Journal of Organometallic Chemistry 694 (2009) 1943–1947

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

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

ARTICLE INFO

*Article history:*
Received 4 February 2009
Received in revised form 17 February 2009
Accepted 18 February 2009
Available online 28 February 2009

*Keywords:*
Asymmetric catalysis
Chiral
Indene
P,N-ligand
Rhodium

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.



## 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$^i$Pr$_2$-2-NMe$_2$-indene (**1**; Scheme 1) can be employed in the synthesis of neutral, cationic, and formally zwitterionic $\kappa^2$-*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 chiral 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.

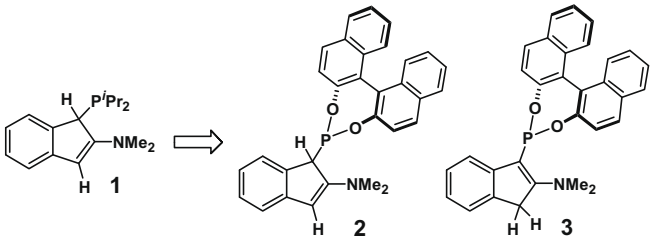
## 2. Experimental

### 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]. $^1$H, $^{13}$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 $^1$H and $^{13}$C) or 85% $H_3PO_4$ in $D_2O$ (for $^{31}$P). $^1$H and $^{13}$C NMR chemical shift assignments are made on the basis of data obtained from $^{13}$C DEPT, $^1$H–$^1$H COSY,

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

0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.02.015




**Scheme 1.**

$^1$H–$^{13}$C HSQC, and $^1$H–$^{13}$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′-binaphthalene-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%. $^1$H NMR ($CD_2Cl_2$): $\delta$ 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{$^1$H} NMR ($CD_2Cl_2$): $\delta$ 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{$^1$H} NMR ($CD_2Cl_2$): $\delta$ 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. $^1$H NMR ($C_6D_6$): $\delta$ 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{$^1$H} NMR ($C_6D_6$): $\delta$ 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{$^1$H} NMR ($C_6D_6$): $\delta$ 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%. $^1$H NMR ($C_6D_6$): $\delta$ 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{$^1$H} NMR ($C_6D_6$): $\delta$ 176.4 ($\kappa^2$-*P,N* ligand C2), 156.8 ($\kappa^1$-*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{$^1$H} NMR ($C_6D_6$): $\delta$ 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**

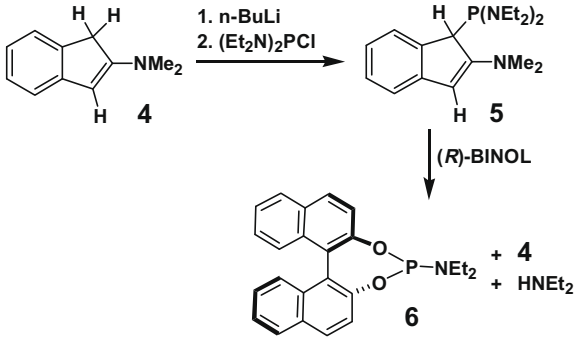
Crystallographic data for this compound were obtained at 173(±2) K on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using a graphite-monochromated Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer.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

and refined with the HKL DENZO and SCALEPACK software [10]. Data reduction and absorption correction (multi-scan) were also performed with the HKL DENZO and SCALEPACK software. The structure was solved by using direct methods, and refined by use of full-matrix least-squares procedures (on $F^2$) with $R_1$ based on $F_o^2 \geq 2\sigma(F_o^2)$ and $wR_2$ based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-H atoms, and all H-atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. The near-zero final refined value of the absolute structure parameter supported that the correct absolute structure had been chosen [11]. The crystal structure diagram in Fig. 1 was generated by use of the ORTEP-3 for Windows program [12].

