Unsymmetrical Bis(iminoethyl)pyridine Metal Complexes with a Pendant Alkenyl Substituent. Part B: Internal Olefin Coordination to Ruthenium†

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A series of unsymmetrically substituted 2,6-bis(iminoethyl)pyridine ligands (**5a**−**d**), each bearing a 2,6-diisopropylphenyl group and a linear alkenyl group (allyl to hexenyl) at their pairs of imino nitrogen atoms, was reacted with ruthenium(II) reagents. The reaction of the allyl-substituted system **5a** with the reagent $[Ru(PPh_3)_3Cl_2]$ gave the $[(\kappa^3N,N',N''$-chelate ligand$)(PPh_3)RuCl_2]$ complex **6a**, featuring a pair of cis chloride ligands. In contrast, the reactions of **5b**−**d** with $[RuCl_2(p$-cymene$)]_2$ yielded the complexes **7b**−**d**. They each feature a pair of trans chloride ligands and an internally coordinated η^2-CH═CH_2 group at the octahedrally coordinated ruthenium center. Treatment of **7c**,**d** with PMe_3 resulted in a replacement of the internally coordinated π-olefin from ruthenium by the phosphine to yield the complexes **8c**,**d**. The compounds **6a**, **7b**−**d**, and **8c**,**d** were characterized by X-ray diffraction.

Introduction

2,6-Bis(iminoalkyl)pyridine chelate ligand systems have been of great use in coordination chemistry and catalysis.[1] A great variety of κ^3N,N',N'' complexes of such tridentate ligands of many metals throughout the periodic table have been reported in the literature.[2−4] Most often, symmetrically substituted ligand systems were employed in these studies, often using pairs of identical aryl substituents bonded to the imine nitrogen atoms. The corresponding bis-*N*-2,6-diisopropylphenyl derivatives of cobalt and especially of iron were shown to be suitable precursors for the generation of very active homogeneous Ziegler−Natta olefin polymerization catalysts.

There are fewer reports about complexes of unsymmetrically substituted 2,6-bis(iminoalkyl)pyridine systems. Examples of such systems (e.g., **1**, see Scheme 1) bearing an aryl substituent at one nitrogen and an alkyl or aryl group at the other imino nitrogen were previously described, for example, by Bianchini and others.[5,6] Some of these systems gave active catalysts for the oligomerization of ethylene upon activation with methylalumoxane. We have just recently described the preparation of a series of related "unsymmetrical" 2,6-bis(iminoethyl)pyridine ligands that carry a combination of the ubiquitous 2,6-diisopropylphenyl substituent and a linear alkenyl substituent at their imino nitrogen atoms. The cobalt and iron complexes (**2**) of a series ranging from allyl to *n*-hexenyl were prepared and characterized, and their ethene polymerization/oligomerization

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† Dedicated to Professor Bernt Krebs on the occasion of his 70th birthday.

‡ X-ray crystal structure analyses.

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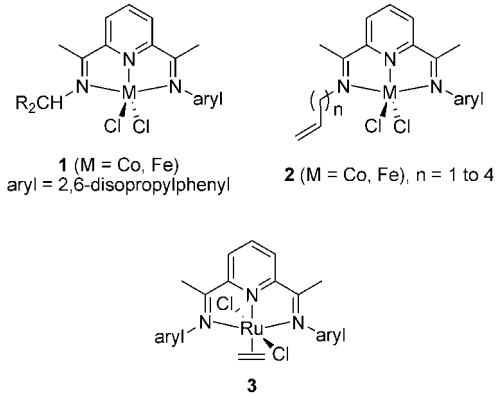
behavior was studied (after MAO activation).[7] That study indicated some involvement of the pendant alkenyl groups in the polymerization process. In order to gain some insight into the possible internal coordination behavior of such pendant alkenyl moieties, we looked for some suitable stable model systems. It is well-known that the corresponding κ^3N,N',N''-bis(iminoalkyl)pyridine complexes of Ru(II), in contrast to their Fe(II) relatives, are diamagnetic and thus amenable to NMR characterization.[8] Since, for example, the bis[*N*-(2,4-diisopropylphenyl)iminoethyl]pyridine−$RuCl_2$ system forms a stable octahedral ethene complex (**3**),[9,10] it was tempting to investigate the role the pendant alkenyl substituents could possibly play in this chemistry. The results of a study using a series of "unsymmetrical" N-alkenyl-substituted bis-(iminoethyl)pyridine ruthenium systems is reported in this account.

