

# Oxazoline chemistry. Part VIII. Synthesis and characterization of a new class of pincer ligands derived from the 2-(*o*-aniliny)-2-oxazoline skeleton — Applications to the synthesis of group X transition metal catalysts<sup>1</sup>

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**Abstract:** The synthesis and characterization of a new and readily synthesized class of potentially anionic pincer ligands with  $C_1$  point group symmetries is described. These materials can be made via amide coupling of a 2-(2'-aniliny)-2-oxazoline unit with picolinic acid; the incorporation of enantiopure oxazoline fragments facilitates the construction of chiral  $C_1$  pincers. Treatment of the free ligands with Pd metal sources leads to the formation of amido-Pd pincer complexes in good yield. One of these Pd complexes has been characterized by single crystal X-ray diffraction methods, which confirms the proposed tridentate binding mode of the ligand and the formation of an amido N—Pd bond. The metal complexes have been shown to be suitable precursors for catalytically active Pd species that are useful for C—C bond forming reactions, notably the Heck reaction under standard conditions.

*Key words:* oxazoline, 4,5-dihydro-2-oxazole, palladium, pincer ligand, amido, Heck reaction.

**Résumé :** On décrit la synthèse facile et la caractérisation d'une nouvelle classe de ligands anioniques à pinces ayant des groupes de symétrie ponctuelle  $C_1$ . Ces produits peuvent être obtenus par couplage d'amide d'une unité 2-(2'-aniliny)-2-oxazoline avec de l'acide picolinique; l'incorporation de fragments oxazolines énantiopurs facilite la formation de ligands à pince de symétrie  $C_1$ . Le traitement des ligands libres avec des sources de palladium métallique conduit à la formation, avec de bons rendements, de complexes amido-Pd pincer. On a caractérisé un de ces complexes du Pd par diffraction des rayons X par un cristal unique et on a ainsi pu confirmer le mode de liaison tridentate du ligand et la formation d'une liaison N—Pd amido. On a montré que les complexes métalliques sont des précurseurs appropriés pour des espèces catalytiquement actives de Pd qui sont utiles dans les réactions de formation de liaisons C—C, particulièrement dans la réaction de Heck dans des conditions standards.

*Mots clés :* oxazoline, 4,5-dihydro-2-oxazole, palladium, ligand à pince, amido, réaction de Heck.

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## Introduction

In recent years, enantiopure ( $C_2$  symmetric) bisoxazolines have become a popular and useful class of ligands for applications in asymmetric synthesis promoted by Lewis acids (1). Oxazolines have been shown to possess a rich transition-metal chemistry (2), and recently the oxazoline fragment has been incorporated into the design of the so-called "pincer" ligand framework. This has resulted in the accessibility of potentially anionic and  $C_2$ -symmetric pincers (3). Pincer ligands have been at the forefront of a number of areas of investigation within organometallic chemistry including

dendrimer chemistry, molecular sensor technology, the study of unusual bonding motifs or metal oxidation states (e.g.,  $Ni^{3+}$ ), and metal-mediated catalysis (4). Despite these advances, there has been increasing interest in ligands of *lower* symmetry; this is due to the fact that in many cases superior enantioselective catalysis can be obtained from species containing such ligands (1a, 1c, 5). Herein, we report the facile syntheses of  $C_1$ -symmetric amide pincer ligands containing a chiral (or achiral) oxazoline group in addition to a secondary binding (pyridine) functionality. In addition, these amides (Fig. 1) are shown to readily deprotonate (to form anionic pincers) on reaction with Pd sources to form Pd-

