New Insight into the Reactivity of Pyridine-Functionalized Phosphine Complexes of Ruthenium(II) with Respect to Olefin Metathesis and Transfer Hydrogenation

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The present paper deals with the synthesis and full characterization of a series of pyridine-functionalized phosphine complexes of Ru(II), namely, $RuCl_2(\mathbf{L^{nx}})(PPh_3)$ ($\mathbf{L^{nx}}$ = $R_2PCH_2(C_5H_2R'R''N)$), differing in the nature of the substituents on the phosphorus (superscript label **n** in $\mathbf{L^{nx}}$ defined as **n** = 1 for R = Ph, **n** = 2 for R = Cy) and/or on the pyridyl group (superscript label **x** in $\mathbf{L^{nx}}$ defined as **x** = **a** for picolyl, noted pic, and **x** = **b** for quinolyl, noted quin) and discloses new aspects of their reactivity with respect to catalysis. The ligands 2-[(diphenylphosphino)methyl]-6-methylpyridine, $\mathbf{L^{1a}}$, 2-[(diphenylphosphino) methyl]quinoline, $\mathbf{L^{1b}}$, 2-[(dicyclohexylphosphino)methyl]-6-methylpyridine, $\mathbf{L^{2a}}$, and 2-[(dicyclohexylphosphino)methyl]quinoline, $\mathbf{L^{2b}}$, were prepared and respectively reacted with $RuCl_2(PPh_3)_3$ under optimized experimental conditions. In a preliminary test, the reaction of $RuCl_2(PPh_3)_3$ with $\mathbf{L^{1a}}$ using a stoichiometric 1/1 metal/ligand ratio gave three complexes, namely, $[RuCl_2(PPh_3)_2]_2$ (**1**), $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(\mathbf{L^{1a}})(PPh_3)]$ ($\mathbf{2_{1a}}$), and $RuCl_2(\mathbf{L^{1a}})_2$ ($\mathbf{3_{1a}}$). These were isolated by fractional crystallization and, at that stage, identified only by single-crystal X-ray diffraction. The formation of **1** and $\mathbf{2_{1a}}$ reflects the existence of the elusive 14 e^- fragment "$RuCl_2(PPh_3)_2$", which tends to relieve its unsaturation by intermolecular association. By contrast, controlled addition of 2-(phosphinomethyl)pyridine type ligands $\mathbf{L^{nx}}$ to $RuCl_2(PPh_3)_2$ leads selectively to the desired 16 e^- species $RuCl_2(\mathbf{L^{nx}})(PPh_3)$ ($\mathbf{4_{nx}}$). For example, with $\mathbf{L^{1b}}$, the green complex $RuCl_2(\mathbf{L^{1b}})(PPh_3)$ ($\mathbf{4_{1b}}$-*trans-Cl*) was identified as the kinetic product of ligand addition. It slowly and irreversibly converts into the more stable isomer $RuCl_2(\mathbf{L^{1b}})(PPh_3)$ ($\mathbf{4_{1b}}$-*cis-Cl*), representing the thermodynamic product. Both isomers were fully characterized by NMR spectroscopy and X-ray diffraction. Similar transformations, taking place at different rates, were observed within the ligand series examined here. All isomeric forms of type $\mathbf{4_{na}}$ complexes react cleanly with a terminal alkyne-like phenylacetylene to give a new complex identified by NMR spectroscopy as the vinylidene species $RuCl_2(\mathbf{L})(CCHPh)(PPh_3)$ ($\mathbf{5_{na}}$). The reaction of $\mathbf{4_{nb}}$-*cis-Cl* with an excess of ethyl diazoacetate at –60 °C gives the novel complex $RuCl_2(\mathbf{L^{na}})\{cis\text{-}EtO(O)C(H)C{=}C(H)C(O)OEt\}$ ($\mathbf{6_{na}}$) with concomitant elimination of the phosphonium ylide, $Ph_3P{=}C(H)C(O)OEt$. Whereas 1 equiv of diazoalkane thus serves as phosphine scavenger, the uptake of two more carbene units by the remaining 14 e^- fragment "$RuCl_2(\mathbf{L^{1a}})$" results in their coupling, providing diethyl maleate, intercepted in $\mathbf{6_{na}}$ as a coordinated ligand. Preliminary catalytic tests indicate that the complexes $\mathbf{4_{nx}}$ act as catalyst precursors for the ROMP of norbornene in the presence of trimethylsilyldiazomethane as the carbene source. The same compounds $\mathbf{4_{nx}}$ are also used as catalyst precursors in the transfer hydrogenation of a series of ketone substrates using alcohol as the hydrogen source. For example, the hydrogenation of cyclohexanone is achieved in 99% yield within 45 s with only 0.01 mol (0.1 mol %) of the precatalyst $RuCl_2(Ph_2PCH_2pic)(PPh_3)$-*trans-Cl* ($\mathbf{4_{1a}}$), representing a turnover frequency of 272 571 h^{-1}. The X-ray structure analyses of **1**, $\mathbf{2_{1a}}$, $\mathbf{3_{1a}}$, $\mathbf{4_{1b}}$ (both *trans*-Cl and *cis*-Cl isomers), and $\mathbf{6_{1a}}$ are reported.

Introduction

In addition to recent investigations on new generations of advanced Grubbs type olefin metathesis catalysts,[1–3] there is also a stimulating challenge in the search for simpler, cheaper, and possibly more archaic systems, albeit in which an active catalytic species could be readily self-generated *in situ* and at low cost upon mixing simple ingredients.[4–6] Remember, in particular, that a number of ill-defined olefin metathesis catalysts of effective industrial relevance are generated *in situ* from precursors as simple as $RuCl_3$ or $[Ru(H_2O)_6](OTs)_2$.[4]

With these considerations in mind, and taking Grubbs' third-generation catalyst ("NHC")$(C_5H_4NBr)_2Cl_2Ru{=}CHPh$[2a,b] as a convenient structural model **A** (see below), the initial objective of the present work was to devise a potentially active hypothetical target species of structural type **B** capable of being "self-assembled" *in situ* from a readily accessible ruthenium precursor and a commercially available carbene source. In brief, it was hoped that a pyridine-functionalized phosphine ligand[7] of the type shown in **B** might constitute a viable alternative to the ideal ligand combination existing in complex **A**, based on a strongly coordinating N-heterocyclic carbene ligand and weakly bound bromopyridine molecules.

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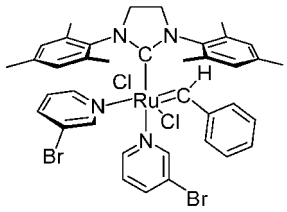

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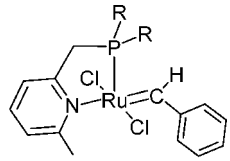

B

A convenient modular approach to a palette of such pyridine-functionalized phosphine ligands was developed some years ago in our laboratory and applied to the synthesis of a number of their Ru and Rh complexes.[8] The procedure allowed multiple variations in the nature of the substituents on the phosphorus, the central methylenic carbon, or the pyridyl group and was even found convenient for the synthesis of optically active versions based on P-chiral or C-chiral centers.[8b–d]

The readily accessible complex $RuCl_2(PPh_3)_3$ was selected as a convenient starting compound for our investigations on account of its well-established substitutional lability, corroborated here by new observations disclosed below.

The present paper describes the directed synthesis and full characterization of new members of the extended family of 16 e^- phosphinopyridine type complexes $RuCl_2(\mathbf{L^{nx}})(PPh_3)$ ($\mathbf{L^{nx}} = R_2PCH_2(C_5H_2R'R''N)$) differing in the nature of substituents on the phosphorus atom (superscript label **n** in $\mathbf{L^{nx}}$ defined as $\mathbf{n} = 1$ for R = Ph, $\mathbf{n} = 2$ for R = Cy) and on the pyridyl group (superscript label **x** in $\mathbf{L^{nx}}$ defined as $\mathbf{x} = \mathbf{a}$ for picolyl, noted pic, and $\mathbf{x} = \mathbf{b}$ for quinolyl, noted quin).[9] It also presents a hitherto unknown aspect of their reactivity toward a diazoalkane, suggesting a realistic rational pathway for the "*in situ*" generation of an active olefin metathesis catalyst. Possibilities and limitations of these complexes as readily available catalyst precursors for the ROMP of norbornene[10] or the transfer hydrogenation of ketones[11] are discussed on the basis of preliminary catalytic tests.

Results and Discussion

Preparation of the Ligands. Both 2-[(diphenylphosphino)methyl]pyridine and 2-[(diphenylphosphino)methyl]-6-methylpyridine ($\mathbf{L^{1a}}$) were previously prepared in good yields by reaction of diphenylchlorophosphine with 2-pyridynylmethyllithium and 6-methyl-2-pyridynylmethyllithium, respectively, at low temperature.[8] Such a procedure was extended here to the synthesis of 2-[(diphenylphosphino)methyl]quinoline ($\mathbf{L^{1b}}$) from Ph_2PCl and 2-quinolynylmethyllithium, 2-[(dicyclohexylphos-

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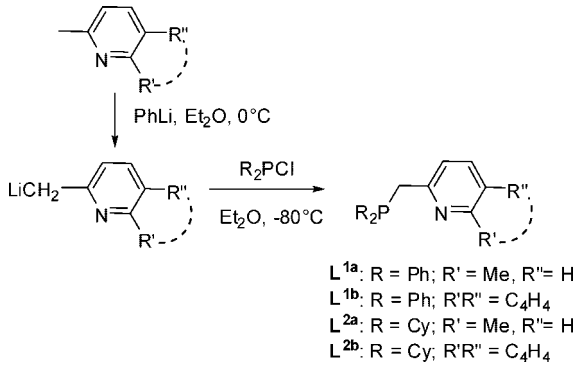
Scheme 1. General Synthetic Procedure and Labeling Scheme for Various 2-(Phosphinomethyl)pyridine Type Ligands



phino)methyl]-6-methylpyridine (**L^{2a}**), and 2-[(dicyclohexylphosphino)methyl]quinoline (**L^{2b}**) by reaction of dicyclohexylchlorophosphine with the appropriate lithiated reagent (see Scheme 1). These reactions are straightforward and afford the corresponding ligands in good yield.

Preliminary Reaction between $RuCl_2(PPh_3)_3$ and 2-[(Diphenylphosphino)methyl]-6-methylpyridine (L^{1a}) under Nonoptimized Conditions, Using a 1/1 Stoichiometric Ratio. The dichlorotris(triphenylphosphine)ruthenium(II) complex $RuCl_2(PPh_3)_3$ has been widely used as a valuable starting material for the preparation of a variety of Ru(II) complexes, including the very popular Grubbs type olefin metathesis catalyst.[12] Its success as a synthetic tool is due both to its direct accessibility from commercial $RuCl_3 \cdot nH_2O$ by a simple and efficient preparative procedure[13] and to its high substitutional lability.[14] Such a property is understood in terms of the existence of an elusive four-coordinate 14 e$^-$ complex "$RuCl_2(PPh_3)_2$" resulting from a spontaneous loss of one PPh_3 ligand observable in solution.[14] Earlier studies have previously led to the proposal that this elusive subcoordinated species tends to relieve its unsaturation by forming a dimeric halide-bridged species, originally mentioned by Wilkinson[14a] and existing also with chelating ligands,[14b–e] but still never fully characterized in the case of triphenylphosphine.

In a preliminary attempt to synthesize a 16 e$^-$ complex of the type $RuCl_2(\mathbf{L^{nx}})(PPh_3)$ capable of serving as a precursor to the desired type **B** catalyst mentioned in the introduction, equimolecular amounts of both the complex $RuCl_2(PPh_3)_3$ and the ligand **L^{1a}** were dissolved in dichloromethane at room temperature, and the reaction mixture was stirred for 4 h. After workup and extraction of the released triphenylphosphine with hexane, a $^{31}P\{^1H\}$ NMR spectrum of the recovered residue revealed the presence of an intricate mixture of complexes. Three main species were subsequently isolated from the mixture by fractional crystallization and identified in the solid state by single-crystal X-ray diffraction analyses. As shown in Scheme 2, these included two dimeric complexes, $[RuCl_2(PPh_3)_2]_2$ (**1**) and $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(\mathbf{L^{1a}})(PPh_3)]$ (**2$_{1a}$**), and the mononuclear complex $RuCl_2(\mathbf{L^{1a}})_2$ (**3$_{1a}$**).

As detailed below, the results of these preliminary experiments proved to be very useful to allow further adjustment of the experimental conditions in such a way to obtain the desired product in a selective manner. Importantly, they also revealed a peculiar aspect of the reactivity of the precursor $RuCl_2(PPh_3)_3$ itself, discussed in the next section.

New Evidence for the High Substitutional Lability of $RuCl_2(PPh_3)_3$: Isolation and Characterization of the Bimetallic Halide-Bridged Complexes $[RuCl_2(PPh_3)_2]_2$ (1) and $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(\mathbf{L^{1a}})(PPh_3)]$ (2$_{1a}$). Characterization of $[RuCl_2(PPh_3)_2]_2$ (1). Among the products isolated from the above reaction (see Scheme 2), one did not contain the ligand **L^{1a}**. Such a complex could be unambiguously formulated as $[RuCl_2(PPh_3)_2]_2$ (**1**) on the basis of an X-ray structure analysis. Relevant crystallographic data are listed in Table 1, whereas a selection of interatomic distances and bond angles is given in Table 2. As shown in Figure 1, this is effectively the bimetallic species originally identified by Wilkinson,[14] now fully characterized here for the first time. Its bimetallic ensemble consists of the juxtaposition of two asymmetric "$RuCl_2(PPh_3)_2$" units related through an inversion center and sharing one of the two chloride atoms, namely, Cl2, thus forming a double μ-Cl bridge. The P1, Cl1, Cl2, and Cl2* atoms constitute the square base of a distorted pyramidal arrangement around the metal center. They are essentially coplanar, with an average deviation from the mean plane of 0.0327 Å (maximum of 0.0341 associated with Cl2). The ruthenium atom lies 0.3895(7) Å above the mean plane thus defined. The observed distortion may be reasonably understood as a result of steric repulsions between the two adjacent triphenylphosphine ligands occupying axial and equatorial sites of the square pyramid, respectively. The overall geometric situation encountered here, with the two edge-sharing pyramids being oriented apart from the basal plane of the dimeric unit, appears to be different from the one originally proposed in Wilkinson's paper.[14a] Such a geometry is also reflecting the need to accommodate steric repulsions and probably represents the only viable isomeric form of this species.

