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Ruthenium(II) Complexes Bearing a Ligand Derived from *P,N*- or *P,N,O*-Diphenylphosphinobenzoxazine: Synthesis, X-ray Characterization, and *cis* Diastereoselectivity in Styrene Cyclopropanation

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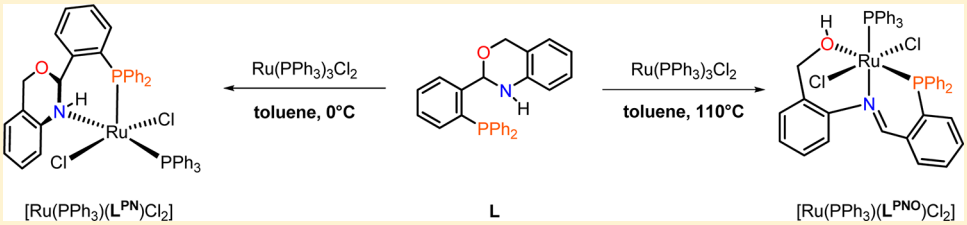
Supporting Information



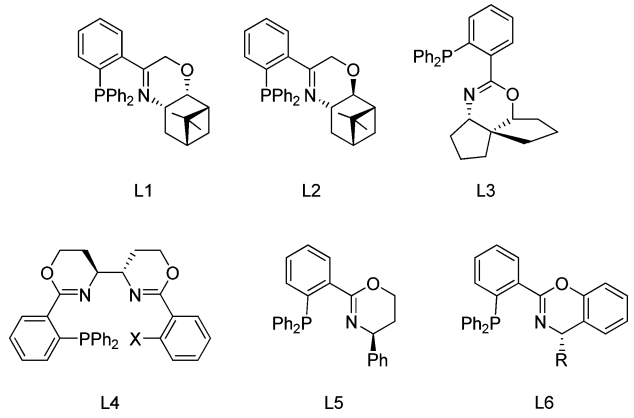
ABSTRACT: A phosphino-oxazine based ligand (**L**; 2-(2-(diphenylphosphino)phenyl)-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazine) showing a temperature-dependent equilibrium between a closed bidentate ($\mathbf{L}^{PN}$) and an opened tridentate ($\mathbf{L}^{PNO}$) form, has been synthesized and its coordination behavior toward ruthenium(II) centers studied. Under different experimental conditions, two different species bearing the ligand in either its bidentate or tridentate coordination mode were isolated by reaction with $Ru(PPh_3)_3Cl_2$. These species, respectively formulated as $[Ru(PPh_3)(\mathbf{L}^{PNO})Cl_2]$ (**1**) and $[Ru(PPh_3)(\mathbf{L}^{PN})Cl_2]$ (**2**), were fully characterized via NMR in solution and by an X-ray structural determination. Notably, compound **2** reacts with an excess of ethyl diazoacetate (EDA) in CH_2Cl_2 to give a stable η^3-diethyl maleate complex, $[Ru(\mathbf{L}^{PN})(cis\text{-}EtO(O)CCH{=}CHC(O)OEt)Cl_2]$ (**3**). The crystal structure of **3** has also been determined. Substitution reactions with 4-picoline (4-Me-py) performed on **1** led to two new complexes: the neutral complex $[Ru(4\text{-}Me\text{-}py)(\mathbf{L}^{PNO})Cl_2]$ (**5**) and the salt $[Ru(4\text{-}Me\text{-}py)_2(\mathbf{L}^{PNO})Cl](Cl)$ (**6a**). The latter compound catalyzed the intermolecular cyclopropanation of styrene with EDA in high yields and with elevated *cis* diastereoselectivity (i.e., *cis*/*trans* = 80/20).

INTRODUCTION

It is well-known that the properties of coordination compounds can be tuned by the appropriate design of multidentate ligands binding the metal center.[1] Special attention has been directed to the use of hetero-multidentate ligands having both hard and soft donor atoms (e.g. P,N, P,O, or P,N,O), since the resulting complexes often showed fascinating coordination chemistry[2] or remarkable properties in catalysis.[3] In the realm of P,N bidentate species,[4] five- or six-membered N-containing heterocycles functionalized with a diphenylphosphino pendant arm have been extensively studied. Since the first synthesis, independently performed by Pfaltz,[5] Helmchen,[6] and Williams,[7] phosphino-oxazoline ligands have been widely used in asymmetric catalysis.[8] More recent examples from Braunstein[9] and Helmchen[10] have also appeared in the literature. Phosphino-oxazine ligands (L1−L6; Chart 1) have received much attention as well. Their complexes exhibit high enantioselectivity when used as catalysts in Pd-catalyzed allylic substitution (L1−L4)[11,12] or in hydrogenation, Heck, or Diels−Alder reactions (L5 and L6).[13]

We recently initiated a study on the coordination chemistry of fully saturated N-containing heterocycles, and we have

Chart 1. Phosphinooxazine Ligands Employed in Catalytic Processes



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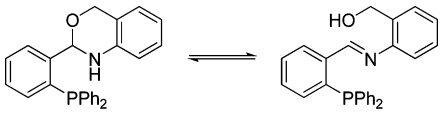
already reported on pyridine-functionalized dihydrobenzoxazine-type ligands[14,15] and on the characterization and catalytic activity of nickel(II) and palladium(II) compounds bearing oxazolidine-based ligands.[16] These species revealed a broad range of coordination modes, giving to the metal centers a variety of coordination environments (e.g., N,N, N,N,O, and N,O). Herein, we report the synthesis of a diphenylphosphinooxazine based ligand, 2-(2-(diphenylphosphino)phenyl)-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazine (**L**; Chart 2), offering either

Chart 2. Equilibrium between the Closed Bidentate L^{PN} and Open Tridentate L^{PNO} Forms of the Ligand L



L^{PN} L^{PNO}

bidentate P,N (L^{PN}) or tridentate P,N,O (L^{PNO}) donation. The coordination behavior of **L** with $Ru(PPh_3)_3Cl_2$ under different conditions has been studied. The reactivity of the resulting complexes toward ethyl diazoacetate and the *cis* diastereoselectivity in styrene cyclopropanation catalyzed by one of their 4-picoline derivatives is also described.

RESULTS AND DISCUSSION

Synthesis of Ligands. The ligand **L** was prepared by condensation of 2-(diphenylphosphino)benzaldehyde with 2-aminobenzyl alcohol, in refluxing ethanol.[17] In the ^1H NMR spectrum (see Table 1 for selected NMR data of the compounds) the AB system centered at 4.85 ppm originates from diastereotopic protons of the methylene group on the heterocyclic ring, whereas the doublet at 6.29 ppm is attributed to the C*H* in position 2 of the oxazine ring (NC*H*O), showing a relatively high coupling with the PPh_2 moiety ($^4J_{PH}$ = 6.6 Hz). The latter results in a singlet at −16.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum (full spectra are given in the Supporting Information, Figures S1−S4).

To first explore the possible conversion of free L^{PN} into L^{PNO}, the product was dissolved in toluene-d_8 and the solution heated to 85 °C, measuring different ^1H NMR spectra at 10 °C intervals (Supporting Information, Figure S5). The appearance and progressive increase of signals attributed to the open iminic form occur, with a 65% extent of conversion of L^{PN} into L^{PNO} at 85 °C. At this stage the signals due to the azomethine proton (9.07 ppm, d, $^4J_{PH}$ = 4.7 Hz), the methylene group (4.65 ppm, s), and O*H* (4.48 ppm, s) are easily identified (Figure 1).

Synthesis of Ruthenium(II) Compounds. Depending on the reaction temperature, it was possible to isolate two different ruthenium(II) complexes, bearing the ligand in either its bidentate (L^{PN}) or tridentate form (L^{PNO}) (Scheme 1).

When a suspension of $Ru(PPh_3)_3Cl_2$ and **L** (in a 1/1.1 molar ratio) was refluxed in toluene, a deep red solid was obtained, later formulated as $[Ru(PPh_3)(L^{PNO})Cl_2]$ (**1**). The presence of the ligand in its tridentate form is proven by solution NMR data (Figures S6−S9 in the Supporting Information): in the ^1H NMR (CD_2Cl_2, 25 °C), the doublet at 2.69 ppm (J_{HH} = 10.9 Hz) is attributed to the OH group and disappears after treatment with D_2O, whereas the H_a and H_b protons of the CH_2OH moiety generate two signals, respectively, at 5.27 ppm (triplet, J_{HH} = 11.0 Hz) and 4.43 ppm (doublet, J_{HH} = 10.8 Hz).