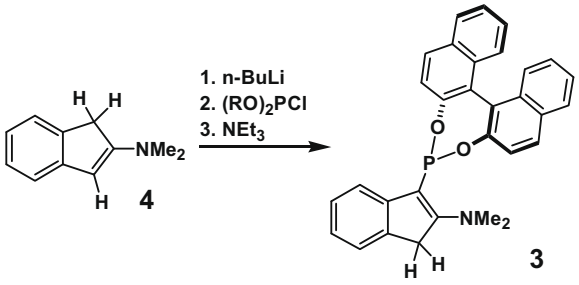
## 3. Results and discussion

### 3.1. Synthetic investigations

The conversion of ($sp^2$-R)P($NEt_2$)$_2$ precursors into ($sp^2$-R)P(BINOL-2H) and $HNEt_2$ upon treatment with BINOL has been successfully exploited in the synthesis of a range of chiral phosphorus-containing compounds [13]. Using this approach, 2-dimethylaminoindene **4** was lithiated, followed by quenching with ClP($NEt_2$)$_2$ to give 1-P($NEt_2$)$_2$-2-$NMe_2$-indene **5** (Scheme 2). While **5** was completely consumed over the course of 24 h upon reaction with (*R*)-BINOL in refluxing toluene, $^1$H and $^{31}$P NMR analysis of the reaction mixture revealed an equimolar mixture of **4**, the known phosphoramidite **6** [14], and $HNEt_2$, rather than the desired product **2** (or the isomer **3**). This product mixture can be viewed as arising from a combination of the desired protonolysis by (*R*)-BINOL of a P–N linkage in **5**, accompanied by unwanted P-C($sp^3$) bond protonolysis. Given that previously reported synthetic protocols of this type have employed precursors that feature more robust P-C($sp^2$) linkages [13], we sought to promote the isomerization of the allylic phosphine **5** to the vinylic phosphine 3-P($NEt_2$)$_2$-2-$NMe_2$-indene; unfortunately, we were unable to effect the clean isomerization




**Scheme 2.**




**Scheme 3.**

of **5** by use of heating and/or treatment with triethylamine [6a]. As such, alternative synthetic inroads to **2** (or **3**) were explored.

In using a protocol similar to that employed in the synthesis of **1** [15], compound **4** was lithiated, followed by quenching with [(*R*)-(1,1′-binaphthalene-2,2′-diyl)]chlorophosphite (represented as (RO)$_2$PCl in Scheme 3). Whereas a mixture of phosphorus-containing products was formed initially (including **3**; $^{31}$P NMR), treatment of this reaction mixture with triethylamine promoted the conversion of at least one of these products (possibly correspond-

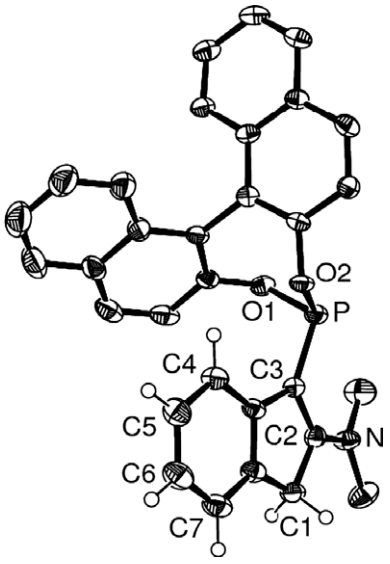



**Fig. 1.** ORTEP diagram of **3**, shown with 50% displacement ellipsoids and with the indene atomic numbering scheme depicted; selected H-atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for **3**: P–C3 1.777(3); P–O1 1.671(3); P–O2 1.669(2); N–C2 1.351(4); N–$CH_3^a$ 1.467(4); N–$CH_3^b$ 1.455(5); C1–C2 1.511(4); C2–C3 1.399(4); C2–N–$CH_3^a$ 120.8(3); C2–N–$CH_3^b$ 123.2(3); $CH_3^a$–N–$CH_3^b$ 115.7(3).

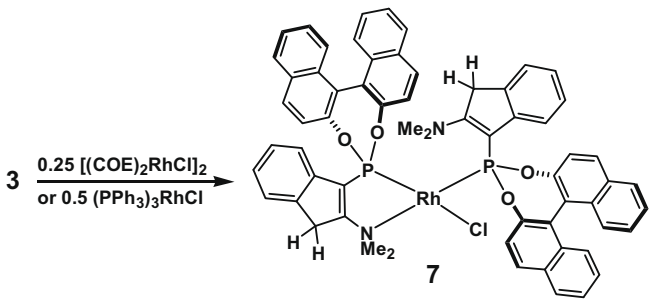
**Table 1**
Crystallographic data for **3**.