The presence of complex **1** under the conditions of the above stoichiometric (1/1) reaction reflects the fact that 2 equiv of the ligand **L^{1a}** were consumed in the formation of the species **3$_{1a}$**, leaving part of the initial complex $RuCl_2(PPh_3)_3$ unreacted. Clearly, this initial complex is engaged in a predissociation equilibrium leading to the formation of a transient 14 e$^-$ complex "$RuCl_2(PPh_3)_2$", which tends to relieve its unsaturation by an intermolecular association involving the formation of halide bridges. The condensation of unsaturated $RuCl_2(PPh_3)_2$ fragments as dimeric units in the solid state appears to be also facilitated by workup with hexane, in which triphenylphosphine is particularly soluble. Let us mention that the formation of edge- or face-sharing bioctahedral species is now common for Ru(II) halide complexes.[15–17]

Characterization of $(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(\mathbf{L^{1a}})(PPh_3)$

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Scheme 2. Preliminary Stoichiometric Reaction of $RuCl_2(PPh_3)_3$ with L^{1a} under Nonoptimized Reaction Conditions

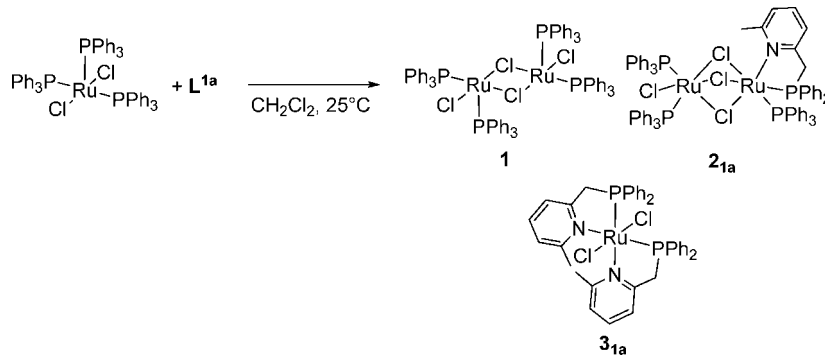


Table 1. Crystal Data and Structure Refinements for Complexes 1, 2_{1a}, 3_{1a}, 4_{2a}-*cis*, 4_{2a}-*trans*, and 6_{1a}

	$1\cdot CH_2Cl_2$	$2_{1a}\cdot 1.5CH_2Cl_2$	$3_{1a}\cdot CH_2Cl_2$	4_{2a}-*cis*$\cdot 3CH_2Cl_2$	4_{2a}-*trans*$\cdot 0.75CH_2Cl_2$	$6_{1a}\cdot 0.33CH_2Cl_2$
empirical formula	$C_{73}H_{62}Cl_6P_4Ru_2$	$C_{74.50}H_{66}Cl_7NP_4Ru_2$	$C_{39}H_{38}Cl_4N_2P_2Ru$	$C_{40}H_{51}Cl_7NP_2Ru$	$C_{37.75}H_{46.5}Cl_{3.5}NP_2RuP$	$C_{82}H_{92}Cl_8N_3O_{12}P_3Ru_3$
molecular weight (g)	1477.95	1549.56	839.52	992.43	801.34	1990.81
temp (K)	180	180	180	180	180	180
λ (Å)						
cryst syst	triclinic	monoclinic	triclinic	monoclinic	monoclinic	trigonal
space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$I2/a$ (#19)	$R\bar{3}$ (#148)
a (Å)	10.793(6)	14.196(2)	11.6100(15)	12.5688(9)	20.306(3)	26.3433(7)
b (Å)	12.856(6)	33.708(3)	12.953(3)	20.0030(13)	12.791(2)	26.3433(7)
c (Å)	13.174(7)	16.8163(14)	13.1890(15)	17.9037(12)	30.984(4)	21.6192(4)
α (deg)	96.96(6)		78.390(19)			
β (deg)	91.14(7)	109.211(11)	80.520(15)	102.123(6)	90.238(19)	
γ (deg)	109.87(6)		86.84(2)			
volume (Å^3)	1702.8(17)	7598.8(15)	1915.8(6)	4400.9(5)	8048(2)	12993.0(5)
Z	1	4	2	4	8	6
$D_{calcd.}$ (g cm^{-3})	1.441	1.354	1.455	1.498	1.323	1.527
μ (mm^{-1})	0.814	0.768	0.802	0.945	0.727	0.878
F_{000}	750	3148	856	2032	3308	6083
instrument	Stoe IPDS	Oxford Inst. Xcalibur	Stoe IPDS	Oxford Inst. Xcalibur	Stoe IPDS	Oxford Inst. Xcalibur
θ_{max} (deg)	26.20	25.00	26.10	32.2	26.01	32.2
completeness to θ_{max}	92.0	99.0	92.0	97.9	99.0	99.0
index range	$-13 < h < 13$	$-16 < h < 12$	$-12 < h < 13$	$-18 < h < 18$	$-24 < h < 24$	$-39 < h < 38$
	$-15 < k < 15$	$-40 < l < 40$	$-15 < k < 16$	$-29 < k < 28$	$-15 < h < 15$	$-35 < h < 38$
	$-16 < l < 16$	$-19 < l < 19$	$-15 < l < 16$	$-26 < l < 24$	$-38 < l < 38$	$-31 < l < 28$
no. of reflns collected	24 217	487 020	20 590	44 137	32 099	47 410
no. of indep reflns	6254	13 339	7004	14 478	7844	9716
no. of data/restraints/params	6254/0/424	13 339/0/626	7004/0/435	14 478/0/416	7844/0/389	9716/0/346
g.o.f.	1.057	0.933	1.03	0.992	1.01	1.04
R, R_w [$I > 2\sigma(I)$]	R1 = 0.0623	R1 = 0.1124	R1 = 0.0413	R1 = 0.0754	R1 = 0.0302	R1 = 0.0693
	wR2 = 0.1691	wR2 = 0.2635	wR2 = 0.1106	wR2 = 0.1295	wR2 = 0.0770	wR2 = 0.0770
R, R_w (all data)	R1 = 0.0729	R1 = 0.2021	R1 = 0.0481	R1 = 0.1811	R1 = 0.0381	R1 = 0.0381
	wR2 = 0.1801	wR2 = 0.3027	wR2 = 0.1152	wR2 = 0.2069	wR2 = 0.0793	wR2 = 0.2267
resid electr dens (e Å^{-3})	1.85/−0.94	2.06/−1.28	0.80/−0.79	1.51/−1.035	0.42/−0.34	1/−0.34

(2_{1a}). Just like the previous complex identified above, the present one belongs to the closely related family of interconvertible edge- and face-sharing bioctahedral species (ESBO/FSBO) of which numerous examples are found in the literature.[15] A less common situation, here, is that the two organometallic fragments fused together are of different nature. Indeed, as shown in Figure 2 (see also Table 1 and Table 3), complex $\mathbf{2_{1a}}$ results from the intermolecular association between the 14 e$^-$ fragment "$RuCl_2(PPh_3)_2$" and the elusive complex $RuCl_2(\mathbf{L^{1a}})(PPh_3)$ ($\mathbf{4_{1a}}$), the latter being in fact the target 16 e$^-$ species we were looking for, and which was ultimately prepared in a selective manner (*vide infra*). It was subsequently verified (see Experimental Part) that complex $\mathbf{2_{1a}}$ can be more conveniently prepared in 43% yield upon reaction of $RuCl_2(PPh_3)_3$ with $\mathbf{4_{1a}}$. It should be noted, however, that, just like **1**, such a complex exists mainly as a solid, whereas a rapid dissociation and redistribution of the fragments takes place in solution. The occurrence of complex $\mathbf{2_{1a}}$ provides further evidence for the ability of the 14 e$^-$

Table 2. Selected Interatomic Distances [Å] and Bond Angles [deg] for Complex 1

Bond Distances	
Ru1−Cl1	2.3646(16)
Ru1−Cl2	2.3932(14)
Ru1−P1	2.2637(14)
Ru1−P2	2.2048(13)
Ru1−Cl2_a	2.4652(14)
Bond Angles	
Cl1−Ru1−Cl2	160.81(6)
Cl1−Ru1−P1	93.00(6)
Cl1−Ru1−P2	95.27(6)
Cl1−Ru1−Cl2_a	89.07(5)
Cl2−Ru1−P1	92.04(6)
Cl2−Ru1−P2	101.97(6)
Cl2−Ru1−Cl2_a	79.70(5)
P1−Ru1−P2	100.65(6)
Cl2_a−Ru1-P1	158.74(5)
Cl2_a −Ru1-P2	100.22(5)
Ru1−Cl2−Ru1_a	100.30(6)

(17) (a) Mashima, K.; Hino, T.; Takaya, H. *J. Chem. Soc., Dalton Trans.* **1992**, 2099. (b) Ohta, T.; Tonomura, Y.; Nozaki, K.; Takaya, H. *Organometallics* **1996**, *15*, 1521. (c) Dias, E. L.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2758. (d) Fabre, S.; Kalck, P.; Lavigne, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1092. Faure, M.; Maurette, L.; Donnadieu, B.; Lavigne, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 518. (f) Hansen, S. M.; Volland, M. A. O.; Rominger, F.; Eisenträger, F.; Hofman, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1273.

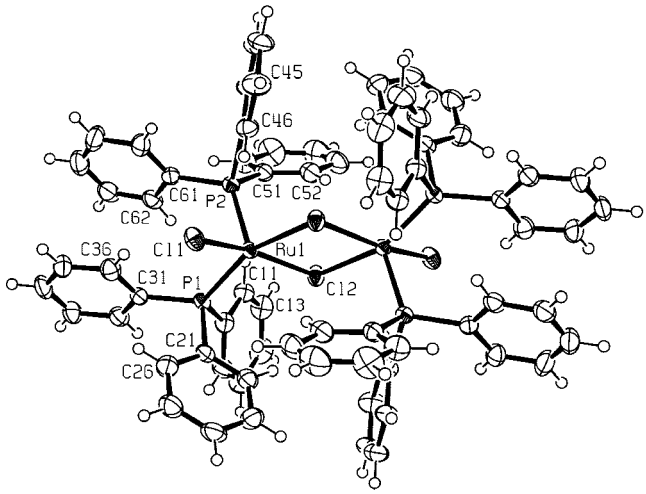


Figure 1. Perspective view of complex $[RuCl_2(PPh_3)_2]_2$ (**1**). Ellipsoids are shown at the 30% probability level.

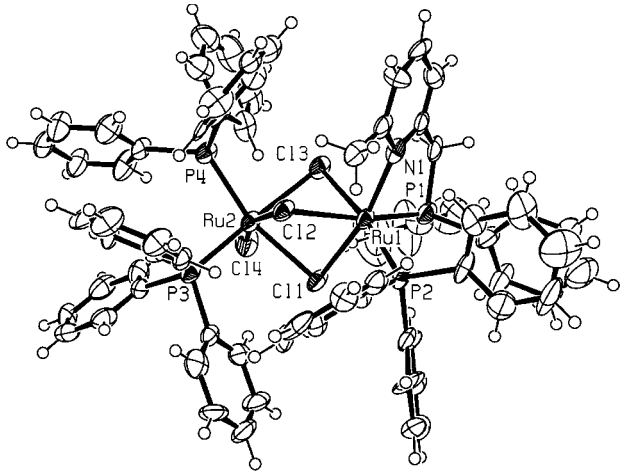


Figure 2. Perspective view of complex $(PPh_3)_2ClRuCl(\mu\text{-}Cl)_3Ru(\mathbf{L^{1a}})(PPh_3)$ ($\mathbf{2_{1a}}$). Ellipsoids are shown at the 30% probability level.

fragment "$RuCl_2(PPh_3)_2$" to form elusive adducts with other well-defined electron-deficient complexes, thereby possibly masking some of their potentially reactive sites. Whereas the formation of halide-bridged bimetallic species has been effectively often regarded as undesirable for the purpose of catalytic applications,[16] opposed evidence has also been obtained in other cases that they may alternatively represent the catalyst's resting state,[17] capable of liberating an active species upon dissociation via halide bridge opening.

Directed Synthesis and Characterization of $RuCl_2(\mathbf{L^{1a}})_2$ ($\mathbf{3_{1a}}$). As predictable from the above preliminary observations, the reaction of $RuCl_2(PPh_3)_3$ with *2* equiv of $\mathbf{L^{1a}}$ produced $\mathbf{3_{1a}}$ in almost quantitative yield. Under such conditions (see Experimental Part), and after extraction of the slight excess of PPh_3, the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture showed only a singlet, consistent with the formulation established by X-ray diffraction, thereby also confirming the existence of only one isomer, unlike what had been previously found in the case of slightly different "PN" ligands of a closely related family.[8] A perspective view of complex $\mathbf{3_{1a}}$ is shown in Figure 3, whereas a selection of interatomic distances and bond angles is displayed in Table 4.