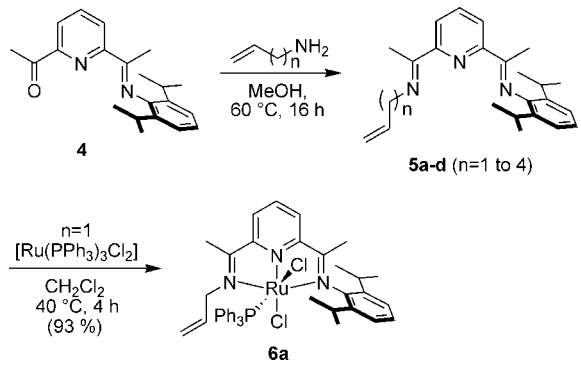
Scheme 1



Results and Discussion

Syntheses and Reactions. Our "unsymmetrical" chelate ligands (**5a**−**d**) were prepared by condensation of **4** with a series of the respective aminoalkenes, as was previously described by us.[7,11] The precursor (**4**) was selectively synthesized by the reaction of 2,6-diacetylpyridine with 2,6-diisopropylaniline, as was recently described by Bianchini et al.[5]

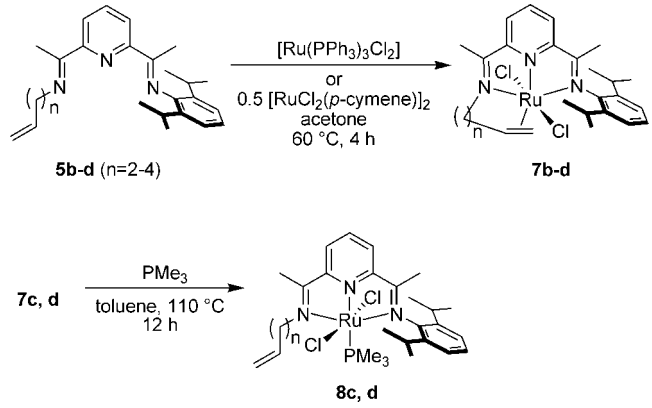
Scheme 2



We first reacted the allyl-substituted ligand (**5a**) with $[Ru(PPh_3)_3Cl_2]$ in dichloromethane at 40 °C. The violet product **6a** was isolated in 84% yield. The diamagnetic complex was characterized by elemental analysis, by spectroscopy, and by an X-ray crystal structure analysis (see below) and was shown to contain a single PPh_3 ligand bonded to ruthenium. The double bond of the allyl substituent is apparently not coordinated to the metal center, either in the crystal or in solution.

The formation of analogous mono-PPh_3 Ru complexes was not observed, at least not in any appreciable amounts, when the ligand systems **5b**−**d**, bearing longer alkenyl substituents at one of their imino nitrogen atoms, were treated with $[Ru(PPh_3)_3Cl_2]$ in refluxing acetone or dichloromethane. Instead, we observed the formation of the phosphine-free products **7b**−**d** (see Scheme 3), which feature an internally coordinated alkenyl unit. These complexes were actually isolated in pure form from the closely related reaction of the systems **5b**−**d** with $[RuCl_2(p\text{-cymene})]_2$.[12] This reaction proceeded much more cleanly and required slightly less forcing reaction conditions. The complexes **7b**−**d** were isolated from these reactions in 30−69% yield as dark purple solids.

Scheme 3



We briefly investigated the stability of the internal η^2-alkenyl coordination toward substitution by the strong PMe_3 donor ligand. Under the applied reaction conditions the butenyl Ru complex **7b** proved to be inert. However, with the complexes **7c**,**d** a slow replacement of the internally coordinated olefinic unit was observed upon exposure to PMe_3. Prolonged treatment of **7c**,**d** with PMe_3 in refluxing toluene (12 h) eventually gave the monophosphine complexes **8c**,**d** in good yields (∼80% isolated, see Scheme 3).