Table 1. Selected ^1H and $^{31}P\{^1H\}$ NMR Spectroscopic Data for Ligands L^{PN} and L^{PNO} and Compounds $[Ru(PPh_3)(L^{PNO})Cl_2]$ (1), $[Ru(PPh_3)(L^{PN})Cl_2]$ (2), $[Ru(L^{PN})(cis\text{-}EtO(O)CCH{=}CHC(O)OEt)Cl_2]$ (3), $[Ru(4\text{-}Me\text{-}py)(L^{PNO})Cl_2]$ (5), and $[Ru(4\text{-}Me\text{-}py)_2(L^{PNO})Cl](Cl)$ (6a)

L^{PN}[a]	
$\delta(^1H)$ (ppm)	4.78 (d, H_a), 4.93 (d, H_b), 9.07 (d, NC*H*O)
$\delta(^{31}P\{^1H\})$ (ppm)	−16.60 (s, PPh_2)
L^{PNO}[b]	
$\delta(^1H)$ (ppm)	4.48 (O*H*), 4.65 (CH_2O), 6.29 (*H*C=N)
$\delta(^{31}P\{^1H\})$ (ppm)	−16.60 (PPh_2)
$[Ru(PPh_3)(L^{PNO})Cl_2]$ (1)[a]	
$\delta(^1H)$ (ppm)	2.69 (O*H*), 4.43 (H_b), 5.27 (H_a), 8.85 (*H*C=N)
$\delta(^{31}P\{^1H\})$ (ppm)	39.9 (PPh_3), 62.1 (PPh_2)
$[Ru(PPh_3)(L^{PN})Cl_2]$ (2)[a]	
$\delta(^1H)$ (ppm)	4.99 (CH_2O), 6.52 (NC*H*O)
$\delta\ ^{31}P\{^1H\}$ (ppm)	44.0 (PPh_3), 75.6 (PPh_2)
$[Ru(L^{PN})(cis\text{-}EtO(O)CCH{=}CHC(O)OEt)Cl_2]$ (3)[a]	
$\delta(^1H)$ (ppm)	1.37 (CH_3), 1.43 (CH_3), 4.24 (CH_2), 4.45 (CH_2), 4.84 (H_b), 4.99 (H_a), 6.52 (*H*C=C), 6.60 (NCHO), 6.68 (*H*C=C)
$\delta(^{31}P\{^1H\})$ (ppm)	51.5 (PPh_2)
$[Ru(4\text{-}Me\text{-}py)(L^{PNO})Cl_2]$ (5)[a]	
$\delta(^1H)$ (ppm)	2.26 (CH_3), 4.49 (O*H*), 4.92 (H_b), 5.64 (H_a), 8.92 (*H*C=N)
$\delta(^{31}P\{^1H\})$ (ppm)	73.3 (PPh_2)
$[Ru(4\text{-}Me\text{-}py)_2(L^{PNO})Cl](Cl)$ (6a)[a]	
$\delta(^1H)$ (ppm)	2.23 (CH_3), 2.24 (CH_3), 2.41 (O*H*), 2.59 (H_b), 4.22 (H_a), 9.01 (*H*C=N)
$\delta(^{31}P\{^1H\})$ (ppm)	61.0 (PPh_2)

[a]Spectra measured in CD_2Cl_2, at 25 °C. [b]Spectrum measured in toluene-d_8, at 85 °C.

The different chemical shifts for H_a and H_b are a consequence of the coordination of the oxygen of the methylene group to the metal center. The triplet for H_a derives from similar coupling constants of this nucleus with both H_b and OH: indeed, the disappearance of coupling with OH after deuteration causes signal simplification into a doublet ($J_{H_a-H_b}$ = 11.2 Hz). Finally, the iminic proton resonates as a doublet at δ 8.85 ppm. The $^4J_{PH}$ value (8.3 Hz) is in the range found for other similar Ru(II) complexes.[18] The presence of a residual PPh_3 coordinated to Ru(II) is confirmed by $^{31}P\{^1H\}$ NMR, where two doublets are observed respectively at 39.9 ppm (J_{PP} = 20.8 Hz, PPh_3) and 62.1 ppm (J_{PP} = 24.2 Hz, PPh_2). These values for coupling constants suggest a *cis* disposition between the phosphorus nuclei, as already reported for other Ru(II) phosphine complexes.[19] The X-ray crystal structure of **1** confirmed these hypotheses (Figure 2).

For complexes bearing *P,N*-iminophosphine ligands, the higher *trans* influence of the phosphorus atom in comparison to that of the imine donor functionality[2b,20] leads to longer distances for bonds *trans* to the phosphorus. On the other hand, in the presence of tridentate P,N,O ligands (with N being an iminic nitrogen) the reverse situation is usually observed;[21] the related bond distances in $[Ru(PPh_3)(L^{PNO})Cl_2]$ (namely, Ru1−O1 = 2.212(3) Å and Ru1−P2 = 2.345(1) Å) follow this rule.

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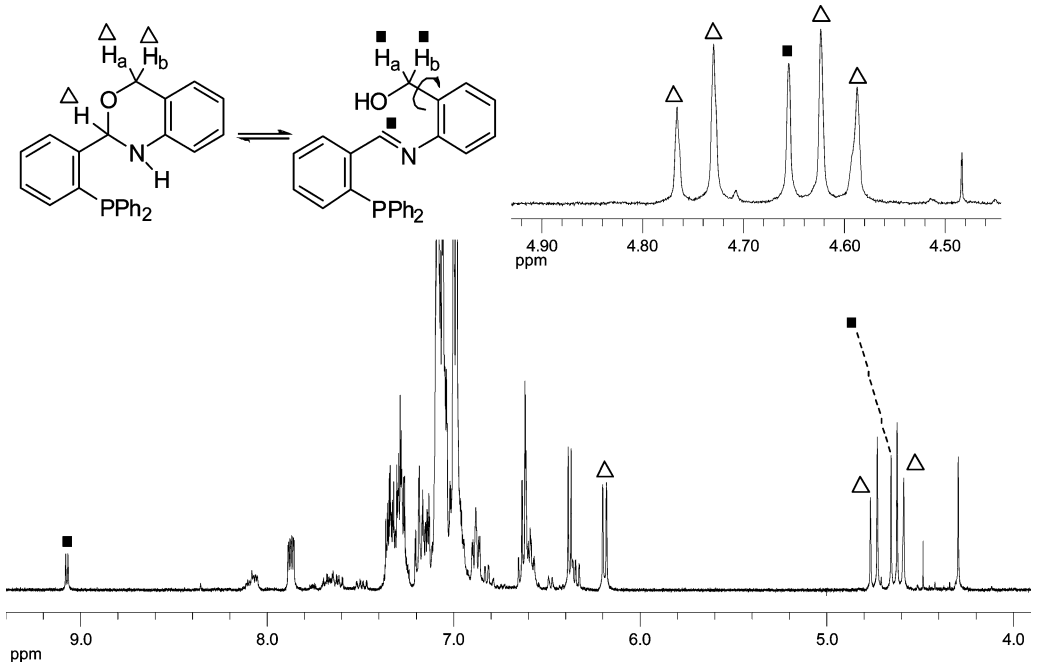
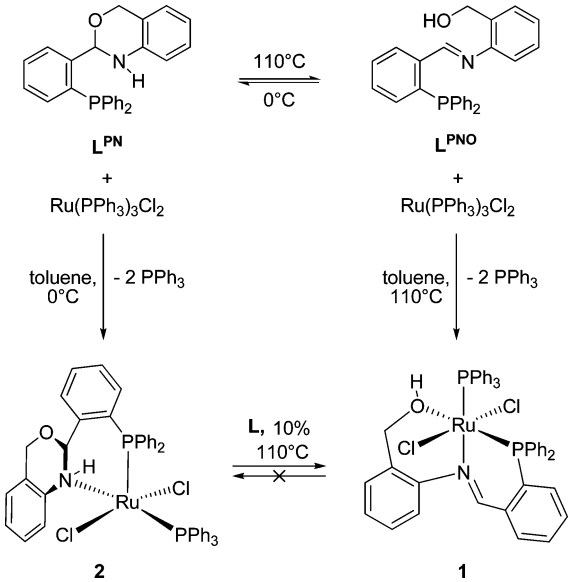


Figure 1. ^{1}H NMR spectrum (toluene-d_8) showing the equilibrium between $\mathbf{L}^{PN}$ (△) and $\mathbf{L}^{PNO}$ (■) present at 85 °C. Inset: expansion of the aliphatic region.

Scheme 1. Syntheses of $[Ru(PPh_3)(L^{PNO})Cl_2]$ (1) and $[Ru(PPh_3)(L^{PN})Cl_2]$ (2)



Alternatively, when the temperature was maintained at 0 °C during the reaction of $Ru(PPh_3)_3Cl_2$ with **L** (1/1.1 molar ratio) in toluene, an emerald green compound was formed, subsequently identified as $[Ru(PPh_3)(L^{PN})Cl_2]$ (**2**). In the ^{1}H NMR (Figure S10, Supporting Information), the pattern of $\mathbf{L}^{PN}$ appears: a quartet at 4.99 ppm, attributable to the methylene group, and a doublet at 6.52 ppm, assigned to the methine of the oxazine ring. This latter resonance does not originate from a coupling with phosphorus, as evidenced by a ^{1}H–^{31}P HMBC experiment (Supporting Information). Thus, it is assumed that in solution complex **2** is present as a mixture of diastereoisomers[22] and the signal relative to NC*H*O appears as a doublet. In the ^{31}P{^{1}H} NMR (Figure S12, Supporting Information) two resonances are seen: one related to the PPh_2 moiety of the ligand (75.6 ppm, J_{PP} = 26.4 Hz) and the other due to PPh_3 (44.0 ppm, J_{PP} = 31.4 Hz). These values for J_{PP} suggest once again a *cis* disposition of the phosphorus atoms, as confirmed by an X-ray structural analysis[23] (Figure 3), which shows the Ru(II) center in **2** to be in a slightly distorted square pyramidal geometry (τ = 0.12).[24]

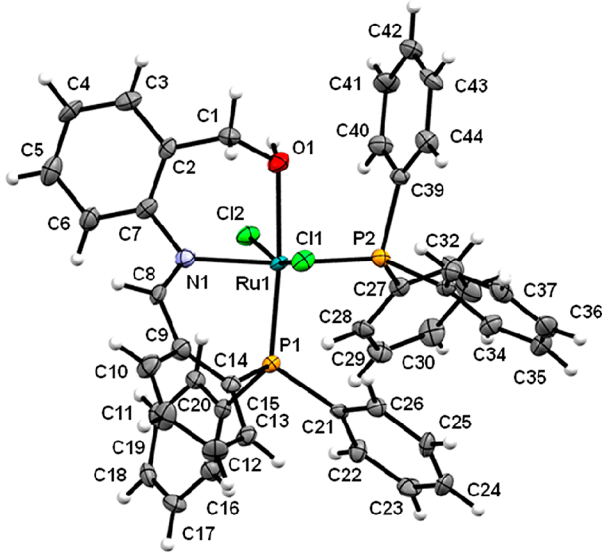


Figure 2. ORTEP representation of **1** at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)–Cl(1) = 2.3924(11), Ru(1)–Cl(2) = 2.4268(11), Ru(1)–P(1) = 2.2253(13), Ru(1)–N(1) = 2.142(4), Ru(1)–O(1) = 2.212(3), Ru(1)–P(2) = 2.3448(14); Cl(1)–Ru(1)–Cl(2) = 164.06(4), N(1)–Ru(1)–Cl(1) = 85.65(10), N(1)–Ru(1)–Cl(2) = 89.54(11), N(1)–Ru(1)–P(1) = 87.70(11), N(1)–Ru(1)–P(2) = 174.12(12), N(1)–Ru(1)–O(1) = 85.31(13), O(1)–Ru(1)–P(1) = 170.72(9), P(1)–Ru(1)–P(2) = 98.03(5).