| | |
|---|---|
| Empirical formula | $C_{31}H_{24}N_1O_2P_1$ |
| Formula weight | 473.82 |
| Crystal dimensions (mm$^3$) | 0.20 × 0.20 × 0.10 |
| Color, habit | Colorless, plate |
| Crystal system | Monoclinic |
| Space group | $P2_1$ |
| $a$ (Å) | 9.4950(6) |
| $b$ (Å) | 7.2100(4) |
| $c$ (Å) | 17.9760(8) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 103.444(3) |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 1196.90(11) |
| $Z$ | 2 |
| Range of transmission | 0.9857–0.9716 |
| 2$\theta$ Limit (°) | 52.74 |
| | $-11 \leqslant h \leqslant 11$ |
| | $-8 \leqslant k \leqslant 9$ |
| | $-22 \leqslant l \leqslant 22$ |
| Independent reflections | 4656 |
| Observed reflections | 3840 |
| Data/restraints/parameters | 4656/1/319 |
| Goodness-of-fit | 1.057 |
| Absolute structure parameter | −0.08(14) |
| $R_1$ [$F_o^2 \geq 2\sigma(F_o^2)$] | 0.0561 |
| $wR_2$ [$F_o^2 \geq -3\sigma(F_o^2)$] | 0.1331 |
| Largest peak, hole (e Å$^{-3}$) | 0.257, −0.270 |

ing to **2**) into **3**. The P,N-indene **3** was obtained as an analytically pure white solid in 71% isolated yield. To complement the solution spectroscopic characterization of **3**, a single-crystal X-ray diffraction experiment was conducted; an ORTEP [12] diagram of **3** is presented in Fig. 1 and crystallographic data are collected in Table 1. The overall geometric features in **3** are comparable to those of the related achiral compound 3-$PPh_2$-2-$NMe_2$-indene [6a]. Notably, the apparent co-planarity of the non-hydrogen indene and dimethylamino atoms, the relatively short N–C2 distance (1.351(4) Å), and the sum of the angles at nitrogen (ca. 360°), collectively indicate that the lone pair of electrons on nitrogen in **3** is in conjugation with the indene π-system. Furthermore, the absolute configuration observed in the crystallographically characterized sample of **3** served to confirm that the stereochemistry of the (*R*)-BINOL synthon is retained in this new P,N-substituted indene.

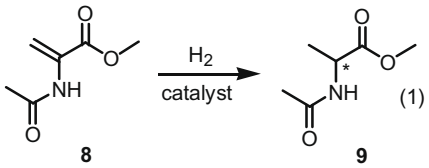
Having successfully prepared the new chiral P,N-indene ligand **3**, we turned our attention to the preparation of rhodium coordination complexes. However, unlike 1-P$^i$Pr$_2$-2-$NMe_2$-indene (**1**), which served as a precursor to the cationic complexes [(COD)Rh(κ$^2$-1/3-P$^i$Pr$_2$-2-*N*$Me_2$-indene)]$^+X^-$ (COD = η$^4$-1,5-cyclooctadiene), as well as the related zwitterion (COD)Rh(κ$^2$-3-P$^i$Pr$_2$-2-*N*$Me_2$-indenide) [4c,15], rather complex reactivity was observed when employing **3** under similar conditions. In this regard, treatment of **3** with either $[(COD)RhCl]_2$ or in situ generated $[(COD)Rh(THF)_2]^+X^-$ afforded an intractable mixture of products. Furthermore, our efforts to generate an indenyl salt of **3** by use of reagents such as *n*-BuLi or $NaN(SiMe_3)_2$ under conditions that proved effective for the metalation of **1**, invariably resulted in the formation of complex reaction mixtures. Although we are presently uncertain as to the identity of the products formed in the latter metalation reactions involving **3**, it is possible that P–O bond cleavage occurs in the presence of the alkali metal reagents employed.

In exploring the reactivity of $[(COE)_2RhCl]_2$ (COE = η$^2$-cyclooctene) with **3**, a 2:1 ligand-to-metal complex **7** was formed invariably ($^{31}$P NMR), even when using a 1:1 stoichiometry of **3**:Rh (Scheme 4); complex **7** was also generated cleanly when using a 2:1 ratio of **3** and $(PPh_3)_3RhCl$. Complex **7** was obtained as an analytically pure light brown solid in 81% isolated yield, and was characterized spectroscopically. Our assignment of **7** as featuring both κ$^2$-*P*,*N*-**3** and κ$^1$-*P*,N-**3** ligands in which the phosphorus atoms are *cis*-disposed is in keeping with the observation of two $^{31}$P NMR resonances that exhibit relatively small $^2J_{PP}$ values (36.4 Hz). This structural assignment is also consistent with the observation of distinct $^1$H and $^{13}$C NMR resonances for each of the inequivalent methyl groups of the κ$^2$-*P*,*N*-**3** ligand, as well as a single set of resonances for the methyl groups of the κ$^1$-*P*,N-**3** ligand which are rendered equivalent by rotation and inversion processes at nitrogen [4c] that are rapid on the NMR timescale. In light of our limited success in preparing isolable rhodium complexes of **3**, asymmetric hydrogenation and hydrosilylation studies (vide infra) were conducting by using primarily catalyst mixtures that were prepared in situ.