Spectroscopic and Structural Characterization of the Products. The [(chelate ligand)(phosphine)]$RuCl_2$ complexes **6a**, and **8c**,**d** were characterized by X-ray diffraction (see Table 1). Complex **6a** was shown to feature a distorted-octahedral coordination geometry at the central Ru atom. The three nitrogen atoms occupy a set of meridional positions. We note that inside the κ^3N,N',N'' coordination the central pyridine N to ruthenium bond is markedly shorter than the pair of lateral imino nitrogen to metal linkages. Both of the imino C═N functions feature typical sp^2 carbon to nitrogen double-bond lengths. The allyl substituent at N24 is rotated away from the central core of the

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Table 1. Selected Structural Parameters of the Ru Phosphine Complexes 6a and 8c,d[a]

	6a	8c	8d
ligand[b]	cis-PPh_3	trans-PMe_3	trans-PMe_3
$-CH=CH_2$	1.311(5)	1.280(5)	1.182(7)[c]
Ru−N1	1.926(3)	1.974(2)	1.992(3)
Ru−N9	2.189(3)	2.139(2)	2.143(2)
Ru−N24	2.049(3)	2.083(2)	2.085(3)
Ru−P	2.331(1)	2.365(1)	2.372(1)
Ru−Cl1	2.449(1)	2.410(1)	2.400(1)
Ru−Cl2	2.462(1)	2.401(1)	2.407(1)
C7−N9	1.295(4)	1.312(3)	1.312(4)
C22−N24	1.303(4)	1.302(3)	1.303(4)
N9−Ru−N24	156.5(1)	154.7(1)	154.8(1)
N1−Ru−P	100.9(1)	179.2(1)	178.4(1)
Cl1−Ru−Cl2	88.1(1)	172.3(1)	172.4(1)
N1−Ru−Cl1	169.1(1)	92.4(1)	87.0(1)
C7−N9−C10−C11	93.5(4)	−91.9(3)	−92.9(3)
C7−N9−C10−C15	−87.0(4)	87.0(3)	86.6(3)

[a] Bond lengths are given in Å and angles in deg. [b] Cis and trans relative to the pyridine nitrogen atom. [c] Bond artificially shortened due to librations at the end of the chain.

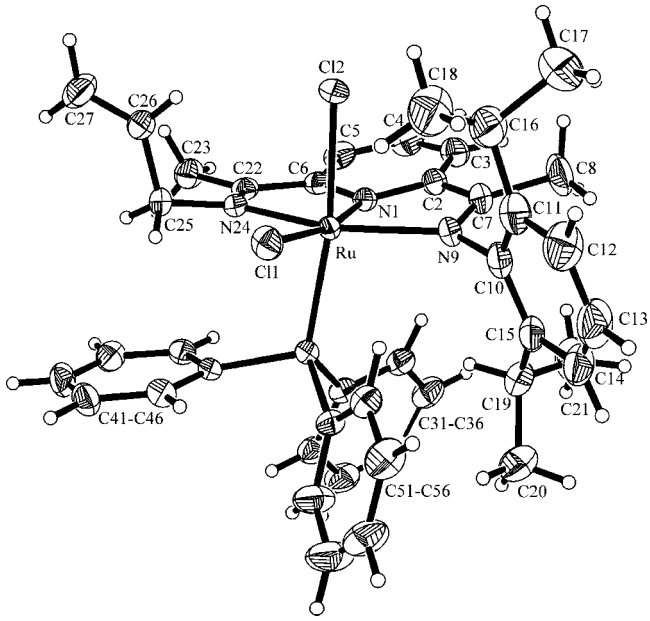

Figure 1. View of the molecular structure of complex **6a**.

complex. The bulky bis-2,6-diisopropylphenyl substituent has its plane oriented normal to the central chelate ligand plane. In complex **6a** the pair of chloride ligands is found to be oriented cis to each other. Consequently, the bulky PPh_3 ligand adopts a position cis to the chelate ligand nitrogen atoms at ruthenium (see Figure 1 and Table 1).

The PMe_3 complexes **8c**,**d** both show structures that are very similar to each other. Therefore, we will discuss here the structural features of the example **8c** (Figure 2). Structural details of its congener **8d** can be found in Table 1, the Experimental Section, and the Supporting Information. Complex **8c** also features a distorted-octahedral structure in the crystal form. The bonding features of the chelate ligand moiety are very similar to those observed for **6a** (see Table 1). Again, the pyridine N to Ru bond is very short and the C=N to Ru linkages are longer. The 2,6-diisopropylphenyl substituent plane is normal to the bis(imino)pyridine ligand plane, and the pentenyl substituent is found in an extended all-antiperiplanar conformation pointing toward the outside. In contrast to the case for complex **6a**, the pairs of chloride ligands in the systems **8c**,**d** are both found in positions trans to each other. Consequently, the PMe_3 donor