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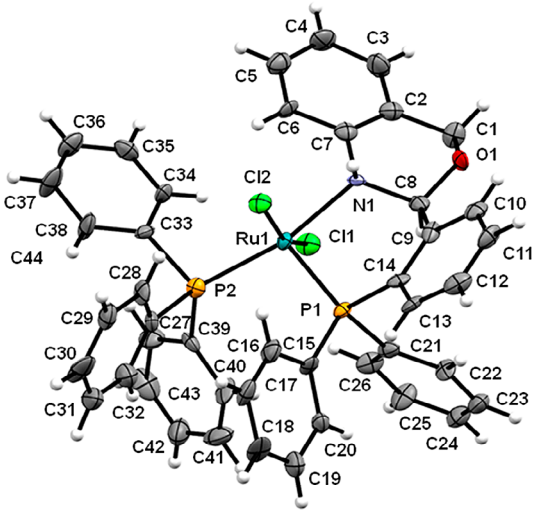


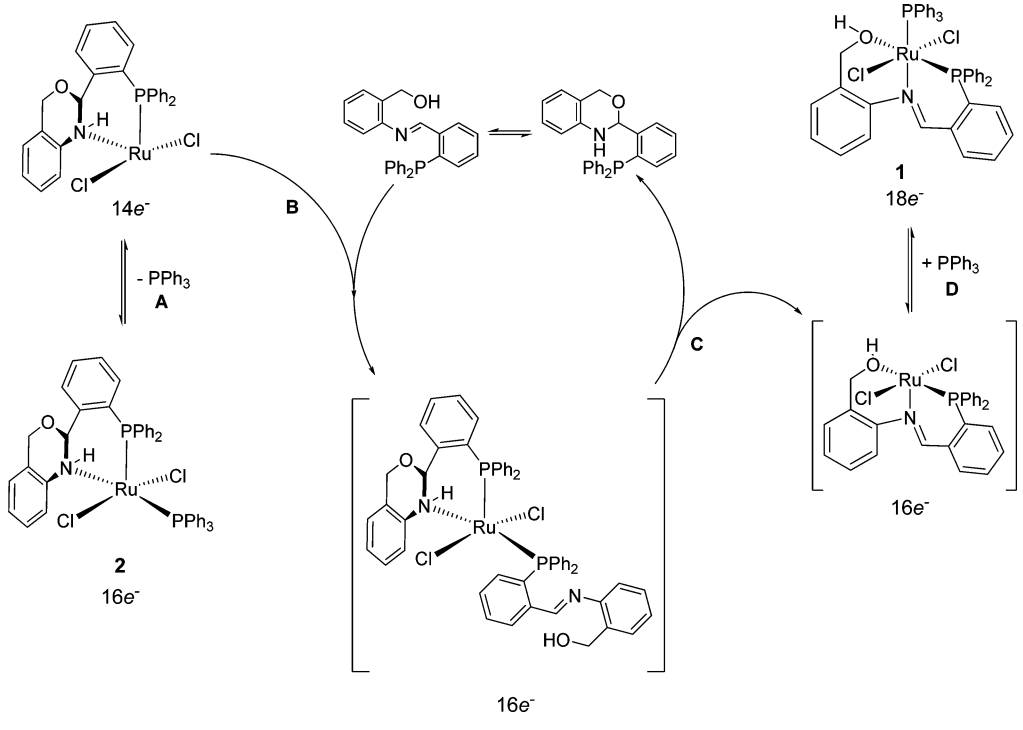
Figure 3. ORTEP representation of **2** at the 50% probability level with dichloromethane molecules omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−Cl(1) = 2.402(3), Ru(1)−Cl(2) = 2.375(3), Ru(1)−P(1) = 2.208(3), Ru(1)−N(1) = 2.176(8), Ru(1)−P(2) = 2.309(3), O(1)−C(8) = 1.398(11); Cl(1)−Ru(1)−Cl(2) = 159.95(10), N(1)−Ru(1)−Cl(1) = 81.1(2), N(1)−Ru(1)−Cl(2) = 86.7(2), N(1)−Ru(1)−P(1) = 91.4(2), N(1)−Ru(1)−P(2) = 166.9(2), P(1)−Ru(1)−P(2) = 101.67(11).

Equilibrium Studies. To shed light on the mechanism leading to **1** and **2**, we investigated the possible conversion of one species into the other. Initially, a suspension of $[Ru(PPh_3)(L^{PN})Cl_2]$ in toluene was heated to reflux, but no structural change was noticed even after a long reaction time (12 h). Thus, once coordinated, the ligand does not undergo ring opening and the mere thermal transformation of **2** into **1** is prevented. As in the original synthesis of **1** a slight excess of **L** was used (1/1.1 Ru/ligand ratio), a suspension of compound **2** in toluene was next refluxed in the presence of a catalytic amount of exogenous ligand (10 mol % relative to [Ru]). This led to a quick change in color from emerald green to deep red, and after stirring for 4 h, a red solid was isolated. All spectroscopic features match those of **1**. Consequently, both temperature and the slight excess of free ligand play a key role in the conversion of **2** into **1**. To prove this assumption, a further reaction of **2** with a slight excess of free **L** was performed, this time with the temperature kept at 20 °C: no transformation was observed, definitely certifying the synergistic influence of temperature and free-ligand excess in the formation of **1**, both in the original preparation from $Ru(PPh_3)_3Cl_2$ and **L** and as a conversion of **2**.

In an additional experiment, a suspension of compound **2** was refluxed in toluene in the simultaneous presence of a catalytic amount of free ligand and 1 equiv (with respect to ruthenium) of exogenous PPh_3. Under these conditions, species **2** did not turn into **1**, meaning that the first step of formation of **1** from **2** is presumably the dissociation of PPh_3 (Scheme 2, **A**). Next, the vacant site in the 14e $[Ru(L^{PN})Cl_2]$ species is occupied by the PPh_2 moiety of the free ligand, which reasonably coordinates in its iminic form, predominant at high temperature (**B**). The subsequent coordination of nitrogen and oxygen forces the ligand in its hetero-tridentate L^{PNO} binding mode, and the concomitant extrusion of the hetero-bidentate L^{PN} form leads to the five-coordinated $[Ru(L^{PNO})Cl_2]$ intermediate (**C**), which readily reacts with PPh_3 still present in the bulk to generate **1** (**D**).

Presumably, the driving force of the reaction is the higher stability of octahedral $[Ru(PPh_3)(L^{PNO})Cl_2]$ with respect to the square-pyramidal $[Ru(PPh_3)(L^{PN})Cl_2]$. Actually, an evaluation of relative energies of species **1** and **2** (DFT; see the Supporting Information) shows complex **1** being 5.69 kcal/mol more stable with respect to complex **2**. As a matter of fact, when it is treated under the described experimental conditions, compound **2** is

Scheme 2. Proposed Mechanism for Conversion of $[Ru(PPh_3)(L^{PN})Cl_2]$ (2) into $[Ru(PPh_3)(L^{PNO})Cl_2]$ (1)



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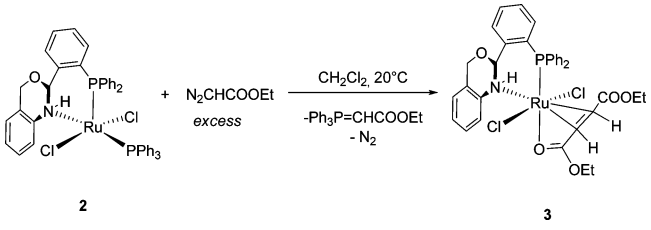
irreversibly converted into **1**. In contrast, when it is suspended in toluene at either 20 or 0 °C, in the presence of a catalytic amount of exogenous ligand (10 mol %), compound **1** did not convert into **2** even after a long reaction time (24 h).

Reactivity with Ethyl Diazoacetate (EDA). In our ongoing exploration of transition-metal-catalyzed cyclopropanation of olefins by means of EDA decomposition,[25] we tested the activity of compounds **1** and **2** as cyclopropanation catalysts. Following an established procedure, [Ru(PPh$_3$)-(**L**^{PNO})Cl$_2$] was first dissolved in dichloromethane (8 mL) in the presence of styrene as substrate (1/200 [Ru]/olefin molar ratio). Ethyl diazoacetate was then added dropwise over a 4 h period (1/100 [Ru]/EDA molar ratio),[26] and the progress of the reaction was monitored via infrared spectroscopy ($\nu_{N\equiv N}$) and GC-MS. Notably, no gas (N$_2$) evolution was noticed and no cyclopropanation products were detected after 24 h. Even performing the reaction at 65 °C (in 1,2-dichloroethane) did not evidence any conversion: indeed, at this temperature the dissociation of PPh$_3$ should take place, generating the pentacoordinate species [Ru(**L**^{PNO})Cl$_2$] with a free coordination site which could enter the catalytic cycle. Thus, the absence of activity of **1** cannot be ascribed to steric hindrance, because the coordinative saturation of the Ru(II) center in **1** is presumably lost at 65 °C (due to dissociation of PPh$_3$). Most likely, electronic contributions made by the diphenylphosphino-imino ligand should be invoked. Probably, the ligand **L**^{PNO} reduces electron density on ruthenium and discourages the formation of the electrophilic carbene [Ru(=CHC(O)OEt)-(**L**^{PNO})Cl$_2$]. As a partial proof, also the square-pyramidal 16e [Ru(PPh$_3$)(**L**^{PN})Cl$_2$], having a free coordination site, did not catalyze styrene cyclopropanation to a significant extent when it was dissolved in dichloromethane under the same conditions as for **1**. To better understand this conduct, [Ru(PPh$_3$)(**L**^{PN})Cl$_2$] was treated with a 10-fold excess of ethyl diazoacetate, in dichloromethane, in the absence of olefin. After the reaction mixture was stirred for 12 h at room temperature, a color change from emerald green to brown was noticed. The solution was evaporated to dryness and the crude residue recrystallized from diethyl ether, affording a light brown solid subsequently identified as [Ru(**L**^{PN})(*cis*-EtO(O)CCH=CHC(O)OEt)Cl$_2$] (**3**) (Scheme 3).