The coordination geometry around the Ru center consists of a distorted octahedron. The two chlorine atoms occupy apical *trans* positions, whereas the P and N donor atoms of the two

Table 3. Selected Interatomic Distances [Å] and Bond Angles [deg] for Complex $\mathbf{2_{1a}}$

Bond Distances	
Ru1−Cl	2.403(3)
Ru1−Cl2	2.499(3)
Ru1−Cl3	2.464(3)
Ru1−P1	2.230(4)
Ru1−P2	2.282(4)
Ru1−N1	2.143(11)
Ru2−Cl1	2.480(3)
Ru2−Cl2	2.398(3)
Ru2−Cl3	2.506(4)
Ru2−Cl4	2.391(5)
Ru2−P3	2.272(4)
Ru2−P4	2.286(4)
P1−C1	1.821(14)
P1−C21	1.846(11)
P1−C31	1.847(11)
P2−C41	1.857(8)
P2−C51	1.873(9)
P2−C61	1.839(10)
P3−C71	1.831(10)
P3−C81	1.857(9)
P3−C91	1.856(9)
P4−C101	1.835(10)
P4−C111	1.857(9)
P4−C121	1.834(9)
N1−C12	1.367(17)
N1−C16	1.397(19)
Bond Angles	
Cl1−Ru1−Cl2	76.94(11)
Cl1−Ru1−Cl3	82.47(12)
Cl1−Ru1−P1	102.29(13)
Cl1−Ru1−P2	89.15(13)
Cl1−Ru1−N1	166.2(3)
Cl2−Ru1−Cl3	77.56(12)
Cl2−Ru1−P1	165.58(14)
Cl2−Ru1−P2	98.56(12)
Cl2−Ru1−N1	95.6(3)
Cl3−Ru1−P1	88.05(14)
Cl3−Ru1−P2	171.36(14)
Cl3−Ru1−N1	84.7(3)
P1 −Ru1-P2	95.82(15)
P1 −Ru1-N1	82.1(3)
P2 −Ru1−N1	103.5(3)
Cl1−Ru2−Cl2	77.39(11)
Cl1−Ru2−Cl3	80.08(12)
Cl1−Ru2−Cl4	84.55(14)
Cl1−Ru2−P3	97.38(13)
Cl1−Ru2−P4	164.24(15)
Cl2−Ru2−Cl3	78.62(11)

chelating units of the $\mathbf{L^{1a}}$ ligand are in equatorial position and mutually adopt a head-to-head arrangement, a situation that can

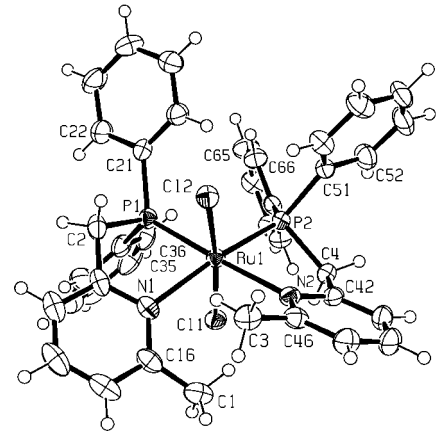


Figure 3. Perspective view of complex $RuCl_2(\mathbf{L^{1a}})_2 \cdot (\mathbf{3_{1a}})$. Ellipsoids are shown at the 30% probability level.

Table 4. Selected Interatomic Distances [Å] and Bond Angles [deg] for Complex 3_{1a}

Bond Distances	
Cl(1)−Ru(1)	2.4021(9)
Cl(2)−Ru(1)	2.4373(9)
N(1)−Ru(1)	2.274(2)
N(2)−Ru(1)	2.313(2)
P(1)−Ru(1)	2.2282(10)
P(2)−Ru(1)	2.2593(9)
Bond Angles	
P(1)−Ru(1)−P(2)	101.78(3)
P(1)−Ru(1)−N(1)	79.18(7)
P(2)−Ru(1)−N(1)	170.95(7)
P(1)−Ru(1)−N(2)	176.31(6)
P(2)−Ru(1)−N(2)	77.97(6)
N(1)−Ru(1)−N(2)	101.69(9)
P(1)−Ru(1)−Cl(1)	91.17(3)
P(2)−Ru(1)−Cl(1)	86.35(3)
N(1)−Ru(1)−Cl(1)	84.63(7)
N(2)−Ru(1)−Cl(1)	92.49(6)
P(1)−Ru(1)−Cl(2)	87.80(3)
P(2)−Ru(1)−Cl(2)	100.51(3)
N(1)−Ru(1)−Cl(2)	88.51(7)
N(2)−Ru(1)-−Cl(2)	88.63(6)
Cl(1)−Ru(1)−Cl(2)	173.13(3)

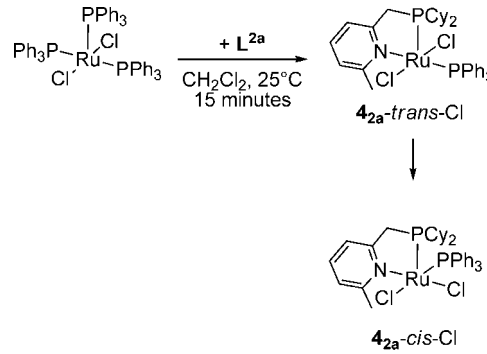
be rationalized in terms of the well-documented "*trans*" effect. Each of the two five-membered rings formed by the chelating bidentate ligand units adopts a half-chair conformation, allowing the two methyl substituents of the pyridyl moieties to be shifted apart from the equatorial plane, an apparent requirement for relieving steric crowding between these groups. As a logical consequence, the molecule possesses a noncrystallographic C_2 symmetry, with the pseudo -C_2 axis bisecting the P−Ru−P (and N−Ru−N) angle(s). Let us remember that the structural arrangement observed here is relatively classical for PN ligands.[18]

Directed Synthesis and Characterization of $RuCl_2(L^{nx})(PPh_3)$ (4_{nx}). The preferential formation of the disubstituted complex 3_{1a}, even from a stoichiometric 1/1 $RuCl_2(PPh_3)_3$/L_{1a} ratio, probably reflects the fact that nucleophilic attack of a second molecule of L_{1a} onto the initial elusive monosubstituted P-bound intermediate "$RuCl_2(PPh_3)_2L_{1a}$" is kinetically preferred over the intramolecular formation of a metallacycle by closure of the Ru−N bond. Thus, a simple way to circumvent the problem would be to maintain the lowest possible ligand-to-metal ratio over the whole reaction course. Effectively, we found that very slow dropwise addition of L^{1a} to a dichloromethane solution of $RuCl_2(PPh_3)_3$ at room temperature over a period of 1 h by using an automatic syringe produces a new compound, 4_{1a}, existing as a mixture of two isomers in a ca. 1/1 ratio. Recrystallization from a dichloromethane/hexane mixture at room temperature gave a pure sample of an orange crystalline material, which was subsequently identified as 4_{1a}-*cis-Cl* (69% isolated yield) on the basis of an X-ray structure analysis (see Experimental Part; structure provided as Supporting Information).

The isolation of the elusive alternate isomer as a solid appeared to be easier in the case of the ligand L^{2a}. In that case, there is no need for a very slow ligand addition, just because the steric bulk of the cyclohexyl group precludes the uptake of a second molecule of L^{2a}, thus preventing the formation of the undesirable hypothetical species 3_{2a}, never detected in our

(18) (a) Shen, J.-Y.; Slugovc, C.; Wiede, P.; Mreiter, K.; Schmid, R.; Kirchner, K. *Inorg. Chim. Acta* **1998**, *268*, 69. (b) Crochet, P.; Gimeno, J.; Garcia-Granda, S.; Borge, J. *Organometallics* **2001**, *20*, 4369. (c) Li, T.; Churlaud, R.; Lough, A. J.; Abdur-Rashid, K.; Morris, R. H. *Organometallics* **2004**, *23*, 6239.

Scheme 3. Stoichiometric Reaction of $RuCl_2(PPh_3)_3$ with L^{2a} Giving $RuCl_2(L^{2a})(PPh_3)$ (4_{2a}-*trans-Cl*) Followed by Isomerization of the Latter to $RuCl_2(L^{2a})(PPh_3)$ (4_{2a}-*cis-Cl*)



experiments. A reaction time of 15 min between $RuCl_2(PPh_3)_3$ and L^{2a} afforded a green solid, recovered in 95% yield. NMR data of the crude material revealed the occurrence of a mixture of the two isomers in a 1/9 ratio, subsequently identified as 4_{2a}-*cis-Cl* and 4_{2a}-*trans-Cl*, respectively. Rapid recrystallization of the green solution from a dichloromethane/hexane mixture at low temperature allowed to intercept the green isomer 4_{2a}-*trans-Cl*, obtained as single crystals that could be unambiguously identified by X-ray diffraction. By contrast, slow recrystallization of the green solution at room temperature produced brown crystals of 4_{2a}-*cis-Cl*, also fully identified by X-ray diffraction (Scheme 3).

The green complex $RuCl_2(L^{2a})(PPh_3)$ (4_{2a}-*trans-Cl*) was thus identified as the kinetic product of ligand addition, progressively converted into the more stable isomer $RuCl_2(L^{2a})(PPh_3)$ (4_{2a}-*cis-Cl*), representing the thermodynamic product. The observation by ^{31}P NMR of J_{PP} coupling constants, of 33 and 40 Hz for 4_{2a}-*trans-Cl* and 4_{2a}-*cis-Cl*, respectively, is consistent with the *cis* arrangement of the two phosphorus atoms observed in both cases in the solid state. For the green isomer, the equivalence of the two methylenic H atoms is consistent with the existence of a mirror plane containing the two phosphorus ligands, thus implying that the chloride atoms are in *trans* position. These observations are corroborated by the X-ray structure analyses of the two complexes (Figure 4 and Table 5; Figure 5 and Table 6). Both complexes exhibit a square-pyramidal geometry where the phosphorus atom of L^{2a} is occupying the apical position, whereas the donor nitrogen atom, the two chlorides, and the remaining triphenyl phosphine are

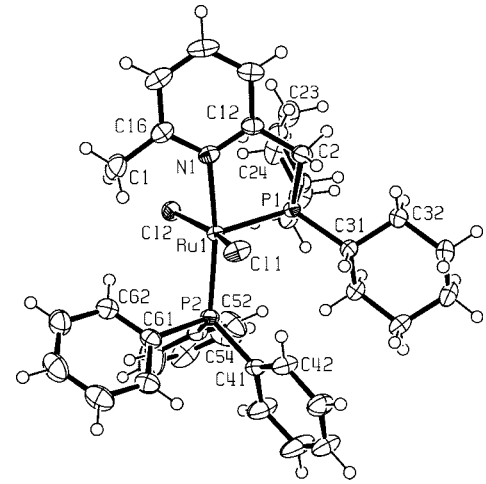


Figure 4. Perspective view of complex $RuCl_2(L^{2a})(PPh_3)$ (4_{2a}-*trans-Cl*). Ellipsoids are shown at the 30% probability level.

Table 5. Selected Interatomic Distances [Å] and Bond Angles [deg] for Complex 4_{2a}-*trans-Cl*

Bond Distances	
Ru1−Cl1	2.3944(7)
Ru1−Cl2	2.3822(7)
Ru1−P1	2.1989(7)
Ru1−P2	2.3031(6)
Ru1−N1	2.1442(17)
P1−C2	1.836(2)
C2−C12	1.490(3)
Bond Angles	
Cl1−Ru1−Cl2	161.84(3)
Cl1−Ru1−P1	96.04(3)
Cl1−Ru1−P2	94.32(3)
Cl1−Ru1−N1	83.86(5)
Cl2−Ru1−P1	99.69(3)
Cl2−Ru1−P2	90.15(3)
Cl2−Ru1−N1	88.92(5)
P1 −Ru1−P2	105.69(3)
P1−Ru1−N1	83.46(5)
P2−Ru1−N1	170.82(5)

all in equatorial position. Let us specify that similar types of isomerization reactions have been observed in the case of other Ru(II)-halide complexes, including alkylidene complexes.[19]

Whereas the same synthetic strategy proved to be convenient for the whole series of phosphino-pyridine type ligands considered in this work, further experiments confirmed that the relative stability of the principal isomers of complex $\mathbf{4_{nx}}$ appears to be strongly dependent on the steric and/or electronic properties of the substituents. Although the complex $RuCl_2(\mathbf{L^{2b}})(PPh_3)$ ($\mathbf{4_{2b}}$-*trans-Cl*) ($\mathbf{L^{2b}} = Cy_2PCH_2quin$) was generated under the same conditions as the previous one, its isomerization into the *cis* derivative $RuCl_2(\mathbf{L^{2b}})(PPh_3)$ ($\mathbf{4_{2b}}$-*cis-Cl*) was found to require a much longer time for completion. The same very slow isomerization of the other quinolynyl derivative, $RuCl_2(\mathbf{L^{1b}})(PPh_3)$ ($\mathbf{4_{1b}}$-*trans-Cl*), was noted.

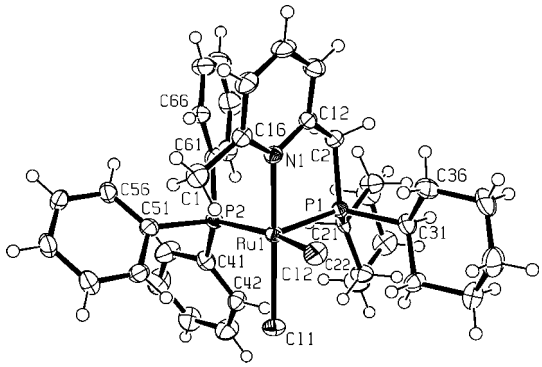
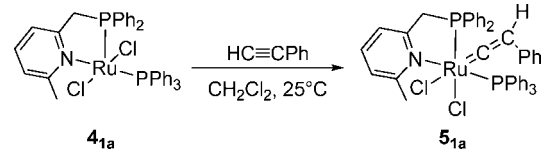


Figure 5. Perspective view of complex $RuCl_2(\mathbf{L^{2a}})(PPh_3)$ ($\mathbf{4_{2a}}$-*cis-Cl*). Ellipsoids are shown at the 30% probability level.