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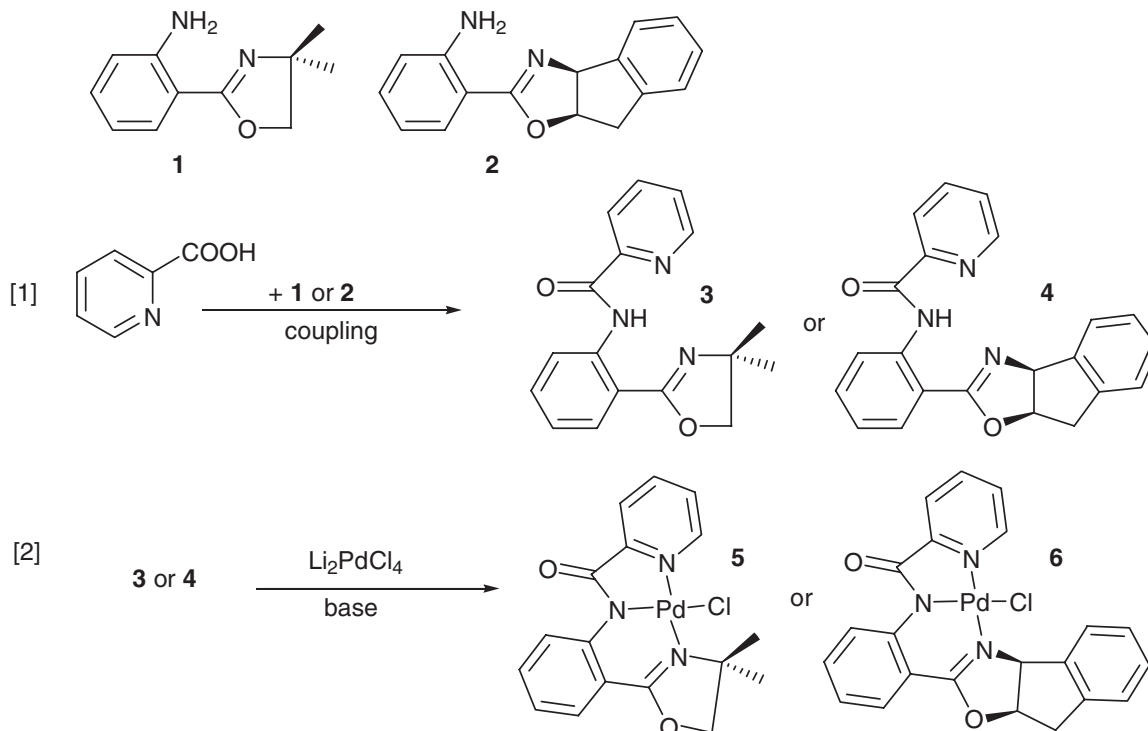
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Fig. 1. Synthetic methodologies for the production of 3–6.



amido complexes; these metal derivatives are shown to be active catalysts for the Heck reaction under standard protocols.

## Results and discussion

The synthesis of amide **3** (Fig. 1) was accomplished using the in situ produced ( $\text{SOCl}_2$ ) acid chloride (6) derivative of picolinic acid (PA), followed by the low temperature addition of readily available 4,4-dimethyl-2-(*o*-aniliny)-2-oxazoline (**1**, Fig. 1, eq. [1]) (**7**). Unfortunately, yields of chiral analogue **4** were found to be variable by the above methodology, but the desired product could be reproducibly synthesized using PA and **2** under DCC–DMAP protocols (Fig. 1, eq. [1], also see Experimental section). Both **3** and **4** can thus be easily produced in large quantities (>1 g). The air-stable nature of these materials makes them easier to handle than many of the sensitive “PCP” or “pincer carbene” ligands (**1**). Facile ligand “tuning” (**8**) can be readily envisioned because of the availability of a number of analogues of **1** and **2** (**7**).

Palladium complexes of deprotonated **3** or **4** are formed in good yield upon treatment of (MeOH) solutions of the ligands with stoichiometric  $\text{Li}_2\text{PdCl}_4$ . These reactions lead to the isolation of solid and air-stable brown-coloured complex **5** (82%) and yellow **6** (91%), respectively (Fig. 1, eq. [2]).  $^1\text{H}$  NMR data on both materials, in combination with elemental analysis, IR data, and the diamagnetic nature of both complexes, strongly suggest the formation of 1:1 adducts of the ligand fragments with  $\text{Pd}^{2+}$ . Specifically, the disappearance of the  $^1\text{H}$  NMR signal assigned to the amide N–H proton and loss of the corresponding IR stretching frequency assigned to this group, imply the formation of complexes of the general formula  $[\text{Pd}(\text{L}-\text{H})\text{Cl}]_x$  (L = **3** or **4**, respectively).