Scheme 3



2 3

The IR spectrum of **3** shows two absorptions, respectively, at 1725 and 1622 cm^{-1}, assigned to C=O of two different ethyl acetate groups. The simultaneous presence of otherwise bonded C(O)OEt groups was also detected in solution by ^{1}H and ^{13}C NMR (Table 1; Figures S13–S15, Supporting Information), showing the concomitant presence in compound **3** of **L**^{PN} and a coordinated diethyl maleate molecule, together with the displacement of the original PPh$_3$. Indeed, a single resonance at 51.5 ppm due to the PPh$_2$ moiety of the ligand is detected in the ^{31}P{^{1}H} NMR. These features were eventually confirmed by X-ray diffraction (Figure 4).

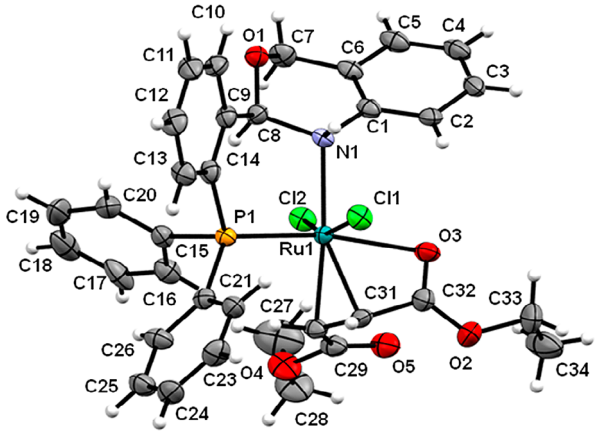


Figure 4. ORTEP representation of **3** at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)–Cl(1) = 2.4127(14), Ru(1)–Cl(2) = 2.3672(13), Ru(1)–P(1) = 2.2578(13), Ru(1)–N(1) = 2.216(4), Ru(1)–O(3) = 2.330(4), Ru(1)–C(31) = 2.126(5), Ru(1)–C(30) = 2.205(5); Cl(1)–Ru(1)–Cl(2) = 160.12(5), N(1)–Ru(1)–Cl(1) = 80.05(11), N(1)–Ru(1)–Cl(2) = 81.73(11), N(1)–Ru(1)–P(1) = 90.32(11), N(1)–Ru(1)–O(3) = 100.21(13), N(1)–Ru(1)–C(30) = 166.80(17), N(1)–Ru(1)–C(31) = 153.72(19), P(1)–Ru(1)–O(3) = 167.19(9).

The formation of such an uncommon Ru–diethyl maleate complex has been previously described by Lugan and Lavigne[27] as a result of the reaction of pyridine-functionalized phosphine Ru(II) complexes with excess ethyl diazoacetate. Despite showing features similar to those of the already reported analogous compound, species **3** presents some relevant differences in its crystal structure: (i) a shorter Ru–O bond (2.330(4) vs 2.414(5) Å) and (ii) a *trans* disposition of the chlorido ligands, in comparison with the *cis*-Ru(Cl)$_2$ fragment in Lavigne's complex.

The commonly accepted mechanism for the generation of such a compound first considers the coordination to ruthenium of the carbene moiety and its coupling with the coordinated PPh$_3$ molecule, with consequent elimination of the phosphonium ylide Ph$_3$P=C(H)COOEt.[28] The resulting 14e species readily coordinates two additional carbene units, ultimately coupling to give the diethyl maleate fragment. We can assume that this is the working mechanism also involved in the reaction between **2** and EDA. Actually, the formation of Ph$_3$P=C(H)C(O)OEt was confirmed by a single resonance at about 18 ppm in the ^{31}P{^{1}H} NMR analysis of the crude bulk product. The stability of the resultant complex **3** is due to electronic contributions, with the extra Ru–O=C bond (Ru–O = 2.330(4) Å) occupying the sixth coordination site on Ru(II). Strong donation from the metal center to the π^* orbitals of the oxazine ring has been previously invoked to justify uncommon behavior of oxazine-containing complexes.[29] This is probably the case with compound **3**, where the **L**^{PN} ligand reduces electron density on the metal, hence favoring carbonyl oxygen coordination. The formation of the stable diethyl maleate species intercepted in the reaction with EDA precludes compound **2** from being an active catalyst in styrene cyclopropanation.

Substitution Reactions with 4-Picoline. As is known, nitrogen-containing heterocyclic ligands such as pyridines are σ

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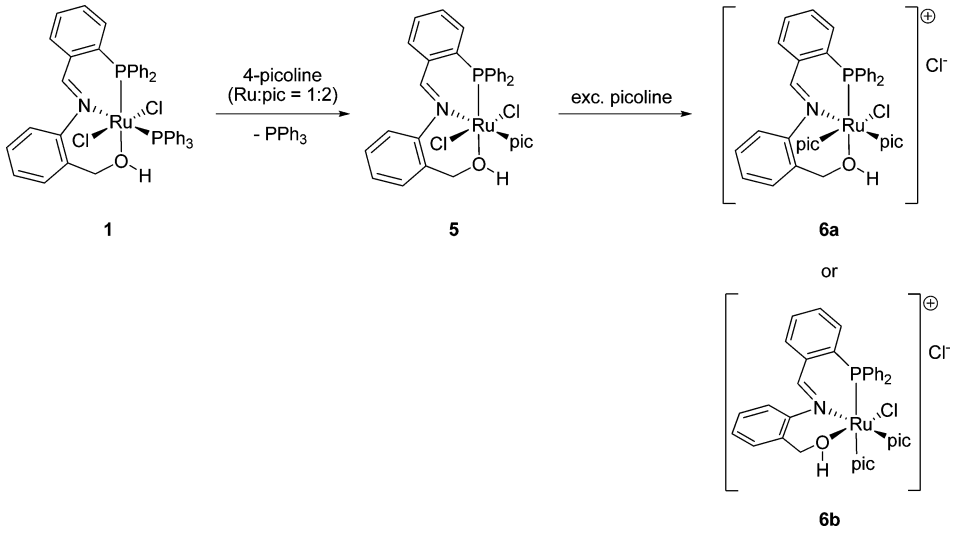
Scheme 4. Suggested Mechanism of Formation of 4-Picoline-Containing Derivatives 5 and 6 Starting from 1



donors with only weak π-acceptor character;[30] thus, we attempted the substitution of PPh_3 with 4-picoline (4-Me-py) with the aim of enhancing electron density on the Ru(II) center. Initially, an emerald green suspension of the pentacoordinated $[Ru(PPh_3)(\mathbf{L}^{PN})Cl_2]$ (**2**) in diethyl ether was reacted with a 2-fold excess of 4-picoline, and the color immediately changed to orange. The product was identified as $[Ru(PPh_3)(4\text{-Me-py})(\mathbf{L}^{PN})Cl_2]$ (**4**) but could not be additionally investigated in solution. Indeed, when **4** is dissolved in CH_2Cl_2, acetone, or toluene, the prompt dissociation of coordinated 4-picoline occurs, restoring an emerald green solution corresponding to complex **2**. Then, an alternative substitution reaction was performed, this time starting from $[Ru(PPh_3)(\mathbf{L}^{PNO})Cl_2]$ (**1**), which was refluxed in toluene in the presence of 4-picoline (1/2 molar ratio) for 6 h. The isolated solid appeared to be a mixture of two products. The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 25 °C) showed two single resonances, respectively, at 73.3 and 61.0 ppm. Such a pattern without any J_{PP} coupling can only originate from two distinct products, each having a single phosphorus atom bound to the metal. In both compounds the ligand is coordinated in the tridentate P,N,O form, as evidenced by the appearance of merely its pattern in the ^1H NMR spectrum. Moreover, the integration of signals allows us to establish different ratios between the ligand and 4-picoline in the two complexes. Later, these were formulated as $[Ru(4\text{-Me-py})(\mathbf{L}^{PNO})Cl_2]$ (**5**) and $[Ru(4\text{-Me-py})_2(\mathbf{L}^{PNO})Cl](Cl)$ (**6**). In principle, two isomers of complex **6** (**6a**, *mer*; **6b**, *fac*) could form in the reaction of **1** or **5** with excess 4-picoline (Scheme 4). Unfortunately, despite several attempts to grow single crystals of these 4-picoline derivatives, no suitable crystals for X-ray determination were obtained. Nevertheless, due to steric constraints the *fac* configuration in **6b** is presumably less favored than the *mer* form encountered in **6a**, which is thought to be the preferred species obtained. Indeed, a comparison of the energies of **6a** and **6b** obtained by optimization of the relative geometries (DFT; see the Supporting Information) reveals species **6a** to be more stable than **6b** by about 14.0 kcal/mol.

