (quat), 147.9 (quat), 142.3 (C3a or C7a), 137.2 (quat), 134.8 (quat), 133.6 (quat), 133.2 (quat), 132.3 (quat), 131.9 (quat), 131.8 (quat), 131.4 (quat), 131.0 (quat), 130.3 (aryl C–H), 130.0 (quat), 129.1 (aryl C–H), 128.4 (aryl C–H), 128.2 (aryl C–H), 128.0 (aryl C–H), 127.3 (aryl C–H), 127.2 (aryl C–H), 127.1 (2 aryl C–Hs), 126.8 (aryl C–H), 126.7 (aryl C–H), 126.0 (aryl C–H), 125.8 (aryl C–H), 125.5 (aryl C–H), 125.3 (aryl C–H), 125.1 (2 aryl C–Hs), 125.0 (aryl C–H), 124.6 (aryl C–H), 124.5 (2 aryl C–Hs), 123.9 (aryl C–H), 123.7 (aryl C–H), 123.5 (aryl C–H), 122.7 (aryl C–H), 122.4 (aryl C–H), 121.6 (aryl C–H), 120.2 (aryl C–H), 117.2 (aryl C–H), 103.4 (aryl C–H), 55.7 (aryl C–H), 55.6 (aryl C–H), 50.7 (bound NMe), 48.5 (bound NMe), 40.8 (unbound NMe_2), 29.7 (CH_2), 29.6 (CH_2); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 199.4 (d of d, $^2J_{PP}$ = 36.4 Hz, $^1J_{RhP}$ = 261.2 Hz), 170.3 (d of d, $^2J_{PP}$ = 36.4 Hz, $^1J_{RhP}$ = 291.6 Hz).

2.5. Crystallographic solution and refinement details for 3

Crystallographic data for this compound were obtained at 173(±2) K on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Cell parameters were initially retrieved using the COLLECT software (Nonius),