To confirm the mononuclear nature of these species, a single crystal X-ray diffraction study was carried out on a sample of complex **5**. A molecular representation of this material is found in Fig. 2. Crystal data can be found in Table 1; Table 2 gives a list of selected bond lengths and angles for complex **5**.

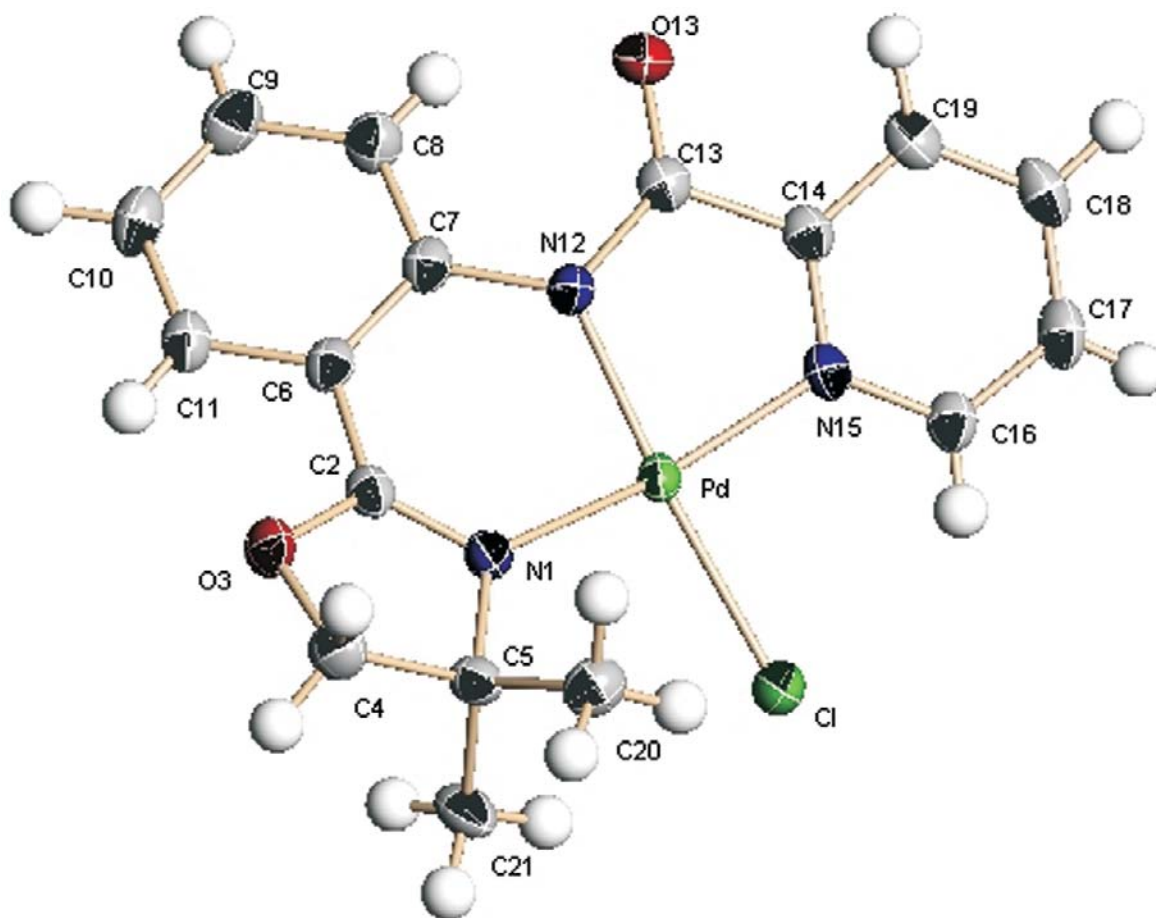
The X-ray data confirm that **5** is a monopalladium complex incorporating deprotonated **3**; bond lengths and angles are typical for a formal  $\text{Pd}^{2+}$  metal centre (1, 9). Of note is the formal amido–Pd interaction in addition to the coordination of both the pyridine and the oxazoline groups forming five- and six-membered rings, respectively; the latter functionality binds through the N atom, as expected (2). Thus, a tridentate ( $\kappa\text{N}$ ,  $\kappa\text{N}'$ ,  $\kappa\text{N}''$ ) bonding motif is presented. The coordination geometry around the Pd atom is best described as distorted square-planar in nature. Therefore, ligands such as **3** do form pincer complexes and in excellent yields.