**Scheme 4.**

**Table 2**
Hydrogenation of methyl-2-acetamidoacrylate.[a]




| Entry | Mol% **3** added | Solvent | %[b] | % *ee*[c] |
|---|---|---|---|---|
| 2-1 | 0 | THF | >99 | <5 |
| 2-2 | 6.0 | THF | >99 | 40 |
| 2-3 | 6.0 | $CH_2Cl_2$ | 26 | <5 |
| 2-4 | 12.0 | THF | 32 | 67 |

[a] Conditions: 24 °C; 1 atm $H_2$; 5.0 mol% $[(COD)Rh(THF)_2]^+BF_4^-$ prepared in situ from 0.5 $[(COD)MCl]_2$ and $AgBF_4$ in THF (COD = η$^4$-1,5-cyclooctadiene).
[b] Percent conversion based on the consumption of methyl-2-acetamidoacrylate (**8**) at 24 h.
[c] Enantiomeric excess of **9** determined on the basis of chiral GC-FID data [9].

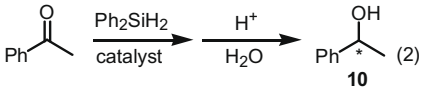
### 3.2. Asymmetric hydrogenation

The rhodium-mediated asymmetric hydrogenation of methyl-2-acetamidoacrylate **8** to afford **9** (Eq. (1)) under mild conditions (24 °C, ca. 1 atm $H_2$, 5.0 mol% Rh) was selected as a test reaction to use in benchmarking the catalytic performance of **3** [16]; representative results of these hydrogenation studies are collected in Table 2. Control experiments confirmed the ability of catalyst mixtures derived from 0.5 $[(COD)RhCl]_2$ and $AgBF_4$ in THF (without added **3**) to efficiently mediate the reduction of **8** (entry 2-1). Under analogous conditions employing 6.0 mol% **3** (1.2 equiv. relative to rhodium) in THF, the quantitative hydrogenation of **8** was also achieved, affording **9** in a modest 40% *ee* (entry 2-2); inferior performance was observed in dichloromethane (entry 2-3). While increasing the amount of **3** to 12.0 mol% provided a rise in enantioselectivity in THF (67% *ee*; entry 2-4), such gains were made at the expense of catalyst productivity (32% conversion). Negligible conversion was achieved by using 6.0 mol% of the isolable Rh complex **7** in either THF or $CH_2Cl_2$ under similar experimental conditions.

### 3.3. Asymmetric hydrosilylation

In an effort to evaluate further the catalytic utility of **3**, we turned our attention to the asymmetric hydrosilylation of ketones [17] – a challenging transformation for which rhodium catalysts supported by appropriately designed chiral κ$^2$-*P*,*N* ligands have proven to be highly effective [18]. Representative results of our catalytic investigations examining the asymmetric hydrosilylation of acetophenone with $Ph_2SiH_2$ (Eq. (2)) are collected in Table 3. In preliminary experiments conducted in THF using catalyst mixtures comprised of 2.5 mol% $[(COD)RhCl]_2$ or $[(COE)_2RhCl]_2$ and 6.0 mol% **3**, conversions of 74% and 63% were achieved (entries 3-1 and 3-2). Altering the conditions to promote the formation of **7** as a pre-catalyst (2.5 mol% $[(COE)_2RhCl]_2$ and 12.0 mol% **3**) offered no reactivity advantages (55%; entry 3-3), and the catalytic performance of pre-formed **7** proved to be identical to this in situ prepared catalyst mixture. While related cationic rhodium catalyst systems did not offer significantly improved performance in THF (30–66%; entries 3-4 to 3-7), in moving to dichloromethane and employing **3**:Rh in an equilmolar ratio, somewhat higher conversions were achieved (57–93%; entries 3-8 to 3-11). However, despite the range