Table 6. Selected Interatomic Distances [Å] and Bond Angles [deg] for Complex 4_{2a}-*cis-Cl*

Bond Distances	
Ru1−Cl1	2.3822(13)
Ru1−Cl2	2.4430(13)
Ru1−P1	2.1956(12)
Ru1−P2	2.2728(12)
Ru1−N1	2.082(4)
P1−C2	1.840(5)
N1−C12	1.351(6)
C2−C12	1.493(7)
Bond Angles	
Cl1−Ru1−Cl2	85.14(4)
Cl1−Ru1−P1	103.27(4)
Cl1−Ru1−P2	94.28(4)
Cl1−Ru1−N1	168.99(11)
Cl2−Ru1−P1	104.27(5)
Cl2−Ru1−P2	160.92(5)
Cl2−Ru1−N1	85.01(11)
P1−Ru1−P2	94.44(4)
P1−Ru1−N1	83.96(11)
P2−Ru1−N1	93.41(11)
Ru1−P1−C2	101.95(17)
Ru1−N1−C12	120.7(3)
P1−C2−C12	110.1(3)
N1−C12−C2	116.7(4)

Scheme 4. Representative Reaction of Type 4_{1x} Phosphinopyridine Ru(II) Complexes with a Terminal Alkyne; Stoichiometric Reaction of $RuCl_2(\mathbf{L^{1a}})(PPh_3)$ ($\mathbf{4_{1a}}$) (mixture of *cis* and *trans* derivatives) with Phenylacetylene Giving the Corresponding Vinylidene Species $RuCl_2(\mathbf{L^{1a}})(CCHPh)(PPh_3)$ ($\mathbf{5_{1a}}$) Obtained as a Unique Single Isomer



$\mathbf{4_{1a}}$ $\mathbf{5_{1a}}$

Reactivity of $RuCl_2(L_{1x})(PPh_3)$ ($\mathbf{4_{1x}}$) toward Alkynes and Formation of Vinylidene $RuCl_2(L_{1x})(=C=CHR)(PPh_3)$ ($\mathbf{5_{1x}}$). It was found that all isomeric forms of $\mathbf{4_{1x}}$ complexes react cleanly with terminal alkynes to afford a new complex $\mathbf{5_{1x}}$ existing under the form of a unique isomer. The latter was identified by NMR spectroscopy as the vinylidene species $RuCl_2(\mathbf{L_{1x}})(=C=CHR)(PPh_3)$ ($\mathbf{5_{1x}}$), exhibiting the geometry shown in Scheme 4. Such a geometry can be reasonably inferred by comparison with that of the allenylidene compound $RuCl_2(\mathbf{L^{2a}})(C=C=CPh_2)(PPh_3)$, exhibiting comparable ^{31}P NMR data, and for which a preliminary X-ray structure analysis was done.[20] As shown in Scheme 4, the vinylidene ligand occupies a coordination site in *cis* position relative to both P and N donor atoms of the PN ligand, whereas the two chloride ligands are in *cis* position. The remaining triphenylphosphine ligand occupies the site *trans* to the nitrogen atom. It is noteworthy that, in contrast to the reaction of terminal alkynes with $RuCl_2(PPh_3)_3$, which was previously shown by Wakatsuki to give the 16 e^- vinylidene complex $RuCl_2(PPh_3)_2(CCHR)$ with concomitant loss of triphenylphosphine,[21] the reaction observed here is an addition rather than a substitution, thus taking place without phosphine displacement and leading to an 18 e^- species. This may be indicative that a phosphinopyridine ligand is less sterically demanding than two phosphines and might then have a lower *cis*-labilizing ability.

Given that vinylidenes can be regarded as "carbenoids",[22] one might reasonably anticipate that the reaction of $\mathbf{4_{1x}}$ with a diazoalkane might generate a potentially metathesis-active carbene species. Indeed, it was previously found by Fogg[5d] that

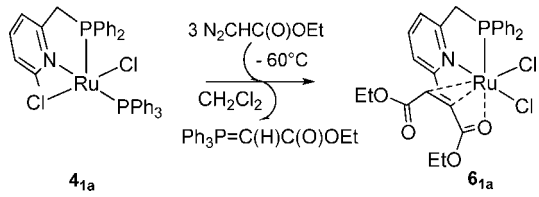
(19) (a) For some examples, see: Queiroz, S. L.; Batista, A. A.; Oliva, G.; Gambardella, M. T.; Santos, R. H. A.; MacFarlane, K. S.; Rettig, S. J.; James, B. R. *Inorg. Chim. Acta* **1998**, *267*, 209. (b) Hansen, S. M.; Volland, M. A. O.; Rominger, F.; Eisenträger, F.; Hofman, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1273. (c) Hansen, S. M.; Rominger, F.; Metz, M.; Hofman, P. *Chem.−Eur. J.* **1999**, *5*, 557. (d) Volland, M. A. O.; Straub, B. F.; Gruber, I.; Rominger, F.; Hofman, P. *J. Organomet. Chem.* **2001**, *617*, 288.

(20) The allenylidene complex $RuCl_2(\mathbf{L^{2a}})(=C=C=CPh_2)(PPh_3)$ was obtained by reaction of $\mathbf{4_{1a}}$ with 1,1-diphenyl-2-propyn-1-ol under the same experimental conditions as those used for the preparation of the vinylidene species. Though not publishable due to the poor quality of the crystals, the X-ray analysis allowed an accurate determination of the overall geometry of the complex (Lugan, N.; Lavigne, G. Unpublished observations).

(21) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105.

(22) (a) Bruce, M. I. *Chem. Rev* **1991**, *91*, 197. (b) Katayama, H.; Ozawa, F. *Coord. Chem. Rev.* **2004**, *248*, 1703.

Scheme 5. Reaction of $RuCl_2(L^{1a})(PPh_3)$ (4_{1a}) (mixture of *cis* and *trans* isomers) with an Excess of Ethyl Diazoacetate Giving the Diethyl Maleate Complex $RuCl_2(L^{1a})$\{*cis*-EtO(O)C(H)C═C(H)C(O)OEt\} (6_{1a}) as a Unique Isomer



closely related complexes $RuCl_2$(diphosphine)(PPh_3) do not require PPh_3 ligand abstraction to achieve high reactivity in ROMP in the presence of a carbene source, possibly meaning that loss of PPh_3 is spontaneous under room-temperature reaction conditions. We were thus led to examine the case of our phosphinopyridine complexes. However, our attempts to use type **5** vinylidene complexes as catalyst precursors for the ROMP of norbornene at room temperature proved to be negative, probably due to the fact that they are fully saturated 18 e^- species.

Reactivity of $RuCl_2(L^{1x})(PPh_3)$ (4_{1x}) toward Ethyl Diazoacetate. The reaction of $RuCl_2(\mathbf{L^{1x}})(PPh_3)$ ($\mathbf{4_{1x}}$) (mixture of *cis*–*trans* isomers) with ethyl diazoacetate was carried out at −60 °C. Monitoring by NMR spectroscopy revealed that total consumption of the precursor complex $\mathbf{4_{1x}}$ required at least 3 equiv of the carbene precursor. Typically, upon addition of an excess of ethyl diazoacetate (5 equiv) at low temperature, the reaction proceeded cleanly toward the formation of a unique complex exhibiting a single phosphorus resonance, along with concomitant elimination of phosphonium ylide Ph_3P═C(H)C(O)OEt. Isolation and characterization of the new complex $\mathbf{6_{1x}}$ by NMR spectroscopy and X-ray diffraction (in the case of $\mathbf{6_{1a}}$) allowed its formulation as $RuCl_2(\mathbf{L^{1x}})$\{*cis*-EtO(O)C(H)C═C(H)C(O)OEt\} ($\mathbf{6_{1x}}$) (Scheme 5, Figure 6, Table 7). The formation of this uncommon olefinic complex can be reasonably understood in terms of a reaction sequence involving (i) the coordination of the incoming carbene moiety to the metal center, (ii) its coupling with the triphenylphosphine ligand to produce the phosphonium ylide Ph_3P═C(H)C(O)OEt, which is readily eliminated, and (iii) the uptake of two more carbene units by the remaining 14 e^- fragment "$RuCl_2(\mathbf{L^{1x}})$", resulting in a metal-mediated CC bond formation between these units to give the coordinated diethyl maleate ligand intercepted here.

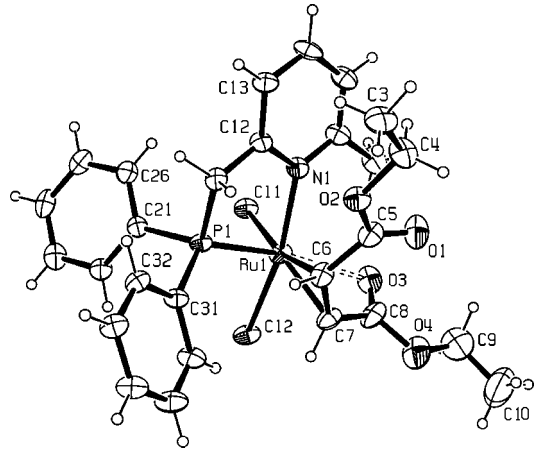


Figure 6. Perspective view of complex $RuCl_2(\mathbf{L^{1a}})$\{*cis*-EtO(O)-C(H)C═C(H)C(O)OEt\} ($\mathbf{6_{1a}}$). Ellipsoids are shown at the 30% probability level.

Table 7. Bond Lengths [Å] and Angles [deg] for Complex 6_{1a}

Bond Distances	
Ru1−Cl1	2.3899(15)
Ru1−Cl2	2.4003(15)
Ru1−P1	2.1987(15)
Ru1−O3	2.414(5)
Ru1−N1	2.142(5)
Ru1−C6	2.179(5)
Ru1−C7	2.131(5)
P1-C2	1.819(5)
P1−C31	1.808(6)
P1−C21	1.808(5)
O1−C5	1.189(9)
O2−C4	1.461(9)
O2−C5	1.345(6)
O3−C8	1.226(9)
O4−C9	1.401(12)
O4−C8	1.355(8)
N1−C12	1.373(6)
C2−C12	1.488(8)
C3−C4	1.502(9)
C5−C6	1.465(10)
C6−C7	1.394(6)
C7−C8	1.440(10)
C9−C10	1.460(13)
Bond Angles	
Cl1−Ru1−Cl2	84.11(5)
Cl1−Ru1−P1	94.59(5)
Cl1−Ru1−O3	98.40(12)
Cl1−Ru1−N1	82.29(12)
Cl1−Ru1−C6	164.73(19)
Cl1−Ru1−C7	153.62(13)
Cl2−Ru1−P1	92.75(6)
Cl2−Ru1−O3	85.33(12)
Cl2−Ru1−N1	165.69(12)
Cl2−Ru1−C6	111.15(18)
Cl2−Ru1−C7	78.72(16)
P1−Ru1−O3	166.59(13)
P1−Ru1−N1	83.94(14)
P1−Ru1−C6	85.44(17)
P1−Ru1−C7	106.02(19)
O3−Ru1−N1	101.04(17)
O3−Ru1−C6	82.91(18)
O3−Ru1−C7	60.6(2)
N1−Ru1−C6	82.5(2)
N1−Ru1−C7	115.58(19)
Ru1−P1−C2	102.41(18)
Ru1−O3−C8	86.5(4)
Ru1−N1−C12	117.4(4)
P1−C2−C12	110.9(3)
Ru1−C6−C5	113.1(5)
Ru1−C6−C7	69.3(3)
C5−C6−C7	121.2(6)
Ru1−C7−C6	73.0(3)
Ru1−C7−C8	93.3(4)
C6−C7−C8	120.9(7)
O4−C8−C7	114.6(6)
O3−C8−O4	125.9(7)
O3−C8−O7	119.5(6)

Interestingly, a comparable reaction pathway involving similar generation of a phosphonium ylide from the cyclopentadienyl Ru(II) complex Cp*RuCl{CHC(O)OEt}(PPh_3) has been previously described by Baratta.[23] It has also been recently shown that one of the identified pathways to decomposition of Grubbs catalysts is a coupling reaction between the propagating carbene and a free phosphine.[24]

(23) (a) Baratta, W.; Del Zotto, A.; Rigo, P. *Organometallics* **1999**, *18*, 5091. (b) Pedro, F. M.; Santos, A. M.; Baratta, W.; Kühn, F. E. *Organometallics* **2007**, *26*, 302.

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Table 8. ROMP of Norbornene Using Complexes 4_{nx} and 2_{1a} as Precatalysts at 22 °C and Trimethylsilyldiazomethane as Initiator

precatalyst[a]	[substr]/[cat.]	time (min) [b]	yield[c]	M_n[d]	PD[d]
$\mathbf{4_{1a}}$	100	30	59	1.81×10^5	2.53
$\mathbf{4_{1b}}$	100	30	61	1.91×10^5	2.30
$\mathbf{4_{2a}}$	100	30	53	1.80×10^5	2.30
$\mathbf{4_{2b}}$	100	30	45	4.41×10^5	1.70
$\mathbf{2_{1a}}$	100	2	50[e]		
$\mathbf{2_{1a}}$	100	8	60[e]		
$\mathbf{2_{1a}}$	100	30	79	4.40×10^4	2.39

[a] General conditions (see Experimental Part): solvent, CH_2Cl_2; reaction initiated by addition of trimethylsilyldiazomethane ([TMSD]/[cat.] = 5). [b] Time at which the polymerization was quenched by addition of 2,6-di(*tert*-butyl)-4-methylphenol in methanol. [c] Isolated by precipitating in methanol. [d] Determined by SEC in microfiltrated THF solutions. [e] The yields obtained for **2a** upon quenching the polymerization at short time are indicative of a fast initiation rate, but the relevant Mn values at intermediate stage were not measured.