The formulation of species **5** and **6a** could be tentatively assigned by NMR investigation in solution. Luckily, it has been possible to prepare pure **5** by boiling a 1/2 suspension of $[Ru(PPh_3)(\mathbf{L}^{PNO})Cl_2]$ and 4-picoline, in *m*-xylene, at 140 °C for 6 h. The methylene signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra of the product (Supporting Information) show a pattern quite similar to that for the corresponding protons in **1** (see the Experimental Section for details). Consequently, compound **5** was identified as $[Ru(4\text{-Me-py})(\mathbf{L}^{PNO})Cl_2]$, deriving from a simple substitution of PPh_3 in **1** with a molecule of 4-picoline. Complex **5** was associated with the singlet at 73.3 ppm in $^{31}P\{^1H\}$ NMR.

The presence of another species bearing two molecules of 4-picoline, as evidenced by ^1H NMR analysis of the initial mixture (namely, **6a**), prompted us to investigate the reaction with increasing amounts of 4-picoline. Indeed, when $[Ru(PPh_3)(\mathbf{L}^{PNO})Cl_2]$ was refluxed in the presence of 4 equiv of 4-picoline for 6 h, the intensity of the signal relative to **6a** increased, and a nearly 5/1 ratio between **6a** and **5** was finally obtained by employing a 1/8 [Ru]/4-picoline molar ratio (Experimental Section). Worthy of note, in addition to the synthesis from **1**, the same selectivity toward **6a** could also be reached by a direct synthesis starting from the formerly isolated complex **5**, in *m*-xylene, in the presence of an excess of 4-picoline. Compound **6a** was then related to the resonance at 61.0 ppm in the $^{31}P\{^1H\}$ NMR.

Most probably, treatment of **1** with 4-picoline initially forms complex **5**, which progressively evolves to complex **6a** due to the excess of heterocyclic amine. The introduction of a donor ligand such as 4-picoline in **5** enhances electron density on ruthenium, thus favoring chloride dissociation. The vacant coordination site generated is then occupied by a second molecule of 4-picoline, giving the cationic **6a**. The ionic nature of **6a** is strongly supported by the molar conductivity (Λ_M = 80.8 Ω^{-1} cm^2 mol^{-1}) measured at 20 °C for a 10^{-3} M solution in methanol; this value falls into the range (80−115 Ω^{-1} cm^2 mol^{-1}) expected for a 10^{-3} M methanol solution of a 1/1 electrolyte type complex.[31]

Compound **6a** was characterized via ^1H and $^{13}C\{^1H\}$ solution NMR (Supporting Information). The main feature of its pattern in ^1H NMR (CD_2Cl_2, 25 °C) is definitely represented by the high proton splitting of the bonded CH_2OH: H_a and H_b are observed respectively at 4.22 and 2.59 ppm, with a separation, Δ_{ppm}, of about 1.63 ppm. This value is almost twice the difference observed in both **1** (Δ_{ppm} = 0.84) and **5** (Δ_{ppm} = 0.72). Both signals appear as doublets of

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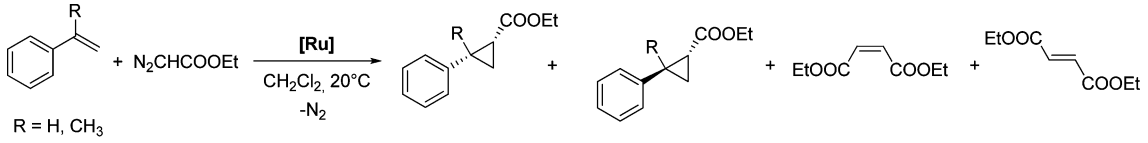
Table 2. Cyclopropanation of Styrene by Means of EDA Decomposition Catalyzed by the Ru(II) Compounds Studied in This Work[a]



A B C D

entry	[Ru]	substrate	A + B (%)[b]	C + D (%)[b]	A/B ratio[c]	C/D ratio[c]
1	**1**	styrene				
2	**2**	styrene				
3	**3**	styrene				
4	**5**	styrene				
5	**6a**	styrene	81	19	79.9/20.1	61.5/38.5
6	**6a**	α-methylstyrene	33	67	69.7/30.3	95.1/4.9
7	**6a**			100		98.2/1.8
8[d]	**6a**+Cl$^-$	styrene	<10	<5		

[a]Conditions: [Ru]/EDA/olefin =1/100/200; CH_2Cl_2 (8 mL), 20 °C. [b]Yields based on EDA consumption (monitored by disappearance of $\nu_{N\equiv N}$ in infrared spectroscopy): (**A** + **B**) + (**C** + **D**) = 100%. [c]Determined by GC-MS analysis after 4 h. [d]Catalyst: **6a** in the presence of 1 equiv of Bu_4NCl.

doublets, H_a and H_b coupling with each other ($^2J_{HH}$ = 11.8 Hz) and with O*H* ($^3J_{HH}$ = 4.6 Hz for H_a and 2.4 Hz for H_b). As was the case for **1** and **5**, also in the case of **6a** the loss of OH coupling after addition of D_2O in the NMR tube induced the simplification of H_a and H_b signals into two doublets. These two resonances also experience a significant upfield shift with respect to **1** and **5**, meaning that the CH_2 moiety is positioned within the shielding cone of the pyridine ring *cis* to it.[32] The O*H* proton signal is highly shielded as well, appearing as a singlet at 2.40 ppm.

As was noted, it was not possible to perform an X-ray structural determination of these species [Ru(4-Me-py)($\mathbf{L}^{PNO}$)-Cl_2] and [Ru(4-Me-py)$_2$($\mathbf{L}^{PNO}$)Cl](Cl), but their catalytic performance in styrene cyclopropanation (vide infra) gave a supplementary corroboration of the proposed formulations.

Cyclopropanation of Styrene. The absence of catalytic activity of species **1**−**3** (Table 2, entries 1−3) in the cyclopropanation of styrene, in the presence of ethyl diazoacetate (EDA) as carbenoid source, has already been discussed in the text. Complexes **5** and **6a** were also tested as catalysts in the same reaction, showing different behavior, as evidenced in Table 2 (entries 4−7). When it was dissolved in a CH_2Cl_2 solution of styrene, at 20 °C, [Ru(4-Me-py)($\mathbf{L}^{PNO}$)Cl_2] (**5**) did not convert the olefin into the corresponding cyclopropylic esters after addition of EDA. In contrast, [Ru(4-Me-py)$_2$($\mathbf{L}^{PNO}$)Cl](Cl) (**6a**) efficiently catalyzed the same reaction in high yields (81%, entry 5) and with elevated *cis* selectivity (*cis*/*trans* ≈ 80/20). In principle, during ruthenium-catalyzed decomposition of diazo compounds in the presence of olefins, a competitive metathesis mechanism could also occur. Notably, when **6a** was employed as the catalyst, no evidence of formation of metathesis products (i.e., PhCH═C(H)C(O)OEt) was observed by GC-MS analysis. Despite a lower yield of conversion into cyclopropanes (33%, entry 6), a similar relatively high *cis* diastereoselectivity was encountered in the cyclopropanation of α-methylstyrene catalyzed by **6a**.

As exhaustively recently reviewed by Perez and co-workers[33] and by Nishiyama,[34] among the numerous Ru complexes which were used as catalysts in the intermolecular cyclopropanation of styrene with ethyl diazoacetate, the large majority induced a certain excess of the thermodynamically preferred *trans* isomer. *cis* diastereoselectivity has been first reported by Katsuki,[35] who employed a [(salen)Ru(NO)$^+$] complex to obtain a 93/7 *cis*/*trans* ratio and later by Mezzetti[36] with cationic complexes bearing tetradentate PNNP ligands and Kim[37] with a catalyst generated in situ from [Ru(dmso)$_4Cl_2$] and ferrocenyl-diphosphane ligands. Then, the present work adds compound **6a** as a further example of the restricted class of *cis*-diastereoselective Ru catalysts for styrene cyclopropanation with EDA. This preference for the *cis* isomer is noticed also in EDA self-coupling: indeed, when **6a** is dissolved in CH_2Cl_2, at 20 °C, in the absence of olefin (entry 7), addition of EDA afforded diethyl maleate as the only product. This conduct somehow resembles the formation of the stable η^3-diethyl maleate complex **3** intercepted in the reaction of **2** with an excess of EDA.

The commonly accepted mechanism for olefin cyclopropanation by EDA contemplates the formation in the catalytic cycle of an active intermediate species bearing a [Ru═C(H)C(O)OEt] fragment. In our case, this could derive from the coordination of the CHC(O)OEt fragment to a vacant site generated from the dissociation of 4-picoline. However, this is in contrast with the dissimilar activity possessed by compounds **5** and **6a**. Indeed, both complexes have a 4-picoline molecule coordinated to Ru(II), being equally predisposed to generate a vacant site on the metal. In addition, compound **5** does not catalyze styrene cyclopropanation, meaning that the higher activity shown by the compound [Ru(4-Me-py)$_2$($\mathbf{L}^{PNO}$)Cl](Cl) (**6a**) has to be ascribed mainly (if not totally) to electronic effects. The replacement of PPh_3 and one chloride in **1** with two molecules of 4-picoline in the inner coordination sphere of ruthenium in **6a** facilitates the progress into the intermediate Ru carbene active species. Presumably, this latter species derives from the initial dissociation of the residual chloride bonded to ruthenium and could be formulated as [Ru(4-Me-py)$_2$($\mathbf{L}^{PNO}$)(═C(H)C-(O)OEt)]$^{2+}$(Cl)$^-_2$. It is known that donor ligands such as pyridines enhance chloride lability in ruthenium complexes, favoring the dissociation of a chloride ligand coordinated to the metal.[38] This could also be the case for **6a**, where the chloride dissociates due to the presence of two molecules of 4-picoline. The resultant cationic fragment [Ru(4-Me-py)$_2$($\mathbf{L}^{PNO}$)]$^{2+}$ readily evolves to the Ru carbene intermediate, ultimately

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leading to cyclopropanation products. To support this hypothesis, we performed a supplementary catalytic run in the presence of exogenous chloride ions, by dissolving 1 equiv of Bu_4NCl in the CH_2Cl_2 mixture of catalyst and styrene, before adding EDA (entry 8). As expected, the catalytic activity of **6a** was reduced to a negligible olefin conversion into products. It is thought that free Cl^- in solution depresses the initial dissociation of chloride, thus preventing the formation of the Ru carbene intermediate. Additional studies will help to extend the scope and limitations of this reaction, hopefully leading to clarify the nature of the complexes involved.