**Table 3**
Addition of diphenylsilane to acetophenone.




| Entry | Metal precursor[a] (5.0 mol% Rh) | Mol% **3** added | Solvent | %[b] |
|---|---|---|---|---|
| 3-1 | $[(COD)RhCl]_2$ | 6.0 | THF | 74 |
| 3-2 | $[(COE)_2RhCl]_2$ | 6.0 | THF | 63 |
| 3-3 | $[(COE)_2RhCl]_2$ | 12.0 | THF | 55 |
| 3-4 | $[(COD)Rh(THF)_2]^+BF_4^-$ | 6.0 | THF | 66 |
| 3-5 | $[(COD)Rh(THF)_2]^+BF_4^-$ | 12.0 | THF | 52 |
| 3-6 | $[(COE)_2Rh(THF)_2]^+BF_4^-$ | 6.0 | THF | 50 |
| 3-7 | $[(COD)Rh(THF)_2]^+BF_4^-$ | 12.0 | THF | 30 |
| 3-8 | $[(COD)RhCl]_2$ | 6.0 | $CH_2Cl_2$ | 84 |
| 3-9 | $[(COE)_2RhCl]_2$ | 6.0 | $CH_2Cl_2$ | 57 |
| 3-10 | $[(COD)Rh(THF)_2]^+BF_4^-$ | 6.0 | $CH_2Cl_2$ | 93 |
| 3-11 | $[(COD)Rh(THF)_2]^+BF_4^-$ | 6.0 | $CH_2Cl_2$ | 90 |

[a] $[(COD)Rh(THF)_2]^+BF_4^-$ and $[(COE)_2Rh(THF)_2]^+BF_4^-$ prepared in situ from 0.5 $[(COD)RhCl]_2$ and 0.5 $[(COE)_2RhCl]_2$ (respectively) and $AgBF_4$ in THF (COD = $\eta^4$-1,5-cyclooctadiene; COE = cyclooctene).

[b] Percent conversion to **10** (following workup) after 18 h at 24 °C; the enantiomeric excess of **10** (in all cases ⩽10%) was determined on the basis of chiral GC-FID data [9].

of conditions and pre-catalyst mixtures surveyed, negligible enantioselectivities (<10% *ee*) were attained in these reactions.

## 4. Summary and conclusions

In conclusion, we have reported herein on the synthesis and characterization of a new enantiopure heterobidentate P,N-indene ligand **3** that is derived from (*R*)-BINOL. In contrast to the established ability of 1/3-$P^iPr_2$-2-$NMe_2$-indene to give rise to isolable neutral, cationic, and formally zwitterionic $\kappa^2$-*P*,*N* rhodium coordination complexes in high yield, more complex reactivity was observed for **3**. In the course of these coordination chemistry studies, the formation of the isolable complex [($\kappa^2$-*P*,*N*-**3**)($\kappa^1$-*P*,N-**3**)RhCl] (**7**) was observed, thereby confirming the propensity of this new ligand to form $L_nRh(\mathbf{3})_2$ complexes; such ligation 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 reported herein.

## Acknowledgements

Acknowledgment is made to Dalhousie University and the Natural Sciences and Engineering Research Council of Canada for their generous support of this work. We also thank Drs. Michael Lumsden and Katherine Robertson (Atlantic Region Magnetic Resonance Center, Dalhousie) for assistance in the acquisition of NMR data.

## Appendix A. Supplementary material

CCDC 719217 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.02.015.