Several Pd pincer compounds are known to be active promoters of selective C–C bond formation (10). We have therefore performed some preliminary tests on complexes **5** and **6** as promoters of the Heck reaction under typical reaction conditions (9). Both complexes catalyse the regioselective coupling of iodobenzene with styrene to give high yields of *trans*-stilbene under standard protocols in the presence of base (NaOAc, see the Experimental section). Notably, these reactions were performed *in open air* and hence these pincer catalysts appear to be highly robust (11) to the high temperature oxidizing conditions employed.

## Conclusions

In conclusion, access to a new and readily synthesized class of potentially anionic pincer ligands has been realised. These compounds can be used to make catalytically active

**Fig. 2.** Image of the molecular structure of complex **5** showing the atomic numbering scheme. Thermal ellipsoids are at the 30% probability level.



Pd species for selective C—C bond forming reactions that can be used in the absence of inert atmosphere conditions. The investigation of other transition-metal complexes of these and related ligands, and their catalytic potentials, will be disclosed in due course.

## Experimental section

### General

All reactions were carried out using standard bench-top laboratory techniques using commercially available, reagent-grade solvents.  $^1\text{H}$  NMR spectra were recorded from chloroform-*d* solutions at 300 MHz using a Bruker Avance 300 NMR spectrometer. Microanalyses were recorded at the analytical services department of the University of Windsor (Windsor, Ontario). IR spectra were obtained as Nujol muls using a PerkinElmer 683 IR spectrometer. Melting point data were obtained using a Mel-Temp II apparatus and reported values are uncorrected. Optical rotation measurements were made on a Bellingham + Stanley Ltd. model ADP220 polarimeter using a 1 dm path length optical cell.

### Syntheses

#### Synthesis of **3**

Thionyl chloride (5.6 g, 50 mmol) was added dropwise to a stirred and cold (0 °C) mixture of PA (6.15 g, 50 mmol)

and  $\text{Et}_3\text{N}$  (7.6 g, 75 mmol) in 35 mL of  $\text{CH}_2\text{Cl}_2$  (6). Stirring was continued for 30 min and then a suspension of **1** (**7a**) (9.5 g, 50 mmol) in 20 mL of  $\text{CH}_2\text{Cl}_2$  was added (at 0 °C). The stirring was continued for a further 3 h as the mixture warmed to room temperature (RT); the reaction vessel was then left standing overnight. Neutralization by the addition of satd. aq.  $\text{Na}_2\text{CO}_3$  was followed by isolation of the organic layer, which was subsequently washed with water (3  $\times$  15 mL) and then evaporated in vacuo. The crude product thus obtained was purified by (flash) chromatography ( $\text{SiO}_2$ , 230–400 mesh) using hexanes – ethyl acetate (3:1, *v/v*) as the eluent ( $R_f = 0.50$ ). The yellow solid *product* was thereafter isolated following solvent evaporation. Yield: 6.63 g (45%); mp 110 °C. IR ( $\text{cm}^{-1}$ ): 3054 (w), 1670 (s), 1645 (s), 1583 (s), 1540 (s).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.51 (s, 6H), 4.12 (s, 2H), 7.15 (t, 1H,  $J = 7.9$  Hz), 7.47–7.58 (m, 2H), 7.87–7.95 (m, 2H), 8.30 (d, 1H,  $J = 7.9$  Hz), 8.69 (d, 1H,  $J = 4.5$  Hz), 9.03 (d, 1H,  $J = 8.3$  Hz). Anal. calcd. for  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2$  (%): C 69.14, H 5.80, N 14.23; found: C 70.03, H 5.82, N 14.57.