■ CONCLUSION

In summary, ruthenium(II) complexes bearing the diphenylphosphinoxazine derived ligand **L** have been prepared and characterized. Depending on the experimental conditions, in the reaction with $Ru(PPh_3)_3Cl_2$, **L** displays different coordination modes, namely a bidentate P,N ($\mathbf{L}^{PN}$) and a tridentate P,N,O form ($\mathbf{L}^{PNO}$), giving rise respectively to $[Ru(PPh_3)(\mathbf{L}^{PNO})Cl_2]$ (**1**) and $[Ru(PPh_3)(\mathbf{L}^{PN})Cl_2]$ (**2**). The electronic properties imposed by the diphenyl-phosphinoxazine ligand strongly influence the reactivity of these species. Actually, in the reaction of **2** with excess ethyl diazoacetate (EDA), the stable η^3-diethyl maleate complex $[Ru(\mathbf{L}^{PN})(cis\text{-}EtO(O)CCH{=}CHC(O)OEt)Cl_2]$ (**3**) was intercepted. Its structural characterization represents the second example known in the literature of such a Ru(II) compound. Substitution reactions with 4-picoline (4-Me-py) were then performed on **1**, and two novel complexes, formulated as $[Ru(4\text{-}Me\text{-}py)(\mathbf{L}^{PNO})Cl_2]$ (**5**) and $[Ru(4\text{-}Me\text{-}py)_2(\mathbf{L}^{PNO})Cl](Cl)$ (**6a**), were isolated. Finally, compound **6a** catalyzed the intermolecular cyclopropanation of styrene with EDA, in good yields and with a high diastereoselectivity toward the *cis* isomer.

■ EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under purified nitrogen using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures prior to use. NMR spectra were recorded with an AVANCE 400 Bruker spectrometer at 400 MHz for ^1H NMR, 100 MHz for $^{13}C\{^1H\}$ NMR, and 162 MHz for $^{31}P\{^1H\}$ NMR. Chemical shifts are given as δ values in ppm relative to residual solvent peaks as the internal reference (for ^1H and ^{13}C NMR) and to external H_3PO_4 (85%) (for ^{31}P NMR). J values are given in Hz. ^{13}C NMR spectra are ^1H decoupled, and the determination of the multiplicities was achieved by the APT pulse sequence. Elemental analyses were obtained with a Perkin-Elmer CHN Analyzer 2400 Series II. Quantitative analyses of products in the catalytic runs were performed on a Finningan Trace GC instrument with a DB-5MS UI capillary column (30 m, 0.25 mm) equipped with a Finningan Trace mass spectrometer. Conductivity measurements were performed with a digital conductimeter (Orion Research Model 101) using platinum electrodes. $Ru(PPh_3)_3Cl_2$[39] and 2-(diphenylphosphino)-benzaldehyde[40] were prepared according to literature methods; 2-aminobenzyl alcohol, ethyl diazoacetate, triphenylphosphine (Aldrich), and 4-picoline (Fluka) were used without further purification. Styrene and α-methylstyrene (Aldrich) employed in catalytic runs were taken from sealed bottles.

2-(2-(Diphenylphosphino)phenyl)-2,4-dihydro-1*H*-benzo[*d*]-[1,3]oxazine (L). To a solution of 2-(diphenylphosphino)-benzaldehyde (1 g, 3.44 mmol) and 2-aminobenzyl alcohol (0.47 g, 3.81 mmol) in ethanol (20 mL) were added 2−3 drops of glacial acetic acid, and the mixture was heated at 70 °C for 12 h. The solvent was removed under reduced pressure, and the residual oil was dissolved in CH_2Cl_2 (50 mL). The solution was then filtered first through a pad of charcoal and then over Celite. The solvent was evaporated to dryness and the residue was recrystallized with several washings with diethyl ether, giving a yellow solid. Yield: 85% (1.16 g). Mp: 68 °C. Anal. Calcd for $C_{26}H_{22}NOP$: C, 78.97; H, 5.61; N, 3.54. Found: C, 78.80; H, 5.66; N, 3.59. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 4.78 (d, J_{HH} = 14.7 Hz, 1H, H_a part of an AB system, CH_2O), 4.93 (d, J_{HH} = 14.7 Hz, 1H, H_b part of an AB system, CH_2O), 6.29 (d, J_{PH} = 6.6 Hz, 1H, NC*H*O), 6.38 (dd, J_{HH} = 8.0 Hz, J_{HH} = 0.6 Hz, 1H, Ar H), 6.79 (dt, J_{HH} = 7.4 Hz, J_{HH} = 1.1 Hz, 1H, Ar H), 6.93 (dd, J_{HH} = 7.6 Hz, J_{HH} = 0.8 Hz, 1H, Ar H), 7.04 (m, 2H, Ar H), 7.31−7.43 (m, 11H, Ar H), 7.48 (dt, J_{HH} = 7.6 Hz, J_{HH} = 1.2 Hz, 1H, Ar H), 7.84 (ddd, J_{HH} = 7.8 Hz, J_{HH} = 3.9 Hz, J_{HH} = 1.3 Hz, 1H, Ar H). ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ 67.59 (CH_2O), 82.42 (d, J_{PC} = 26.7 Hz, NCHO), 116.05 (Ar C), 119.14 (Ar C), 121.69 (Ar C), 124.76 (Ar C), 126.55 (d, J_{PC} = 5.0 Hz, Ar C), 127.16 (Ar C), 128.49 (d, J_{PC} = 6.8 Hz, Ar C), 128.69 (Ar C), 128.98 (d, J_{PC} = 6.4 Hz, Ar C), 129.39 (Ar C), 133.68 (d, J_{PC} = 18.6 Hz, Ar C), 134.14 (d, J_{PC} = 20.2 Hz, Ar C), 135.72 (d, J_{PC} = 17.3 Hz, Ar C), 136.76 (d, J_{PC} = 10.2 Hz, Ar C), 142.20 (Ar C), 143.49 (d, J_{PC} = 22.3 Hz, Ar C). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ −16.60 (s, PPh_2).

$[Ru(PPh_3)(\mathbf{L}^{PNO})Cl_2]$ (1). A suspension of $Ru(PPh_3)_3Cl_2$ (1 g, 1.04 mmol) in toluene (15 mL) was treated with **L** (0.45 g, 1.14 mmol) and the mixture was gently refluxed for 8 h. During this time the color changed to purple-red. After it was cooled to room temperature, the suspension was filtered and the red solid was thoroughly washed with diethyl ether. Yield: 74% (0.64 g). Anal. Calcd for $C_{44}H_{37}Cl_2NOP_2Ru$: C, 63.69; H, 4.49; N, 1.69. Found: C, 63.59; H, 4.43; N, 1.72. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 2.69 (d, J_{HH} = 10.9 Hz, 1H, O*H*), 4.43 (d, J_{HH} = 10.8 Hz, 1H, H_b of CH_2O), 5.27 (t, J_{HH} = 11.0 Hz, 1H, H_a of CH_2O), 6.70 (t, J_{HH} = 6.5 Hz, 2H, Ar H), 6.84 (dd, J_{HH} = 7.5 Hz, J_{HH} = 0.7 Hz, 1H, Ar H), 7.00 (t, J_{HH} = 8.4 Hz, 1H, Ar H), 7.05 (t, J_{HH} = 6.5 Hz, 1H, Ar H), 7.15 (dt, J_{HH} = 7.9 Hz, J_{HH} = 1.8 Hz, 6H, Ar H), 7.25−7.43 (m, 19H, Ar H), 7.56 (ddd, J_{HH} = 7.5 Hz, J_{HH} = 3.6 Hz, J_{HH} = 1.0 Hz, 1H, Ar H), 7.78 (t, J_{HH} = 8.7 Hz, 2H, Ar H), 8.85 (d, $^4J_{PH}$ = 8.3 Hz, 1H, *H*C═N). ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ 64.33 (CH_2O), 123.46 (Ar C), 127.03 (d, J_{PC} = 8.9 Hz, Ar C), 127.52 (d, J_{PC} = 10.0 Hz, Ar C), 128.81 (Ar C), 128.94 (Ar C), 129.12 (Ar C), 129.50 (Ar C), 129.60 (Ar C), 129.91 (Ar C), 130.82 (Ar C), 131.31 (Ar C), 132.06 (d, J_{PC} = 6.1 Hz, Ar C), 133.84 (d, J_{PC} = 8.5 Hz, Ar C), 134.27 (Ar C), 134.64 (d, J_{PC} = 11.7 Hz, Ar C), 135.25 (d, J_{PC} = 8.9 Hz, Ar C), 135.91 (d, J_{PC} = 7.8 Hz, Ar C), 171.28 (d, J_{PC} = 4.2 Hz, HC═N) (it was not possible to identify the NMR signal of four quaternary carbons). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 39.9 (d, J_{PP} = 20.8 Hz, PPh_3), 62.1 (d, J_{PP} = 24.2 Hz, PPh_2). Single crystals suitable for an X-ray determination were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution of **1**, at 20 °C.