Spectroscopic and crystallographic data reveal that the olefinic bond of the newly assembled diethyl maleate ligand is π-bound to the Ru center and is coordinated in *cis* position relative to both the phosphorus and the nitrogen atom of the ancillary PN ligand. Maleate and fumarate ligands have been previously used as suitable leaving groups in a series of ruthenium complexes prepared by Kondo and Mitsudo.[25] Here, an additional bonding interaction is seen to occur between one of the donor oxygens of the diethyl maleate unit and the ruthenium center, thereby blocking the coordination site opposite to the phosphorus ligand. The octahedral basis set of the complex is completed by the two chloride ligands adopting a *cis*- arrangement.

On the basis of the expectation that the olefin is only weakly bound to the metal, we were reasonably anticipating that further reaction of $\mathbf{6_{1a}}$ with one more equivalent of diazoalkane would result in the formation of a carbene complex via simple displacement of the coordinated ester function of the olefin. Surprisingly, however, additional experiments indicated that such a reaction does not spontaneously occur (at least under ambient conditions), which probably reflects a rather high stability of the complex inherent to the chelating coordination mode of the diethyl maleate ligand. Preliminary experimental tests under catalytic conditions effectively confirmed that complex $\mathbf{6_{1a}}$ is inefficient as a catalyst precursor for the ROMP of norbornene, at least under ambient conditions.

With this in mind, we were logically prompted to carry out further catalytic experiments by using a carbene source devoid of potentially coordinating oxygen. Trimethylsilyldiazomethane, also commercially available, was thus logically selected as an alternate carbene source for that purpose. The results of relevant catalytic tests are reported in the next section.

ROMP of Norbornenes Using $RuCl_2(L_{nx})(PPh_3)$ (4_{nx}-*cis*-*Cl*) and Related Species as Catalyst Precursors in the Presence of Trimethylsilydiazomethane as the Carbene Source. Noëls and co-workers[5b,e,l] have previously shown that a number of noncarbene Ru(II) precursors are prone to catalyze the ROMP of norbornenes upon *in situ* activation by trimethylsilyl diazomethane, and we have recently exploited such a strategy in a published report showing that some alkynylphosphine complexes can act similarly as fast ROMP precatalysts.[5j] Attempts to evaluate the efficiency of our new complexes were thus made under the same experimental conditions. The results, listed in Table 8, indicate that our "*in situ*" generated catalysts exhibit a moderate activity at room temperature in nonoptimized standard tests where the polymerization was quenched after 30 min. It is noteworthy that the complexes are more active than the precursor $RuCl_2(PPh_3)_3$, known to polymerize norbornene only at 50 °C.[5h] Changes in the nature of the substituents on the ligand affect only moderately the activity of the catalyst. Interestingly, the bimetallic species $\mathbf{2_{1a}}$ is also seen to be active as a catalyst precursor, exhibiting the fastest initiation rate (50% conversion after 2 min). However, in that case, considering that both a $14e^-$ fragment, "$RuCl_2(PPh_3)_2$" (the latter possibly acting as a phosphine scavenger) and a 16 e^- fragment "$RuCl_2(\mathbf{L_{1a}})(PPh_3)$" may be liberated in solution upon dissociation of the bimetallic unit, a complicating factor arises from the fact that both fragments are prone to be attacked by the incoming carbene and may thus each produce an independent active species propagating at a different rate.

The precatalysts studied in this work tolerate small amounts of HCl, but are dramatically altered by the presence of traces of base, such as residues that might incidentally remain on the glassware after cleansing treatment with an ethanolic KOH bath (this is avoided by routine neutralization of the glassware with an aqueous HCl bath). The deleterious effect of bases noted here may be understood in terms of pioneering observations made by Grubbs on the ROMP reaction initiated by well-defined Ru carbene complexes.[10a] The degradation of the catalyst in that case may be ascribed to the facile displacement of the chlorides by anionic ligands,[26] a transformation that may be exploited for other types of catalytic reactions, as exemplified below in the next section. Let us mention here that a positive effect of acid additives on the performances of well-defined ROMP precatalysts has been observed by Grubbs[27] and recently investigated in depth by Schanz.[28]

At the present stage of our investigation, the principal drawback of these *in situ* generated catalysts is that they are unable to polymerize more synthetically useful cyclic olefins being less strained than norbornene. One reason for such a limitation might be that, contrary to our original expectations, the pyridyl group does not behave as a hemilabile ligand and probably remains coordinated to the metal, even in the active form of the catalyst. In this respect, the introduction of bromo substituents on the pyridyl ring (as seen in third-generation Grubbs' catalyst) might allow enhancing its leaving group properties. So, it is no doubt that further modifications of the ligand backbone will be needed in view of future improvements (see our conclusions).

Transfer Hydrogenation of Ketones Using $RuCl_2(L_{nx})(PPh_3)$ (4_{nx}) as a Catalyst Precursor. A number of authoritative recent reviews have highlighted the importance of chemoselective transition-metal-catalyzed transfer hydrogenation of ketones,[11] which has now gained considerable significance and has been successfully applied to selective organic transforma-

(25) (a) Mitsudo, T.; Suzuki, T.; Zhang, S.-W.; Imai, D.; Fujita, K.; Manabe, T.; Shiotsuki, M.; Watanabe, Y.; Wada, K.; Kondo, T. *J. Am. Chem. Soc.* **1999**, *121*, 1839. (b) Shiotsuki, M.; Suzuki, T.; Kondo, T.; Wada, K.; Mitsudo, T. *Organometallics* **2000**, *19*, 5733.

(26) Hong, S. H.; Wenzel, A. G.; Salguero, T. T.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 7961.

(27) Lynn, D. M.; Mohr, B.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6601.

(28) P'Pool, S. J.; Schanz, H.-J. *J. Am. Chem. Soc.* **2007**, *129*, 14200.

(29) (a) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466. (b) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931. (c) Pamies, O. Bäckvall.; J.-E., *Chem.−Eur. J.* **2001**, *7*, 5052. (d) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 15104. (e) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201. (f) Samec, J. S.; Ell, A. H.; Aberg, J. B.; Privalov, T.; Eriksson, L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2006**, *128*, 14293. (g) Comas-Vives, A.; Ujaque, G.; Llenos, A. *Organometallics* **2007**, *26*, 4135.

tions including enantioselective reactions. Significantly, according to these reviews, there is not one, but several types of operative specific mechanisms for transfer hydrogenation,[29] depending both on the classes of transition-metal complexes used as precatalysts and on the peculiar ligand combinations adopted in the construction of such complexes. Since the early pioneering reports of Sasson and Blum,[30] where $RuCl_2(PPh_3)_3$ was used for the first time as a catalyst precursor for the transfer hydrogenation from alcohols to ketones, and the equally very important work by Bäckvall,[31] who originally defined the most convenient experimental conditions, a multitude of ruthenium complexes were investigated and proved to function as efficient catalyst precursors.[11] Significantly, the reports by Noyori[32] on the spectacular performances of $RuCl_2$(diamine)(diphosphine) complexes, giving rise to "bifunctional" RuH/NH_2 catalysts capable of promoting a concerted transfer of proton and hydride to the incoming ketone, have oriented the quest for ligand acceleration effects toward diverse combinations of soft phosphines and hard nitrogen ligands as well as hybrid "PN" ligands.[33–35] Some of the relevant complexes, however, are implying mechanisms different from that proposed by Noyori. A representative example is the case of Ru(II) complexes of the chiral ferrocenyloxazolinylphosphine ("FOXAP"),[34] sometimes generated *in situ*, and subsequently formulated as $RuCl_2$(FOXAP)(PPh_3), which were found to be of particular efficiency for various highly enantioselective reduction reactions including hydrogen transfer.

Among numerous approaches,[11,30–36] including several early reports by two of us,[8a,b] the Ru-based systems recently reported by Baratta,[35] in particular those involving a terdentate pincer ligand or a cyclometallated N-heterocyclic carbene,[35d,e] are of spectacular efficiency and presently remain the best transfer hydrogenation catalysts reported so far.

Table 9. Transfer Hydrogenation of Various Ketones, Using Complexes 4_{nx} as Precatalysts[a]

substrate	catalyst	TOF(h^{-1})	yield after 60s	final yield[b]
Cyclohexanone				
	4_{1a}	**273 000**	99%	99%
	4_{2a}	239 000	99%	99%
	4_{1b}	172 000	93%	99%
	4_{2b}	140 000	98%	99%
2-Hexanone				
	4_{1a}	200 000	90%	91%
	4_{2a}	164 000	91%	92%
	4_{1b}	**225 000**	92%	92%
	4_{2b}	211 000	91%	91%
Acetophenone				
	4_{1a}	99 000	83%	88%
	4_{2a}	**124 000**	77%	88%
	4_{1b}	82 000	74%	88%
	4_{2b}	100 000	70%	88%
5-Methyl-5-hexen-2-one				
	4_{1a}	78 000	75%	94%
	4_{2a}	35 000	52%	92%
	4_{1b}	**129 000**	87%	94%
	4_{2b}	100 000	84%	93%
Benzophenone				
	4_{1a}	93 000	69%	93%
	4_{2a}	29 000	49%	57%
	4_{1b}	**150 000**	90%	94%
	4_{2b}	49 000	55%	60%

[a] Reactions were carried out on a 10 mmol scale, using 0.01 mole of catalyst in 10 mL *i*PrOH at T = 82 °C under N_2 with [NaOH]/[RU] = 22.5. The conversion rates were determined by GC from samplings made every 15 seconds. Turnover frequencies, corresponding to the number of moles of ketone converted per mole of catalyst per hour, were determined at 50% conversion. The table gives both the intermediate yield obtained within 60 seconds and the final maximum yield reached. [b] Final yields were respectively measured after 2 min for cyclohexanone, 5 min for 2-hexanone and acetophenone, 10 min for 5-methyl-5-hexen-2-one, and 30 min for benzophenone.

With the above literature data in mind, we were curious to examine whether a very simple metal–ligand system using our series of type **4_{nx}** complexes as catalyst precursors could compete with the more elaborated catalyst prototypes cited above. From an experimental point of view and for comparative purposes, all catalytic tests were made under Bäckvall's conditions. In such a way to ascertain our results, we cautiously made a blank test, keeping in mind that hydrogen transfer is also known to proceed without catalyst, but then at much slower rates, and via a different mechanism.[37] The blank test, carried out on acetophenone under the experimental conditions of all our catalytic runs, albeit in the absence of catalyst, gave 0.6% yield in 5 min, 1.3% yield in 10 min, and 94% yield in 70 h.

The results of our catalytic experiments carried out with complexes **4_{nx}-*cis*-*Cl*** (Table 9, Figure 7) reveal that these rank

(30) Sasson, Y.; Blum, J. *J. Org. Chem.* **1975**, *40*, 1887.

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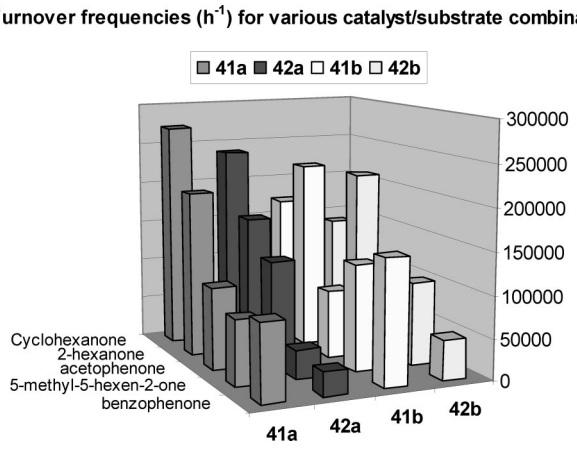

Figure 7. TOF values (h^{-1}) recorded for type $\mathbf{4_{nx}}$ precatalysts in the transfer hydrogenation of various ketone substrates.

among the fastest precatalysts reported so far for this reaction. They appear to exhibit higher efficiency than the already excellent Ru(II)/PCP-pincer complexes reported by Fogg[33h] and van Koten,[33e,q] with the additional advantage that they are simpler and do not require any pretreatment. Our results also indicate that for a given ketonic substrate it is certainly possible to select the fastest catalyst within the present family. However, one must admit that subtle variations of the electronic and steric properties of the ligands are only moderately affecting the performances of the catalyst. In particular, the comparative diagram displayed in Figure 7 reveals that, whereas electron-rich ligands have been previously shown to exhibit particular efficiency, this does not appear to be the case here, where $\mathbf{4_{1a}}$ and $\mathbf{4_{1b}}$ are even often slightly better than $\mathbf{4_{2a}}$ and $\mathbf{4_{2b}}$. Our best result was recorded with the precatalyst $\mathbf{4_{1a}}$, using cyclohexanone as the substrate. The latter ketone was hydrogenated in 99% yield within 45 s with only 0.01 mol (1×10^{-3} mol %) of $\mathbf{4_{1a}}$, representing a turnover frequency of 272 571 h^{-1}. The TOF was indeed measured at 50% conversion, namely, after 7 s in the present case! Indeed, the first sampling at 15 s already gave 89.8% yield. Such performances rank only slightly below those recorded with Baratta's catalysts, and it is noteworthy that the turnover rates obtained with our new ligands are about 2 times higher than those recorded with the bulkier and more sophisticated "P−N−O" ligand "1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane" previously tested in our group.[8b] Though no mechanistic studies were made during the course of the present work, it can be reasonably assumed that the mechanism previously established by Bäckvall for $RuCl_2(PPh_3)_3$ and involving the formation of a dihydride species[31c] is also operative for the present catalytic system.