#### Synthesis of **4**

In a round-bottomed flask containing chilled (10 °C)  $\text{CH}_2\text{Cl}_2$  (160 mL) was added **2** (**7a**) (2.136 g, 11.2 mmol) and PA (1.674 g, 13.6 mmol). The mixture was stirred under an inert atmosphere for 25 min at 0 °C. To this mixture was added DMAP (0.412 g, 3.2 mmol) and DCC (3.492 g,

**Table 1.** X-ray diffraction data for complex **5**.

Formula weight	436.18
Formula	C <sub>17</sub> H <sub>16</sub> ClN <sub>3</sub> O <sub>2</sub> Pd
Temperature (K)	198(1)
$\lambda$ (Å)	0.710 73
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>
Unit cell dimensions:	
<i>a</i> (Å)	11.231 8(6)
<i>b</i> (Å)	17.399 1(10)
$\beta$ (°)	95.515(1)
<i>c</i> (Å)	8.421 0(5)
Volume (Å <sup>3</sup> )	1 638.04(16)
<i>Z</i>	4
Density (calcd., Mg/m <sup>3</sup> )	1.769
Absorption coefficient (mm <sup>-1</sup> )	1.311
<i>F</i> (000)	872
Crystal size (mm <sup>3</sup> )	0.40 × 0.25 × 0.20
$\theta$ Range for data collection (°)	1.82–27.50
Index ranges	–13 ≤ <i>h</i> ≤ 14, –20 ≤ <i>k</i> ≤ 22, –10 ≤ <i>l</i> ≤ 10
Reflections	11 291
Independent reflections	3 679
<i>R</i> (int)	0.020 6
Completeness to $\theta$ (°)	97.6% (27.50)
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	3 679 / 0 / 281
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.066
Final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	
<i>R</i> <sub>1</sub>	0.020 0
<i>wR</i> <sub>2</sub>	0.052 3
<i>R</i> indices (all data)	
<i>R</i> <sub>1</sub>	0.023 6
<i>wR</i> <sub>2</sub>	0.054 3
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.612 and –0.185

**Note:** where  $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[F_o^4]\}^{1/2}$ ,  $R_1 = \sum|F_o| - |F_c| / \sum|F_o|$ . Weight =  $1/[\sigma^2(F_o^2) + (0.0303P)^2 + (0.6142P)]$ , where  $P = (\max(F_o^2, 0) + 2F_c^2)/3$ .

16.8 mmol) and the mixture was then stirred for an additional 25 min at 0 °C. The cooling bath was removed and the solution warmed up to RT. After being stirred for 48 h, the mixture was filtered (thrice) to yield a clear filtrate. The filtrate was then washed with water (4 × 300 mL), 5% aq. HOAc (160 mL), and again with water (4 × 200 mL). The organic layer was then dried (MgSO<sub>4</sub>), filtered, and then all volatile components were removed on a rotary evaporator. The crude product thus obtained was purified by flash silica gel chromatography (230–400 mesh) using hexanes – ethyl acetate (75:25, *R<sub>f</sub>* = 0.61) as the eluent, following by solvent evaporation. Yield: 1.79 g (45%); mp 189 °C.  $[\alpha]_D$  (300 K, *c* 0.5, CH<sub>2</sub>Cl<sub>2</sub>) –74°. IR (cm<sup>-1</sup>): 1680 (s), 1636 (s), 1579 (s), 1520 (s). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.45 (s, 1H), 3.54 (d, 1H, *J* = 6.7 Hz), 5.49 (m, 1H), 5.97 (d, 1H, *J* = 7.9 Hz),

**Table 2.** Selected bond lengths (Å) and angles (°) for complex **5** (esds in brackets).

Bond lengths (Å)	
Pd—N1	2.0254(14)
Pd—Cl	2.3248(5)
Pd—N12	2.0077(14)
Pd—N15	2.0236(15)
Bond angles (°)	
N1—Pd—N15	169.07(6)
Cl—Pd—N12	171.55(4)
N12—Pd—N1	90.01(6)
N12—Pd—N15	81.76(6)

7.15 (t, 1H, *J* = 8.0 Hz), 7.27 (m, 3H), 7.49–7.57 (m, 2H), 7.67 (t, 1H, *J* = 4.1 Hz), 7.90–7.95 (m, 2H), 8.31 (d, 1H, *J* = 7.8 Hz), 8.90 (d, 1H, *J* = 4.3 Hz), 9.01 (d, 1H, *J* = 8.3 Hz). Anal. calcd. for C<sub>22</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub> (%): C 74.35, H 4.82, N 11.82; found: C 74.91, H 4.63, N 12.26.