$[Ru(PPh_3)(\mathbf{L}^{PN})Cl_2]$ (2). A suspension of $Ru(PPh_3)_3Cl_2$ (0.1 g, 1.04 mmol) in toluene (15 mL) was treated with **L** (0.45 g, 1.14 mmol), and the mixture was stirred at 0 °C for 6 h. During this time the color changed to emerald green. Then the suspension was filtered and the green solid was thoroughly washed with diethyl ether. Yield: 91% (0.79 g). Anal. Calcd for $C_{44}H_{37}Cl_2NOP_2Ru$: C, 63.69; H, 4.49; N, 1.69. Found: C, 63.55; H, 4.41; N, 1.74. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 4.99 (q, J_{HH} = 14.3 Hz, 2H, CH_2O), 6.52 (d, 1H, NC*H*O), 6.66 (dd, J_{HH} = 9.8 Hz, J_{HH} = 3.7 Hz, 1H, Ar H), 6.79 (m, 2H, Ar H), 6.92 (m, J_{HH} = 9.7 Hz, J_{HH} = 8.0 Hz, J_{HH} = 0.8 Hz, 1H, Ar H), 6.99−7.49 (m, 26H, Ar H), 7.61 (m, 2H, Ar H), 8.17 (dd, J_{HH} = 7.7 Hz, J_{HH} = 3.5 Hz, 1H, Ar H). ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ 67.95 (CH_2O), 87.10 (d, J_{PC} = 9.1 Hz, NCHO), 121.81 (Ar C), 125.06 (Ar C), 125.45 (d, J_{PC} = 8.9 Hz, Ar C), 125.63 (Ar C), 126.98 (d, J_{PC} = 10.5 Hz, Ar C), 127.69 (d, J_{PC} = 9.3 Hz, Ar C), 127.83 (Ar C), 128.48 (d, J_{PC} = 7.7 Hz, Ar C), 128.94 (Ar C), 129.48 (Ar C), 130.15 (d, J_{PC} = 13.6 Hz, Ar C), 130.52 (Ar C), 130.78 (d, J_{PC} = 16.9 Hz, Ar C), 133.81 (Ar C), 134.23 (Ar C), 134.60 (d, J_{PC} = 9.9 Hz, Ar C), 134.60 (d, J_{PC} = 10.1 Hz, Ar C), 134.99 (d, J_{PC} = 10.1 Hz, Ar C), 140.19 (Ar C), 140.29 (Ar C). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 44.0 (d, J_{PP} = 31.4 Hz, PPh_3), 75.6 (d, J_{PP} = 26.4 Hz, PPh_2). Single crystals suitable for an X-ray determination were grown by slow diffusion of hexane into a CH_2Cl_2 solution of **2**, at 20 °C.

$[Ru(\mathbf{L}^{PN})(cis\text{-}EtO(O)CCH{=}CHC(O)OEt)Cl_2]$ (3). Complex **2** (0.4 g, 0.48 mmol) was dissolved in CH_2Cl_2 (10 mL), and a large excess of ethyl diazoacetate (510 μL, d = 1.085 g/mL, 4.85 mmol) was added in

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Table 3. Crystallographic and Selected Experimental Data for 1, 2·2CH_2Cl_2, and 3

	1	2·2CH_2Cl_2	3
chem formula	$C_{44}H_{37}Cl_2NOP_2Ru$	$C_{46}H_{41}Cl_6NOP_2Ru$	$C_{34}H_{34}Cl_2NO_5PRu$
formula wt	829.66	999.51	739.56
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
cryst color and shape	orange block	orange block	orange block
cryst size (mm)	0.22 × 0.16 × 0.15	0.20 × 0.16 × 0.13	0.25 × 0.20 × 0.17
a (Å)	11.1458(7)	11.9642(8)	10.1641(6)
b (Å)	12.3496(8)	9.9035(6)	10.2585(6)
c (Å)	14.1942(10)	37.701(3)	16.5236(10)
α (deg)	86.394(5)	90	74.473(5)
β (deg)	75.615(5)	102.818(6)	78.171(5)
γ (deg)	75.546(5)	90	71.912(4)
V (Å^3)	1832.6(2)	4355.8(5)	1563.94(16)
Z	2	4	2
T (K)	173(2)	173(2)	173(2)
D_c (g cm^{-3})	1.504	1.524	1.570
μ (mm^{-1})	0.698	0.839	0.767
scan range (deg)	3.40 < 2θ < 58.38	3.50 < 2θ < 58.46	4.26 < 2θ < 58.38
no. of unique rflns	9881	11 418	8411
no. of rflns used ($I > 2\sigma(I)$)	5671	4090	5519
R_{int}	0.1539	0.3739	0.1557
final R1 and wR2 indices ($I > 2\sigma(I)$)[a]	0.0671, 0.0752	0.1244, 0.1459	0.0683, 0.1259
R1 and wR2 indices (all data)	0.1419, 0.0886	0.2826, 0.1901	0.1192, 0.1423
goodness of fit	0.925	0.961	0.988
max, min $\Delta\rho$ (e Å^{-3})	0.527, −0.771	0.840, −1.119	0.921, −1.105

[a]Structures were refined on F_o^2: wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

small portions. The resulting mixture was stirred at room temperature for 12 h, during which time gas evolution (N_2) was noticed. Then the solvent was carefully removed under reduced pressure, and the residue was treated with diethyl ether, affording a light brown precipitate. Yield: 75% (0.27 g). Anal. Calcd for $C_{34}H_{34}Cl_2NO_5PRu$: C, 55.22; H, 4.63; N, 1.89. Found: C, 55.11; H, 4.69; N, 1.83. IR: ν_{max}/cm^{-1} 1725 (O═COEt), 1622 (Ru−O═COEt). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 1.37 (t, J_{HH} = 7.2 Hz, 3H, CH_3), 1.43 (t, J_{HH} = 7.2 Hz, 3H, CH_3), 4.24 (m, 2H, CH_2), 4.45 (m, J_{HH} = 28.0 Hz, J_{HH} = 10.7 Hz, J_{HH} = 7.1 Hz, 2H, CH_2), 4.84 (d, J_{HH} = 13.8 Hz, 1H, H_b part of an AB system, CH_2O), 4.99 (d, J_{HH} = 13.7 Hz, 1H, H_a part of an AB system, CH_2O), 6.52 (t, J_{HH} = 9.2 Hz, 1H, HC═C), 6.60 (d, 1H, NCHO), 6.68 (ddd, J_{HH} = 10.7 Hz, J_{PH} = 7.7 Hz, J_{HH} = 0.9 Hz, 1H, HC═C), 7.09 (dd, J_{HH} = 7.2 Hz, J_{HH} = 0.6 Hz, 1H, Ar H), 7.16 (t, J_{HH} = 7.2 Hz, 1H, Ar H), 7.24 (dt, J_{HH} = 7.3 Hz, J_{HH} = 1.2 Hz, 2H, Ar H), 7.37−7.57 (m, 10H, Ar H), 7.67 (tt, J_{HH} = 7.7 Hz, J_{HH} = 1.2 Hz, 2H, Ar H), 8.13 (dd, J_{HH} = 7.8 Hz, J_{HH} = 4.0 Hz, 2H, Ar H). ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ 13.83 (CH_3), 14.51 (CH_3), 60.43 (CH_2CH_3), 63.48 (HC═C), 63.87 (CH_2CH_3), 64.09 (HC═C), 68.63 (CH_2O), 88.37 (d, J_{PC} = 13.6 Hz, NCHO), 124.05 (Ar C), 124.62 (d, J_{PC} = 8.6 Hz, Ar C), 125.34 (d, J_{PC} = 9.2 Hz, Ar C), 127.24 (Ar C), 127.89 (d, J_{PC} = 10.4 Hz, Ar C), 128.59 (d, J_{PC} = 10.1 Hz, Ar C), 128.81 (d, J_{PC} = 11.6 Hz, Ar C), 129.06 (d, J_{PC} = 7.7 Hz, Ar C), 129.34 (Ar C), 130.05 (Ar C), 130.92 (Ar C), 131.15 (Ar C), 131.20 (Ar C), 131.37 (Ar C), 133.17 (d, J_{PC} = 5.3 Hz, Ar C), 134.07 (d, J_{PC} = 12.7 Hz, Ar C), 139.65 (d, J_{PC} = 11.6 Hz, Ar C), 140.19 (Ar C), 171.91 (C(O)OEt), 178.51 (C(O)OEt). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ 51.5 (s, PPh_2). Single crystals suitable for an X-ray determination were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution of **3**, at 20 °C.

[Ru(PPh$_3$)(4-Me-py)(L^{PN})Cl$_2$] (4). Compound **2** (0.2 g, 0.241 mmol) was suspended in diethyl ether (10 mL), and 4-picoline (47 μL, 0.482 mmol) was added in one portion. The suspension was stirred for 6 h, and then the orange solid was filtered off, washed with diethyl ether (10 mL), and then dried under vacuum. Yield: 86% (0.191 g). Anal. Calcd for $C_{50}H_{44}Cl_2N_2OP_2Ru$: C, 65.08; H, 4.81; N, 3.04. Found: C, 64.92; H, 4.98; N, 3.19.

[Ru(4-Me-py)(L^{PNO})Cl$_2$] (Mixture of 5 and 6a). Complex **1** (0.2 g, 0.241 mmol) was suspended in 10 mL of solvent (toluene, 1,2-dichloroethane, THF, or CH_3CN), and 4-picoline (47 μL, 0.482 mmol) was added in one portion. The suspension was refluxed for 6 h, and then the solid was filtered off and washed with diethyl ether. ^{31}P{^{1}H} NMR revealed the crude product as being a mixture with different proportions of two compounds, identified as [Ru(4-Me-py)(L^{PNO})Cl$_2$] (**5**) and [Ru(4-Me-py)$_2$(L^{PNO})Cl](Cl) (**6a**).