Conclusion

At a time where tandem catalysis is attracting growing attention,[38] the ability for a given transition-metal complex to catalyze several types of substrate transformations is appearing as a valuable property. In the present investigation, we have shown that certain phosphinopyridine complexes of the type $RuCl_2\{R_2PCH_2(C_5H_2R'R''N)\}(PPh_3)$ where the pyridyl moiety is a picolyl or a quinolyl group are simple and readily accessible at low cost from $RuCl_2(PPh_3)_3$ under a simple experimental protocol, which has now been precisely defined. They were designed as probe systems enabling convenient preliminary assays in metathesis, and, in this respect, our initial objective is only partly attained. Indeed, though the corresponding "*in situ*" generated catalysts proved to be moderately efficient initiators for the ROMP of norbornene under ambient conditions, they still do have some important limitations, being in particular unable to polymerize unstrained cyclic olefins such as cyclooctene or to catalyze other types of metathesis reactions.

Importantly, however, one outgrowth of the present investigation is to provide insight into the mechanism by which an active olefin metathesis catalyst can be generated *in situ* upon reaction of a phosphine-containing Ru(II) complex with a carbene source. Indeed, a typical diazoalkane such as ethyl diazoacetate was seen to act not only as the effective source of the propagating carbene but also as a phosphine scavenger, via concomitant formation of the corresponding phosphonium ylide, thereby contributing to the creation of an unsaturation, as obviously required for olefin coordination and metathesis.

In parallel, we have also shown that most complexes within the series $RuCl_2\{R_2PCH_2(C_5H_2R'R''N)\}(PPh_3)$ are acting as remarkably efficient "instant" catalysts for the transfer hydrogenation of ketones, matching the performances of the best catalytic system reported so far, and in particular those based on more sophisticated ligands. Of course, further modifications of our ligands by introduction of chiral centers are still required in view of developing relevant synthetically useful applications in catalytic hydrogenation.

More generally, a logical continuation of this work in our laboratory is currently involving the parallel design and development of related *in situ* generated catalysts based on pyridine-functionalized N-heterocyclic carbene ligands, which are also easily available.[39] Relevant results will be published in due course.

Experimental Part

General Considerations. THF and diethyl ether were distilled from sodium/benzophenone ketyl just before use. Toluene, pentane, and dichloromethane were dried and distilled following standard procedures and stored under nitrogen. $RuCl_2(PPh_3)_3$[40] and 2-[(diphenylphosphino)methyl]-6-methyl-pyridine,[8c] ($\mathbf{L^{1a}}$) were prepared following literature procedures. Other reagent grade chemicals such as 2-picolin, 2,6-lutidin, 2-methylquinolin, phenylacetylene, ethyl diazoacetate, and ^{n}BuLi (1.6 M solution in hexane) were obtained from Aldrich and used without further purification. All synthetic manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. A liquid N_2/2-propanol slush bath was used to maintain samples at the desired low temperature. NMR spectra were recorded on Bruker AC200, WM250, DPX300, AV300, AMX400, or AV500 spectrometers and were referenced to the residual signals of the deuterated solvent. Infrared spectra were obtained as solutions on Perkin-Elmer 1725 FT-IR or 983G spectrometers with 0.1 mm cells equipped with CaF_2 windows. Microanalyses of C, H, and N elements were performed by the Laboratoire de Chimie de Coordination Microanalysis Service on a Perkin-Elmer 2400 CHN analyzer. *Note: Most of the compounds isolated in this work were found by X-ray diffraction to contain*

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nonstoichiometric amounts of dichloromethane in the lattice (vide infra). The presence of such volatile molecules in the solid samples is believed to affect the precision of microanalyses. The characterization of polynorbornene was carried out by size exclusion chromatography: Analytical SEC data were obtained at 298 K using a SFD RI 2000 differential refractometer, a multiangle laser light scattering detector (Wyatt Technology, miniDAWN), a PLgel 5 μm MIXED-D column (300 × 7.5 mm), and microfiltrated THF as eluant with a nominal flow of 0.85 mL/min; results are reported relative to poly(styrene) standards. The products of transfer hydrogenation were analyzed by gas chromatography on a Hewlett-Packard HP4890AHP equipped with a flame ionization detector and an Alltech EC-1000 column (0.32 mm i.d., 15 m long).

Synthesis of Ph_2PCH_2quin (L^{1b}), Ph_2PCH_2pic (L^{2a}), and Cy_2PCH_2quin (L^{2b}). The typical procedure for the preparation of these ligands is exemplified here by the case of $\mathbf{L^{2a}}$. A solution containing 2.5 mL of 2,6-lutidine (21.5 mmol) in 20 mL of Et_2O was added dropwise at 0 °C to a solution containing 1 molar equiv of 1.6 M ^{n}BuLi diluted in 13.5 mL of hexane. The resulting solution was found to gradually turn red-orange during the addition. At the end of the addition, it was stirred for 30 min more at 0 °C, then allowed to warm to room temperature. The resulting solution of $picCH_2Li$ thus prepared was added dropwise over a period of 3 h by means of an automatic syringe to a solution containing 5 g of dicyclohexylchlorophosphine (21.5 mmol) in 100 mL of Et_2O maintained at −80 °C. At the end of the addition, the cold bath was removed in such a way as to allow warming of the solution to ambient temperature. Degased water (100 mL) was added to the reaction medium, and the phosphine was extracted with ether. The organic phase was dried over $MgSO_4$ and then evaporated under high vacuum, leaving a pale yellow oil ultimately producing a solid residue when stored at −30 °C in a freezer. This residue was subsequently recrystallized at −30 °C from a Et_2O/hexane mixture, producing the pure phosphine Cy_2PCH_2pic ($\mathbf{L^{2a}}$, 4.6 g, 1.40 mmol, 71% yield).

The other two new phosphinomethyl pyridine ligands, namely, Ph_2PCH_2quin ($\mathbf{L^{1b}}$) and Cy_2PCH_2quin ($\mathbf{L^{2b}}$), were synthesized according to the same preparative procedure, using on one hand the chlorophosphines Ph_2PCl and Cy_2PCl for $\mathbf{L^1}$ and $\mathbf{L^2}$, respectively, and on the other hand, 2-methylquinoline.

$\mathbf{L^{1b}}$ (pale yellow solid, 56% yield). NMR ^{1}H (250 MHz, CD_2Cl_2): δ 7.97 (d, 1H, J_{HH} = 7 Hz, C_9H_6N), 7.62 (d, 1H, J_{HH} = 7 Hz, C_9H_6N), 7.75 (d, 1H, C_9H_6N), 7.65 (t, 1H, C_9H_6N), 7.53 (t, 1H, C_9H_6N), 7.17 (d, 1H, C_9H_6N), 3.82 (s, 2H, CH_2), 7.48–7.35 (m, 5H, Ph). NMR ^{31}P{^{1}H} (101 MHz, CD_2Cl_2): δ −9.33. Anal. Calcd for $C_{22}H_{18}NP$: C, 80.72; H, 5.54; N, 4.28. Found: C, 80.39; H, 5.35; N, 4.23.

$\mathbf{L^{2a}}$ (white solid, 71% yield). NMR ^{1}H (250 MHz, CD_2Cl_2): δ 7.39 (t, 1H, J_{HH} = 9.6 Hz, C_5H_3N), 7.07 (d, 1H C_5H_3N), 6.86 (d, 1H, C_5H_3N), 2.94 (d, 2H, CH_2, J_{PH} = 3.7 Hz), 2.45 (s, 3H, CH_3). NMR ^{31}P (101 MHz, CD_2Cl_2): δ 5.89. Anal. Calcd for $C_{19}H_{30}NP$: C, 75.21; H, 9.97; N, 4.62. Found: C, 75.00; H, 9.62; N, 4.38.

$\mathbf{L^{2b}}$ (pale yellow solid, 68% yield). NMR ^{1}H (250 MHz, CD_2Cl_2): δ 8.05 (d, 1H, J_{HH} = 7 Hz, C_9H_6N), 9.97 (d, 1H, J_{HH} = 7 Hz, C_9H_6N), 7.79 (d, 1H, C_9H_6N), 7.66 (t, 1H, C_9H_6N), 7.53 (t, 1H, C_9H_6N), 7.47 (d, 1H, C_9H_6N), 3.18 (s, 2H, CH_2), 1.30–1.75 (m, 11H, C_6H_{11}). NMR ^{31}P (101 MHz, CD_2Cl_2): δ 6.11. Anal. Calcd for $C_{22}H_{30}NP$ C, 77.84; H, 8.91; N, 4.13. Found: C, 77.56; H, 8.68; N, 4.02.

Reaction of Ph_2PCH_2pic (L_{1a}) with $RuCl_2(PPh_3)$ under Nonoptimized Conditions. Crystals of $RuCl_2(PPh_3)_3$ (95 mg, 0.10 mmol) and Ph_2PCH_2pic ($\mathbf{L_{1a}}$, 29 mg, 0.10 mmol) were introduced in a Schlenk flask equipped with a stirring bar, and dichloromethane (15 mL) was added at room temperature. After stirring for 4 h, the dichloromethane was removed under vacuum. The brown residue was washed with *n*-hexane (2 × 10 mL) and dried under vacuum. Recrystallization from a dichloromethane/hexane mixture afforded a heterogeneous crystalline material, from which single crystals of $[RuCl_2(PPh_3)_2]_2$ (**1**), $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(\mathbf{L^{1a}})(PPh_3)]$ ($\mathbf{2_{1a}}$), and $RuCl_2(\mathbf{L^{1a}})_2(\mathbf{3_{1a}})$ were selected for X-ray diffraction analyses.

Synthesis of $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(L^{1a})(PPh_3)]$ (2_{1a}). Complex $RuCl_2(Ph_2PCH_2pic)(PPh_3)$ ($\mathbf{4_{1a}}$, as ca. 1:1 mixture of *cis/trans* isomers (*vide infra*), 73 mg, 0.10 mmol) and crystals of $RuCl_2(PPh_3)_3$ (95 mg, 0.10 mmol) were introduced in a Schlenk flask and dissolved in 15 mL of dichloromethane at room temperature. After stirring for 4 h, the solvent was eliminated under reduced pressure and the resulting brown residue was washed with *n*-hexane (2 × 10 mL) and dried under vacuum. Recrystallization from a dichloromethane/hexane mixture afforded a homogeneous dark orange crystalline material, which analyzed as $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(\mathbf{L^{1a}})(PPh_3)]$ ($\mathbf{2_{1a}}$) (60 mg, 0.043 mmol, 43% yield).

$\mathbf{2_{1a}}$. Anal. Calcd for $C_{73}H_{63}Cl_4NP_4Ru_2$: C, 61.65; H, 4.47; N, 0.98. Anal. Calcd for $[C_{73}H_{63}Cl_4NP_4Ru_2 + 1.5CH_2Cl_2]$ (X-ray structure analysis): C, 57.74; H, 4.29; N, 0.90. Found: C, 56.05; H, 3.86; N, 0.83.

Synthesis of $RuCl_2(L^{1a})_2$ (3_{1a}). Crystals of $RuCl_2(PPh_3)_3$(95 mg, 0.10 mmol.) and Ph_2PCH_2pic ($\mathbf{L_{1a}}$, 58 mg, 0.20 mmol) were introduced in a Schlenk flask, and 15 mL of dichloromethane was added at room temperature. After stirring overnight, the dichloromethane was removed under vacuum. The orange residue was washed with *n*-hexane (2 × 10 mL) and dried under vacuum. Recrystallization from a dichloromethane/hexane mixture afforded $RuCl_2(\mathbf{L^{1a}})_2$ ($\mathbf{3_{1a}}$) as a microcrystalline material (69 mg, 0.092 mmol, 92% yield).

$\mathbf{3_{1a}}$. NMR ^{1}H (500 MHz, CD_2Cl_2, 25 °C): δ 7.47–7.00 (m, 26H, C_6H_5*and*MeC_5H_3N), 5.44 (dt, 2H, J_{HH} = 15 Hz, J_{HP} = 5 Hz, C*H*H), 3.98 (dt, 2H, J_{HH} = 15 Hz, J_{HP} = 10 Hz, CH*H*), 2.83 (s, 6H, MeC_5H_3N). NMR ^{31}P{^{1}H} (101 MHz, CD_2Cl_2, 25 °C): δ 63.6 (s). Anal. Calcd for $C_{38}H_{36}Cl_2N_2P_2Ru$: C, 60.48; H, 4.81; N, 3.71. Anal. Calcd for $C_{38}H_{36}Cl_2N_2P_2Ru$: C, 60.48; H, 4.81; N, 3.71. Anal. Calcd for $[C_{38}H_{36}Cl_2N_2P_2Ru + CH_2Cl_2]$ (X-ray analysis): C, 55.79; H, 4.56; N, 3.35. Found: C, 55.89; H, 4.34; N, 3.12.