### Synthesis of **5**

To a 10 mL solution (MeOH) of in situ formed Li<sub>2</sub>PdCl<sub>4</sub> (0.5 mmol, prepared by boiling 0.088 g (0.5 mmol) of PdCl<sub>2</sub> and 0.127 g of LiCl (3 mmol)) was added **3** (0.145 g, 0.5 mmol). The mixture was stirred at RT for 48 h and the resulting brown complex isolated by filtration, washed with MeOH and ether, and then dried at 60 °C overnight. Yield: 0.179 g (82%), mp 251 to 252 °C. IR (cm<sup>-1</sup>): 1646 (s), 1614 (s), 1485 (s), 520 (w), 340 (w). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.79 (s, 6H), 4.30 (s, 2H), 7.02 (t, 1H, *J* = 7.7 Hz), 7.41–7.53 (m, 2H), 7.82 (t, 1H, *J* = 8.1 Hz), 8.04 (m, 2H), 8.49 (d, 1H, *J* = 8.6 Hz), 9.27 (d, 1H, *J* = 5.5 Hz). Anal. calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub>ClPd·1/2H<sub>2</sub>O (%): C 45.86, H 3.85, N 9.44; found: C 45.53, H 3.64, N 9.68.

### Synthesis of **6**

As described above for complex **5** using Li<sub>2</sub>PdCl<sub>4</sub> (0.5 mmol) and **4** (0.145 g, 0.5 mmol). Yield: 0.225 g (91%) of a yellow powder; mp > 300 °C.  $[\alpha]_D$  (300 K, *c* 0.49, CH<sub>2</sub>Cl<sub>2</sub>) –385°. IR (cm<sup>-1</sup>): 1623 (s), 1598 (s), 1482 (s), 530 (w), 335 (w). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.50 (t, 1H, *J* = 5.1 Hz), 3.57 (s, 1H), 5.49 (m, 1H), 6.43 (d, 1H, *J* = 7.1 Hz), 6.98 (t, 1H, *J* = 8.1 Hz), 7.25–7.37 (m, 3H), 7.43–7.47 (m, 1H), 7.50–7.55 (m, 1H), 7.86 (dd, 1H, *J* = 8.1 Hz), 8.03–8.05 (m, 2H), 8.43 (d, 1H, *J* = 8.4 Hz), 8.53 (t, 1H, *J* = 5.3 Hz), 9.23 (d, 1H, *J* = 5.6 Hz). Anal. calcd. for C<sub>22</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub>ClPd (%): C 53.25, H 3.25, N 8.47; found: C 53.68, H 3.17, N 9.25.

### Catalysis

#### Heck coupling reactions of iodobenzene and styrene using **5** or **6**<sup>4</sup>

Iodobenzene (25 mmol), styrene (30 mmol), *N,N*-dimethylformamide (25 mL), sodium acetate (30 mmol), and 0.5 mg (~1  $\mu$ mol) of **5** or **6** were combined in a round-bottomed flask equipped with a reflux condenser (9). The mixture was heated, in open air, to 140–150 °C for 24 h. After cooling to RT, 0.1 L of dil. aq. HCl was added and the

<sup>4</sup>Nota bene: no attempt was made to optimize the reaction conditions.

organic components were extracted with ethyl acetate (3 × 100 mL). The organic layer was washed (brine) and dried (Na<sub>2</sub>SO<sub>4</sub>). After filtration, volatiles were removed (vacuo) and the product *trans*-stilbene (correct mp and <sup>1</sup>H NMR) was purified by flash column chromatography (hexanes–EtOAc, 9:1). Yield: 95% (using **5**); 89% (using **6**).

### X-ray crystallography of complex **5**<sup>5</sup>

Single crystals were coated with Paratone-N oil, mounted using a glass fibre, and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using  $\omega$  and  $\theta$  scans with a scan width of 0.3° and 10 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT) (12) and corrected for absorption (SADABS) (13). The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  (SHELXTL) (14). Hydrogen atoms were included in calculated positions and refined using a riding model.

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<sup>5</sup>Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 4011. For more information on obtaining material refer to [http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub\\_e.shtml](http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml). CCDC 263208 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).