## References

[1] (a) N.B. Johnson, I.C. Lennon, P.H. Moran, J.A. Ramsden, Acc. Chem. Res. 40 (2007) 1291;
(b) V. Farina, J.T. Reeves, C.H. Senanayake, J.J. Song, Chem. Rev. 106 (2006) 2734;
(c) H.-U. Blaser, B. Pugin, F. Spindler, J. Mol. Catal. A 231 (2005) 1;
(d) H.-U. Blaser, F. Spindler, M. Studer, Appl. Catal. A 221 (2001) 119.
[2] (a) K. Källström, I. Munslow, P.G. Andersson, Chem. Eur. J. 12 (2006) 3194;
(b) P.J. Guiry, C.P. Saunders, Adv. Synth. Catal. 346 (2004) 497;
(c) G. Chelucci, G. Orrù, G.A. Pinna, Tetrahedron 59 (2003) 9471;
(d) K.N. Gavrilov, A.I. Polosukhin, Russ. Chem. Rev. 69 (2000) 661.
[3] (a) A. Pfaltz, W.J. Drury III, Proc. Natl. Acad. Sci. 101 (2004) 5723;
(b) G. Helmchen, A. Pfaltz, Acc. Chem. Res. 33 (2000) 336.
[4] (a) R.J. Lundgren, M.A. Rankin, R. McDonald, M. Stradiotto, Organometallics 27 (2008) 254;
(b) R.J. Lundgren, M.A. Rankin, R. McDonald, G. Schatte, M. Stradiotto, Angew. Chem., Int. Ed. 46 (2007) 4732;
(c) J. Cipot, R. McDonald, M.J. Ferguson, G. Schatte, M. Stradiotto, Organometallics 26 (2007) 594.
[5] (a) L. Eberhardt, D. Armspach, J. Harrowfield, D. Matt, Chem. Soc. Rev. 37 (2008) 839;
(b) A.J. Minnaard, B.L. Feringa, L. Lefort, J.G. de Vries, Acc. Chem. Res. 40 (2007) 1267;
(c) J.G. de Vries, L. Lefort, Chem. Eur. J. 12 (2006) 4722.
[6] (a) We viewed **2** and **3** as being equally suitable ligand targets, in light of our observation that the introduction of the allylic phosphine 1-$P^iPr_2$-2-$NMe_2$-indene **1**, or alternatively mixtures of **1** and the vinylic phosphine 3-$P^iPr_2$-2-$NMe_2$-indene, to a transition metal fragment is often accompanied by ligand isomerization to give coordination complexes of 3-$P^iPr_2$-2-$NMe_2$-indene. For discussions of such ligand isomerization phenomena, see: J. Cipot, D. Wechsler, M. Stradiotto, R. McDonald, M.J. Ferguson, Organometallics 22 (2003) 5185;
(b) Ref. [4] herein.
[7] (a) U. Edlund, G. Bergson, Acta Chem. Scand. 25 (1971) 3625;
(b) J. Klosin, W.J. Kruper Jr., P.N. Nickias, G.R. Roof, P. De Waele, K.A. Abboud, Organometallics 20 (2001) 2663.
[8] R. Sablong, C. Newton, P. Dierkes, J.A. Osborn, Tetrahedron Lett. 37 (1996) 4933.
[9] D. Wechsler, M. Stradiotto, Can. J. Chem. 87 (2009) 72.
[10] HKL DENZO and SCALEPACK v1.96: Z. Otwinowski, W. Minor, in: C.W. Carter, R.M. Sweet (Eds.), Macromolecular Crystallography, Part A, vol. 276, Academic Press, San Diego, 1997, pp. 307–326.
[11] The Flack absolute structure parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration: H.D. Flack, G. Bernardinelli, J. Appl. Crystallogr. 33 (2000) 1143.
[12] ORTEP-3 for Windows Version 1.074: L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[13] (a) Selected recent examples: D. Sirbu, G. Consiglio, S. Gischig, J. Organomet. Chem. 691 (2006) 1143;
(b) I.D. Kostas, K.A. Vallianatou, J. Holz, A. Börner, Appl. Organomet. Chem. 19 (2005) 1090;
(c) G. Franciò, D. Drommi, C. Graiff, F. Faraone, A. Tiripicchio, Inorg. Chim. Acta 338 (2002) 59;
(d) M.T. Reetz, D. Moulin, A. Gosberg, Org. Lett. 3 (2001) 4083.
[14] L.A. Arnold, R. Imbos, A. Mandoli, A.H.M. de Vries, R. Naasz, B.L. Feringa, Tetrahedron 56 (2000) 2865.
[15] M. Stradiotto, J. Cipot, R. McDonald, J. Am. Chem. Soc. 125 (2003) 5618.
[16] I.D. Gridnev, T. Imamoto, Acc. Chem. Res. 37 (2004) 633.
[17] H. Brunner, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, vol. 2, Wiley-VCH, New York, 1998, pp. 131–140.
[18] (a) For some noteworthy examples, see: B. Tao, G.C. Fu, Angew. Chem., Int. Ed. 41 (2002) 3892;
(b) D.K. Heldmann, D. Seebach, Helv. Chim. Acta 82 (1999) 1096;
(c) Y. Nishibayashi, K. Segawa, K. Ohe, S. Uemura, Organometallics 14 (1995) 5486.