Synthesis of $RuCl_2(Ph_2PCH_2pic)(PPh_3)$ (4_{1a}). Crystals of $RuCl_2(PPh_3)_3$(95 mg, 0.10 mmol) were introduced in a Schlenk flask and dissolved in 15 mL of dichloromethane at room temperature. A solution of the ligand Ph_2PCH_2pic ($\mathbf{L_{1a}}$, 29 mg, 0.10 mmol) in 5 mL of degassed CH_2Cl_2 was prepared separately and introduced slowly into the previous one over a period of 4 h, using an automatic syringe. At the end of the addition, the solvent was evaporated under reduced pressure and the resulting brown solid was washed twice with *n*-hexane (10 mL) and dried under vacuum. NMR data of the crude product revealed the occurrence of a mixture of *cis*-Cl and *trans*-Cl isomers in a ca. 1/1 ratio. Recrystallization from a CH_2Cl_2/hexane mixture at room temperature gave pure samples of $\mathbf{4_{1a}}$-*cis-Cl* isolated as an orange crystalline material (50 mg, 0.069 mmol, 69% yield), subsequently used for the catalytic runs.

$\mathbf{4_{1a}}$-*trans-Cl* (from a $\mathbf{4_{1a}}$-*cis-Cl* /$\mathbf{4_{1a}}$-*trans-Cl* mixture). NMR ^{1}H (250 MHz, CD_2Cl_2, 25 °C): δ 8.15–6.91 (m, C_6H_5*and*MeC_5H_3N), 4.33 (d, 2H, J_{HP} = 10.3 Hz, CH_2), 2.69 (s, 3H, MeC_5H_3N). NMR ^{31}P{^{1}H} (101 MHz, CD_2Cl_2, 25 °C): δ 88.9 (d, J_{PP} = 44.0 Hz, Ph_2P), 50.7 (d, J_{PP} = 44.0 Hz, PPh_3).

$\mathbf{4_{1a}}$-*cis-Cl*. NMR ^{1}H (250 MHz, CD_2Cl_2, 25 °C): δ 8.15–6.91 (m, C_6H_5*and*MeC_5H_3N), 3.88 (dd, 1H, J_{HH} = 14 Hz, J_{HP} = 11 Hz, C*H*H), 3.07 (dd, 1H, J_{HH} = 14 Hz, J_{HP} = 10 Hz, CH*H*), 2.14 (s, 3H, MeC_5H_3N). NMR ^{31}P{^{1}H} (101 MHz, CD_2Cl_2, 25 °C): δ 86.2 (d, J_{PP} = 37 Hz, Ph_2P), 47.3 (d, J_{PP} = 37 Hz, PPh_3). Anal. Calcd for $C_{37}H_{33}Cl_2NP_2Ru$: C, 61.25; H, 4.58; N, 1.93. Anal. Calcd for $[C_{37}H_{33}Cl_2NP_2Ru + CH_2Cl_2]$ (X-ray analysis):[41] C, 56.31; H, 4.35; N, 1.73. Found: C, 57.61; H, 3.97; N, 1.53.

(41) Crystal data for $\mathbf{4_{1a}}$-*cis-Cl*·CH_2Cl_2: monoclinic, a = 10.530(5) Å, b = 13.425(5) Å, c = 25.056(5) Å, β = 95.832(5)°, V = 35242 Å^{-3}, T = 180 K, space group $P2_1/n$, Z = 4, μ(MoKα) = 0.868 mm^{-1}, 26 159 reflections measured, 6816 unique R_{int} = 0.0458, which were used in all calculations. The final $wR(F^2)$ was 0.0428 for all data.

Synthesis of $RuCl_2(Cy_2PCH_2pic)(PPh_3)$ ($\mathbf{4_{2a}}$). Crystals of $RuCl_2(PPh_3)_3$ (239 mg, 0.25 mmol) and of the ligand Cy_2PCH_2pic ($\mathbf{L_{2a}}$, 75 mg, 0.25 mmol) were introduced in a Schlenk flask and dissolved in 20 mL of dichloromethane under a nitrogen atmosphere. After 15 min, the solution was evaporated to dryness, and the resulting green solid was washed twice with *n*-hexane (10 mL) and dried *in vacuo* (70 mg, 0.95 mmol, 95%). At this stage, NMR data of the crude product revealed the occurrence of a mixture of *cis*-Cl and *trans*-Cl isomers in a ca. 1/9 ratio. Rapid recrystallization from a CH_2Cl_2/hexane mixture in the cold mixture gave pure $\mathbf{4_{1a}}$-*trans-Cl* as a dark green crystalline material, some single crystals being suitable for X-ray diffraction analyses. Alternatively, slow recrystallization from a CH_2Cl_2/hexane mixture at room temperature eventually gives pure $\mathbf{4_{1a}}$-*cis-Cl* as an orange crystalline material, which was used for both the X-ray diffraction analysis and the catalytic tests.

$\mathbf{4_{2a}}$-*trans-Cl*. NMR ^{1}H (250 MHz, CD_2Cl_2, 25 °C): δ 7.83–7.02 (m, C_6H_5 *and* MeC_5H_3N), 3.61 (d, 2H, J_{HP} = 12 Hz, CH_2), 2.58 (s, 3H, MeC_5H_3N), 2.12–1.05 (m, 22H, C_6H_{11}). NMR ^{31}P (101 MHz, CD_2Cl_2, 25 °C): δ 99.9 (d, J_{PP} = 33.5 Hz, PCy_2), 45.7 (d, J_{PP} = 33.5 Hz, PPh_3). Anal. Calcd for $C_{37}H_{45}Cl_2NP_2Ru$: C, 60.24; H, 6.15; N, 1.90. Anal. Calcd for $[C_{37}H_{45}Cl_2NP_2Ru + 0.75CH_2Cl_2]$ (X-ray analysis): C, 58.54; H, 6.01; N, 1.83. Found: C, 57.52; H, 5.91; N, 1.73.

$\mathbf{4_{2a}}$-*cis-Cl*. NMR ^{1}H (250 MHz, CD_2Cl_2, 25 °C): δ 7.81–7.15 (m, C_6H_5*and*MeC_5H_3N), 2.89 (dd, 1H, J_{HH} = 14 Hz, J_{HP} = 11 Hz, C*H*H), 2.67 (m(br), 1H, CH*H*), 2.07 (s, 3H, MeC_5H_3N), 1.84–1.03 (m, 22H, C_6H_{11}). NMR ^{31}P (101 MHz, CD_2Cl_2, 25 °C): δ 105.7 (d, J_{PP} = 40 Hz, PCy_2), 53.7 (d, J_{PP} = 40 Hz, PPh_3). Anal. Calcd for $C_{37}H_{45}Cl_2NP_2Ru$: C, 60.24; H, 6.15; N, 1.90. Anal. Calcd for $[C_{37}H_{45}Cl_2NP_2Ru + 3CH_2Cl_2]$ (X-ray analysis): C, 48.41; H, 5.18; N, 1.41. Found: C, 55.89; H, 5.46; N, 1.56.

Synthesis of $RuCl_2(Ph_2PCH_2quin)(PPh_3)$ ($\mathbf{4_{1b}}$). Crystals of $RuCl_2(PPh_3)_3$ (143 mg, 0.15 mmol.) were introduced in a Schlenk flask and dissolved in 5 mL of dichloromethane at room temperature. A solution of the ligand Ph_2PCH_2quin ($\mathbf{L_{1b}}$, 49 mg, 0.15 mmol) in 5 mL of degassed CH_2Cl_2 was prepared separately and introduced slowly into the previous one over a period of 1 h, using an automatic syringe. At the end of the addition, magnetic agitation was maintained for about 30 min more. The solvent was then removed under vacuum, and the resulting brown residue was washed twice with 10 mL of *n*-hexane and dried under vacuum. NMR data of the crude product revealed the occurrence of a mixture of *cis*-Cl and *trans*-Cl isomers in a ca. 1/9 ratio. Slow recrystallization from a CH_2Cl_2 hexane mixture at room temperature gave pure $\mathbf{4_{1b}}$-*cis-Cl* as an orange crystalline material (85 mg, 0.11 mmol, 74% yield). Such samples were subsequently used for the catalytic runs.

$\mathbf{4_{1b}}$-*trans-Cl* (from a $\mathbf{4_{1b}}$-*cis*-Cl/$\mathbf{4_{1b}}$-*trans-Cl* mixture). NMR ^{1}H (250 MHz, CD_2Cl_2, 25 °C): δ 9.25–6.46 (m, C_6H_5 and C_9H_6N), 4.57 (d, 2H, J_{PH} = 12 Hz, CH_2). NMR ^{31}P (101 MHz, CD_2Cl_2, 25 °C): δ 88.1 (d, J_{PP} = 37.0 Hz, PPh_2), 49.6 (d, J_{PP} = 37.0 Hz, PPh_3).

$\mathbf{4_{1b}}$-*cis-Cl*. NMR ^{1}H (250 MHz, CD_2Cl_2, 25 °C): δ 9.25–6.46 (m, C_6H_5 and C_9H_6N), 4.10 (dd, 1H, J_{HH} = 19 Hz, J_{HP} = 13 Hz, CH_2), 3.36 (dd, 1H, J_{HH} = 19 Hz, J_{HP} = 12 Hz, CH_2). NMR ^{31}P (101 MHz, CD_2Cl_2, 25 °C): δ 90.7 (d, J_{PP} = 44 Hz, PPh_2), 51.8 (d, J_{PP} = 44 Hz, PPh_3). Anal. Calcd for $C_{40}H_{33}Cl_2NP_2Ru$: C, 63.08; H, 4.37; N, 1.84. Anal. Calcd for $[C_{40}H_{33}Cl_2NP_2Ru + CH_2Cl_2]$: C, 58.17; H, 4.17; N, 1.65. Found: C, 58.19; H, 3.96; N, 1.64.

$RuCl_2(Cy_2PCH_2quin)(PPh_3)$ ($\mathbf{4_{2b}}$-*trans*). Crystals of $RuCl_2(PPh_3)_3$ (479 mg, 0.5 mmol) and of the ligand Cy_2PCH_2quin ($\mathbf{L_{2b}}$, 168 mg, 0.5 mmol) were introduced in a Schlenk flask and dissolved in 20 mL of degassed dichloromethane. The resulting green solution was stirred for 1 h and concentrated to dryness, giving a green powder, which was washed twice with *n*-hexane (10 mL) and dried *in vacuo* (350 mg, 0.09 mmol, 90% yield). NMR analysis showed the material to consist of a ca. 1/9 mixture of *trans*-Cl and *cis*-Cl isomers. Slow recrystallization from a CH_2Cl_2/hexane mixture at room temperature eventually gave pure $\mathbf{4_{1a}}$-*cis-Cl* as an orange crystalline material, which was used for the catalytic runs.

$\mathbf{4_{2b}}$-*trans-Cl* (from a $\mathbf{4_{2b}}$-*cis-Cl*/$\mathbf{4_{2b}}$-*trans-Cl* mixture). NMR ^{1}H (250 MHz, CD_2Cl_2, 25 °C): δ 8.21–7.44 (m, 11H, C_6H_5 and C_9H_6N), 3.83 (d, 2H, J_{HP} = 12 Hz, CH_2), 2.17–1.04 (m, 22H, C_6H_{11}). NMR ^{31}P (101 MHz, CD_2Cl_2, 25 °C): δ 102.8 (d, J_{PP} = 32 Hz, PCy_2), 46.5 (d, J_{PP} = 32 Hz, PPh_3).

$\mathbf{4_{2b}}$-*cis-Cl*. NMR NMR ^{1}H (250 MHz, CD_2Cl_2, 25 °C): δ 8.19–7.04 (m, C_6H_5), 3.02 (dd, 1H, J_{HH} = 18 Hz, J_{HP} = 13 Hz, CH_2), 2.81 (m, 1H, CH_2); 2.12–0.88 (m, 22H, C_6H_{11}). NMR ^{31}P (101 MHz, CD_2Cl_2, 25 °C): δ 106.9 (d, J_{PP} = 40 Hz, PCy_2), 54.2 (d, J_{PP} = 40 Hz, PPh_3). Anal. Calcd for $C_{40}H_{45}Cl_2NP_2Ru$: C, 62.09; H, 5.86; N, 1.81. Anal. Calcd for $[C_{40}H_{45}Cl_2NP_2Ru + CH_2Cl_2]$ (X-ray analysis):[42] C, 57.35; H, 5.52; N, 1.63. Found: C, 61.11; H, 5.36; N, 1.71.43.

Synthesis of $RuCl_2(CCHPh)(Ph_2PCH_2pic)(PPh_3)$ ($\mathbf{5_{1a}}$) and $RuCl_2(CCHPh)(Ph_2PCH_2quin)(PPh_3)$ ($\mathbf{5_{1b}}$). In a typical experiment, the complex $\mathbf{4_{1a}}$ (as a ca. 1:1 mixture of *cis*-Cl and *trans*-Cl isomers, 108 mg, 0.15 mmol) was introduced in a Schlenk flask and dissolved in 20 mL of degassed CH_2Cl_2. Phenylacetylene (0.33 mL, 3 mmol) was added, and the resulting mixture was stirred overnight at room temperature. The solvent was then evaporated to dryness and the resulting brown-orange solid was washed twice with *n*-hexane (10 mL) and dried under vacuum. Recrystallization from a CH_2Cl_2/hexane mixture afforded $RuCl_2(CCHPh)(Ph_2PCH_2pic)(PPh_3)$ ($\mathbf{5_{1a}}$) as a brown microcrystalline material (90 mg, 0.11 mmol, 72% yield).

Complex $RuCl_2(CCHPh)(Ph_2PCH_2quin)(PPh_3)$ ($\mathbf{5_{1b}}$) was obtained in 83% yield following a similar procedure starting from $\mathbf{4_{1b}}$ (as a ca. 1/9 mixture of *cis*-Cl and *trans*-Cl isomers, 115 mg, 0.15 mmol).