[Ru(4-Me-py)(L^{PNO})Cl$_2$] (5). Complex **1** (0.2 g, 0.241 mmol) was suspended in 10 mL of *m*-xylene, and 4-picoline (47 μL, 0.482 mmol) was added in one portion. Refluxing the suspension for 6 h afforded a deep red solid, which was washed thoroughly with Et_2O and dried in vacuo. Yield: 67% (0.107 g). Anal. Calcd for $C_{32}H_{29}Cl_2N_2OPRu$: C, 58.19; H, 4.43; N, 4.24. Found: C, 58.31; H, 4.59; N, 4.79. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 2.26 (s, 3H, CH_3), 4.49 (d, $^3J_{HH}$ = 11.0 Hz, 1H, OH), 4.92 (dd, $^2J_{HH}$ = 11.6 Hz $^3J_{HH}$ = 1.6 Hz, 1H, H_b of CH_2O), 5.64 (t, $^2J_{HH}$ = $^3J_{HH}$ = 11.4 Hz, 1H, H_a of CH_2O), 6.67 (m, J_{HH} = 8.2 Hz, J_{HH} = 1.5 Hz, 1H, Ar H), 6.76 (d, J_{HH} = 6.1 Hz, 2H, picoline H_m), 6.97 (t, J_{HH} = 8.4 Hz, 1H, Ar H), 7.08 (t, J_{HH} = 6.9 Hz, 2H, Ar H), 7.25 (t, J_{HH} = 6.9 Hz, 1H, Ar H), 7.30−7.59 (m, 13H, Ar H), 8.64 (d, J_{HH} = 11.0 Hz, 2H, picoline H_o), 8.92 (s, 1H, HC═N). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C): 20.34 (CH_3), 65.84 (CH_2O), 121.88 (Ar C), 123.77 (picoline C_m), 127.19 (Ar C), 127.59 (d, J_{PC} = 9.4 Hz, Ar C), 127.89 (Ar C), 128.35 (Ar C), 129.41 (AR-c), 129.67 (Ar C), 130.61 (Ar C), 130.12 (d, J_{PC} = 13.2 Hz), 131.35 (Ar C), 131.67 (d, J_{PC} = 5.9 Hz, Ar C), 133.69 (d, J_{PC} = 9.0 Hz, Ar C), 134.05 (d, J_{PC} = 9.2 Hz, Ar C), 134.54 (d, J_{PC} = 7.9 Hz, Ar C), 138.39 (d, J_{PC} = 14.2 Hz, Ar C), 146.72 (Ar C), 154.65 (Ar C), 155.49 (picoline C_o), 170.93 (s, HC═N). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ 73.3 (s, PPh_2).

[Ru(4-Me-py)$_2$(L^{PNO})Cl](Cl) (6a) (5/1 Mixture with Compound 5). Compound **1** (0.2 g, 0.241 mmol) was suspended in 10 mL of *m*-xylene, and an 8-fold excess of 4-picoline (190 μL, 1.952 mmol) was added in one portion. Refluxing the suspension for 6 h afforded a deep red solid, which was washed thoroughly with Et_2O and dried in vacuo. Data for compound **6a** are as follows. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 2.23 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.41 (d, $^3J_{HH}$ = 3.2

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Hz, 1H, OH), 2.59 (dd, $^2J_{HH}$ = 11.8 Hz $^3J_{HH}$ = 2.4 Hz, 1H, H_b of CH_2O), 4.22 (dd, $^2J_{HH}$ = 11.9 Hz $^3J_{HH}$ = 4.6 Hz, 1H, H_a of CH_2O), 6.77−7.75 (m, 22H, Ar H), 8.44 (d, J_{HH} = 2.9 Hz, 2H, picoline H_o), 8.58 (d, J_{HH} = 3.4 Hz, 2H, picoline H_o), 9.01 (s, 1H, HC═N). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 25 °C): 20.46 (CH_3), 20.48 (CH_3), 62.70 (CH_2O), 118.93 (Ar C), 124.34 (picoline C_m), 124.63 (picoline C_m), 127.06 (Ar C), 127.84 (d, J_{PC} = 9.5 Hz, Ar C), 128.89 (d, J_{PC} = 1.8 Hz, Ar C), 129.02 (d, J_{PC} = 2.8 Hz, Ar C), 129.84 (d, J_{PC} = 2.7 Hz, Ar C), 130.51 (Ar C), 130.70 (Ar C), 131.91 (Ar C), 132.15 (d, J_{PC} = 6.3 Hz, Ar C), 132.36 (Ar C), 132.76 (Ar C), 133.26 (d, J_{PC} = 9.7 Hz, Ar C), 134.29 (d, J_{PC} = 8.0 Hz, Ar C), 138.32 (d, J_{PC} = 13.5 Hz, Ar C), 147.63 (Ar C), 147.83 (Ar C), 153.04 (picoline C_o), 155.50 (picoline C_o), 171.97 (d, J_{PC} = 4.5 Hz, HC═N). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 61.0 (s, PPh_2).

Synthesis of 6a from 5. Compound **5** (0.15 g, 0.227 mmol) was suspended in 10 mL of *m*-xylene, and a 4-fold excess of 4-picoline (90 μL, 0.925 mmol) was added in one portion. Refluxing the suspension for 6 h afforded **6a** as the major product (as evidenced by $^{31}P\{^1H\}$ NMR of the bulk product).

General Procedure for Cyclopropanation of Styrene and α-Methylstyrene. In a standard experiment, to a solution of catalyst (0.02 mmol) in dichloromethane (8 mL) at room temperature and under an inert atmosphere was added the olefin (4 mmol) in one portion (catalyst/olefin molar ratio 1/200). Then, ethyl diazoacetate (2 mmol) was added dropwise over a period of 4 h, and the reaction mixture was stirred at 20 °C for an additional 4 h. The consumption of EDA was monitored by infrared spectroscopy ($\nu_{N\equiv N}$). Yields and diastereoselectivity (*cis*/*trans* ratio) were determined by GC-MS analysis of the bulk product by comparison with pure samples.[25d]

Computational Details. Geometries were optimized, without symmetry constraints, employing the standard B3LYP hybrid functional as implemented in the ADF 2012.01 program suite.[41] AE-TZ2P basis sets (C, H, N, P, Cl) combined with the AE-QZ4P basis set (Ru) were used. Scalar relativistic effects on ruthenium atoms were treated by applying the zeroth-order regular approximation (ZORA).[42] Starting geometries for **1** and **2** were taken from experimental Cartesian coordinates obtained by the X-ray diffraction data, while the PM6 semiempirical method,[43] as implemented in the MOPAC2009[44] program package, was employed to preoptimize geometries for **6a** and **6b** cations. All geometry optimizations were performed simulating a CH_2Cl_2 solvation using the COSMO dielectric continuum model as implemented in ADF. Frequency analyses were performed to ensure all optimized molecular structures were real minima (no imaginary frequencies) (see the Supporting Information).

X-ray Crystallographic Study. Crystals of **1**, **2**·2CH_2Cl_2, and **3** were mounted on a Stoe Mark II-Image Plate Diffraction System, using Mo Kα graphite-monochromated radiation, image plate distance 135 mm, 2θ range from 2.4 to 51.3°, D_{max}−D_{min} = 16.029−0.836 Å. The structures were solved by direct methods using the program SHELXS-97.[45] Refinement and all further calculations were carried out using SHELXL-97.[45] The H atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least squares on F^2. Despite several attempts to get better crystals of complex **2** and a better data set, only poor-quality data were obtained. Nevertheless, the molecular structure of **2** confirms the suggested structure based on the compiled NMR data. Crystallographic details are summarized in Table 3. Figures 2−4 (ORTEP drawings) were drawn with Mercury CSD 3.0 software.

CCDC-881236 (**1**), CCDC-881237 (**2**·2CH_2Cl_2), and CCDC-881238 (**3**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax (internat.) +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving full NMR spectra (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^1H−^{31}P HMBC) of L^{PN} and complexes **1**−**3**, **5**, and **6a**, crystallographic data for compounds **1**−**3**, illustrations of the possible diastereoisomers of **2** and **3**, computational details, and a full list of authors for ref 42. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(22) $\mathbf{L}^{\mathbf{PN}}$ has a stereogenic center in position 2 of the oxazine ring; however, due to the equilibrium involving the ligand, it was not possible to isolate the ligand in an enantiomerically pure form, and $\mathbf{L}^{\mathbf{PN}}$ was always used as a racemic mixture. Additionally, its coordination to Ru(II) prevents inversion at the N atom, thus generating a second stereogenic center: as a result, compounds **2** and **3** are always present in solution as a mixture of diastereoisomers (see the Supporting Information for further details).
(23) The elevated R_{int} value observed for complex **2** (see the Experimental Section) is due to the fact that the crystal was weakly diffracting, so that a large proportion of essentially unobserved reflections were used in the refinement. We have tried to obtain a better data collection using other crystals; however, we were unable to get a better data set. Nevertheless, we believe that the X-ray data were important to insert in the paper, despite their poor quality, and overall were essential for the study and support our findings.
(24) The index of degree of trigonality, τ, is defined by the equation $\tau = (\beta - \alpha)/60$, where α and β are the two major angles of a five-coordinate system (with $\beta > \alpha$). Thus, for an ideal square-pyramidal geometry $\tau = 0$ ($\alpha = \beta = 180°$), whereas for a perfect trigonal-bipyramidal geometry $\tau = 1$ ($\alpha = 120°$, $\beta = 180°$). For further explanation see: Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.
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(26) Together with the desired products, diethyl maleate and diethyl fumarate, derived from EDA self-coupling, are always detected. In order to minimize these side reactions, a large excess of olefin (namely, a Ru/EDA/olefin = 1/100/200 molar ratio), and dropwise addition of EDA are employed.
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