$\mathbf{5_{1a}}$. NMR ^{1}H (250 MHz, $CDCl_3$, 25 °C): δ 7.78–6.56 (m, C_6H_5 and MeC_5H_3N), 5.33 (dd, 1H, J_{HH} = 17 Hz, J_{HP} = 10 Hz, CH_2), 3.96 (dd, 1H, J_{HH} = 17 Hz, J_{HP} = 10 Hz, CH_2), 3.32 (s, 3H, MeC_5H_3N), 2.69 (t, J_{HP} = 4 Hz, =C*H*Ph). NMR ^{13}C (63 MHz, CD_2Cl_2, 25 °C): δ 351.5 (dd, J_{CP} = 22 Hz, J_{CP} = 17 Hz, Ru=*C*), 145.5–118.6 (C_6H_5 and MeC_5H_3N), 111.9 (d, J_{CH} = 154 Hz, =*C*HPh), 48.7 (dt, J_{CP} = 36 Hz, J_{CH} = 133 Hz, CH_2), 28.8 (q, J_{CH} = 138 Hz, MeC_5H_3N). NMR ^{31}P{^{1}H} (101 MHz, CD_2Cl_2, 25 °C): δ 42.9 (d, J_{PP} = 27 Hz, PPh_2), 33.8 (d, J_{PP} = 27 Hz, PPh_3). IR (CH_2Cl_2): 1623 ($\nu_{C=C}$). Anal. Calcd for $C_{45}H_{39}Cl_2NP_2Ru$: C, 65.30; H, 4.75; N, 1.69. Found: C, 65.12; H, 4.65; N, 1.65.

$\mathbf{5_{1b}}$. NMR ^{1}H (250 MHz, CD_2Cl_2, 25 °C): δ 9.77–6.64 (m, C_6H_5 and C_9H_6N), 5.46 (dd, 1H, J_{HH} = 17 Hz, J_{HP} = 10 Hz, CH_2), 4.33 (dd, 1H, J_{HH} = 17 Hz, J_{HP} = 13 Hz, CH_2), 2.83 (t, J_{HP} = 4 Hz, =CPh*H*). NMR ^{13}C (63 MHz, CD_2Cl_2, 25 °C): δ 350.6 (dd, J_{CP} = 21 Hz, J_{CP} = 15 Hz, Ru=*C*), 154.5–119.6 (C_6H_5 and C_9H_6N), 112.0 (d, J_{CH} = 154 Hz, =*C*HPh), 49.9 (dt, J_{CP} = 38 Hz, J_{CH} = 134 Hz, CH_2). NMR ^{31}P (101 MHz, CD_2Cl_2, 25 °C): δ 46.0 (d, J_{PP} = 29 Hz, PCy_2), 40.7 (d, PPh_3). IR (CH_2Cl_2): 1623 ($\nu_{C=C}$). Anal. Calcd for $C_{48}H_{39}Cl_2NP_2Ru$: C, 66.75; H, 4.55; N, 1.62. Found: C, 66.55; H, 4.46; N, 1.60.

Synthesis of $RuCl_2(\eta^3$-EtO(O)CH=CHC(O)OEt)(Ph_2PCH_2pic) ($\mathbf{6_{1a}}$) and $RuCl_2(\eta^3$-EtO(O)CH=CHC(O)OEt)(Ph_2PCH_2quin) ($\mathbf{6_{1b}}$). In a typical experiment, complex $\mathbf{4_{1a}}$ (as a ca. 1/9 mixture of *cis*-Cl and *trans*-Cl isomers, 145 mg, 0.20 mmol) was introduced in a Schlenk flask and dissolved in 20 mL of degassed CH_2Cl_2. The solution was cooled to −60 °C, and an excess of ethyl diazoacetate (0.210 mL, 2 mmol) was syringed into the flask. The solution was then allowed to slowly warm to room temperature over a period of ca. 4 h, after which the solvent was removed under vacuum. A ^{31}P NMR spectrum of the crude reaction mixture showed a singlet at

(42) Crystal data for $\mathbf{4_{2b}}$-*cis-Cl*·CH_2Cl_2: monoclinic, a = 13.0145 Å, b = 16.2875 Å, c = 18.698(5) Å, β = 95.832(5)°, V = 39372 Å^{-3}, T = 180 K, space group $P2_1/n$, Z = 4, μ(Mo Kα) = 0.782 mm^{-1}, 40 155 reflections measured, 12 968 unique (R_{int} = 0.1666), which were used in all calculations. The final $wR(F^2)$ was 0.1671 for all data.

65.6 ppm attributed to the newly formed complex **6$_{1a}$** and two relatively broad singlets at 18.6 and 20.18 ppm, which were attributed to the phosphonium ylide $Ph_3P{=}CH\text{-}C(O)OEt$ by comparison with an authentic sample. The yellow solid residue was then recrystallized from a dichloromethane/hexane mixture at room temperature to afford $RuCl_2(\eta^3\text{-}EtO(O)CH{=}CHC(O)OEt)(Ph_2PCH_2pic)$ (**6$_{1a}$**) as a yellow crystalline material (70 mg, 0.11 mmol, 56% yield).

Complex **6$_{1b}$** was obtained in 43% yield following a similar procedure starting from **4$_{1b}$** (as a ca. 1/9 mixture of *cis*-Cl and *trans*-Cl isomers, 78 mg, 0.10 mmol).

6$_{1a}$. NMR ^{1}H (500.3 MHz, $CDCl_3$, 25 °C): δ 7.89–7.20 (m, C_6H_5 and MeC_5H_3N), 4.735 (d, 1H, J_{HH} = 8.5 Hz, CH=CH), 4.529 (ABX_3pattern, 2H, $-OCH_2CH_3$), 4.419 (ABX pattern, 2H, J_{HaHb} = 16.8 Hz, J_{HaP} = 10.3 Hz, J_{HbP}= 13.4 Hz, PCH_2), 3.921 (dd, 1H, J_{HH} = 8.5 Hz, J_{HP} = 4.5 Hz, CH=C*H*), 3.635 (dq, 1H, $-OCHHCH_3$, J_{HH} = 10.9 Hz, $J_{HH(Me)}$ = 7.2 Hz), 3.085 (dd, 1H, $-OCHHCH_3$, J_{HH} = 10.9 Hz, J_{HH} = 7.2 Hz), 2.63 (s, 3H, MeC_5H_3N), 1.44 (t, J_{HH} = 7.2 Hz, $-OCH_2CH_3$), 0.85 (t, J_{HH} = 7.2 Hz, $-OCH_2CH_3$). NMR ^{13}C (125.8 MHz, $CDCl_3$, 25 °C): δ 176.61; 171.49 (C=O), 167.09–120.26 (C_6H_5 and MeC_5H_3N), 70.79 (d, J_{CH} = 177 Hz, HC=C*H*), 63.60 (t, J_{CH} = 142 Hz, CH_2), 60.61 (d, J_{CH} = 162 Hz, HC=C*H*), 60.62 (t, J_{CH} = 147 Hz, CH_2), 43.86 (dt, J_{CP} = 35 Hz, J_{CH} = 130 Hz, PCH_2), 25.36 (q, J_{CH} = 130 Hz, MeC_5H_3N), 13.89 (q, J_{CH} = 128 Hz, CH_3), 13.47 (q, J_{CH} = 128 Hz, CH_3). NMR ^{31}P{^{1}H} (202.6 MHz, CD_2Cl_2, 25 °C): δ 63.48 (s). Anal. Calcd for $C_{27}H_{30}Cl_2NO_4PRu$: C, 51.03; H, 4.76; N, 2.20. Anal. Calcd for $[C_{27}H_{30}Cl_2NO_4PRu + 0.33CH_2Cl_2]$ (X-ray analysis): C, 49.46; H, 4.66; N, 2.11. Found: C, 49.61; H, 4.45; N, 2.06.

6$_{1b}$. NMR ^{1}H (250 MHz, $CDCl_3$, 25 °C): δ 8.58–7.15 (m, C_6H_5 and C_9H_6N), 4.74 (d, 1H, J_{HH} = 9 Hz, *H*C=C*H*), 4.58 (m, 2H, PCH_2), 4.53 (ABX_3 pattern, 2H, J_{HaHb} = 11 Hz, $J_{HaH(Me)}$ = $J_{HbH(Me)}$ = 7 Hz, OCH_2CH_3), 3.89 (dd, 1H, J_{HH} = 9 Hz, J_{HP} = 4 Hz, HC=C*H*), 2.62 (m, 2H, OCH_2CH_3), 1.40 (t, 3H, J_{HH} = 7 Hz, OCH_2CH_3), 0.56 (t, 3H, J_{HH} = 7 Hz, OCH_2CH_3). NMR ^{13}C (63 MHz, $CDCl_3$, 25 °C): δ 176.9, 170.8 (C=O), 167.09–120.26 (C_6H_5 and C_9H_6N), 69.8 (d, J_{CH} = 178 Hz, HC=C*H*), 63.9 (t, J_{CH} = 142 Hz, CH_2), 62.7 (J_{CH} = 160 Hz, HC=C*H*), 60.2 (J_{CH} = 148 Hz, CH_2), 45.9 (dt, J_{CP} = 33 Hz, J_{CH} = 131 Hz, PCH_2), 14.0 (q, J_{CH} = 128 Hz, CH_3), 13.3 (q, J_{CH} = 127 Hz, CH_3). NMR ^{31}P{^{1}H} (101 MHz, CD_2Cl_2, 25 °C): δ 65.56 (s). Anal. Calcd for $C_{30}H_{30}Cl_2NO_4PRu$: C, 53.66; H, 4.50; N, 2.09. Found: C, 53.12; H, 4.32; N, 1.98.

X-Ray Diffraction Studies. Crystals of **1**, **2$_{1a}$**, **3$_{1a}$**, **4$_{2a}$**-*cis*-*Cl*, **4$_{2a}$**-*trans*-*Cl*, and **6$_{1a}$** suitable for X-ray diffraction were obtained by recrystallization of the relevant compounds from dichloromethane/hexane solutions in the cold. Additional X-ray data for compounds **4$_{1a}$**-*cis*-*Cl* and **4$_{2b}$**-*cis*-*Cl* are also available as Supporting Information. Intensity data were collected at low temperature (see Table 1 for exact temperature and specific conditions) on a Stoe IPDS diffractometer (for **1**, **3$_{1a}$**, and **4$_{2a}$**-*trans*-*Cl*) or an Oxford Diffraction Xcalibur (**2$_{1a}$**, **4$_{2a}$**-*cis*-*Cl*, and **6$_{1a}$**) diffractometer. All calculations were performed on a PC-compatible computer using the WinGX system.[43] Full crystallographic data are given in Table 1. The structures were solved by using the SIR92 program,[44] which revealed in each instance the position of most non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses by using the SHELXL97 program.[45] Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for Ru, P, and Cl atoms were included in F_c. All non-hydrogen atoms were allowed to vibrate anisotropically. All hydrogen atoms were introduced in idealized positions (R_3CH, C−H = 0.96 Å; R_2CH_2, C−H = 0.97 Å; RCH_3, C−H = 0.98 Å; $C(sp^2)$−H = 0.93 Å; U_{iso} 1.2 or 1.5 time greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached) and refined as "riding" atoms. After completing the initial structure solution for **2$_{1a}$**, it was found that 26% of the total cell volume was filled with disordered solvent molecules, which could not be modeled in terms of atomic sites. From this point on, residual peaks were removed and the solvent region was refined as a diffuse contribution without specific atom positions by using the PLATON[46] module SQUEEZE,[47] which subtracts electron density from the void regions by appropriately modifying the diffraction intensities of the overall structure. An electron count over the solvent region provided an estimate for the number of solvent molecules removed from the cell. The number of electrons thus located, namely, 148 per unit cell, was assigned to 1.00 and 0.50 molecule of dichloromethane on two different sites per molecule of **2$_{1a}$** (148/4 = 37 electrons per molecule of **2$_{1a}$**; 1.5 molecules of dichloromethane would give 37.5 electrons) and were included in the formula, formula weight, calculated density, absorption coefficient, and *F*(000). Applying this procedure led to a dramatic improvement in all refinement parameters and a minimization of residuals. The SQUEEZE module was also used to treat disordered solvent molecules in the structure of **4$_{1b}$**-*trans*-*Cl*. In that case, 142 electrons per unit cell were located and were assigned to 0.50 and 0.25 molecule of dichloromethane on two different sites per molecule of **4$_{1b}$**-*trans*-*Cl* (142/8 = 17.75 electrons per molecule of **4$_{1b}$**-*trans*-*Cl*; 0.75 molecule of dichloromethane would give 18.75 electrons) and were included in the formula, formula weight, calculated density, absorption coefficient, and *F*(000).

ROMP Procedure. The reactions were carried out under inert atmosphere. To the monomer solution (2.5 mmol) in 10 mL of CH_2Cl_2 was added the precatalyst (0.01 equiv) and then the initiator Me_3SiCHN_2 (0.05 equiv) by means of a syringe. The polymerization was quenched after 1 h, and the polymer was precipitated by adding 40 mL of a solution of 2,6-di(*tert*-butyl)-4-methylphenol in methanol. The resulting polymer was dried under vacuum, weighted, and analyzed by size exclusion chromatography (*vide supra*).

Catalytic Transfer Hydrogenation. The catalyst precusrsor (0.01 mmol) was dissolved in 2-propanol (8 mL), and the solution was heated under reflux. After 10 min, distilled ketone (10 mmol) was added. After an additional 10 min, the transfer hydrogenation was initiated by addition of sodium hydroxide (9.9 mg, 0.24 mmol) dissolved in 2 mL of 2-propanol. The progress of the reaction was monitored by gas chromatographic analysis on periodic sampling every 15 s.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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