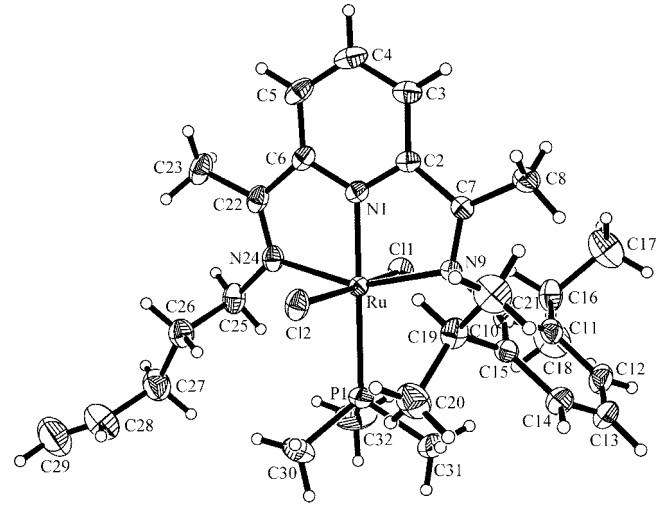

Figure 2. Molecular structure of the [(chelate ligand)(PMe_3)-*trans*-Cl_2Ru] complex **8c**.

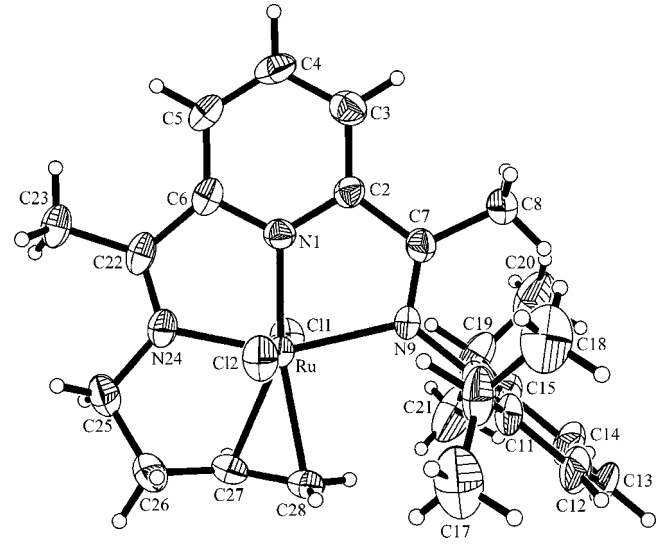

Figure 3. Projection of the molecular structure of the internal olefin Ru complex **7b**.

ligand is placed at a trans coordination site relative to the central pyridine nitrogen atom.

All three internal η^2-alkenyl Ru complexes **7b**−**d** were characterized by X-ray diffraction. Complex **7b** (see Figure 3 and Table 2) features a distorted-octahedral coordination geometry. The terminal butenyl C=C double bond occupies a coordination site trans to the pyridine nitrogen atom. The carbon−ruthenium bond lengths are found around 2.22 Å. In complex **7b** the Ru to CH_2 linkage of the Ru(η^2-CH=CH_2) moiety is slightly longer than the internal Ru to CH bond. The C=C bond length has lengthened considerably upon coordination to the heavy group 8 metal (see Table 2). The chloride ligands in complex **7b** are trans to each other. Again the Ru−N bond lengths increase markedly in the order Ru−N1 < Ru−N24 < Ru−N9. The 2,6-diisopropylphenyl ligand plane in complex **7b** is oriented normal to the plane of the pyridine chelate ligand. The conformational arrangement of the NCH_2CH_2-η^2-CH=CH_2 tether seems to represent a compromise between the desire of the olefin π ligand to have the C−C vector oriented in the meridional plane and the connecting $-CH_2CH_2-$ linker to attain optimum staggering.

Table 2. Selected Structural Parameters of Internal Olefin Ru Complexes 7b−d[a]

	7b[b]	7c	7d
n	2	3	4
−CH=CH_2	1.382(8)	1.383(7)	1.353(5)
Ru−CH=	2.192(5)	2.236(4)	2.254(3)
Ru−CH_2=	2.230(5)	2.212(4)	2.209(3)
Ru−N1	1.954(45	1.973(3)	1.966(2)
Ru−N9	2.166(4)	2.131(3)	2.137(2)
Ru−N24	2.017(4)	2.075(3)	2.088(3)
Ru−Cl1	2.399(1)	2.393(1)	2.403(1)
Ru−Cl2	2.396(1)	2.408(1)	2.390(1)
C7−N9	1.296(6)	1.307(4)	1.293(4)
C22−N24	1.293(7)	1.311(6)	1.298(4)
N9−Ru−N24	155.6(2)	154.9(1)	153.8(1)
N1−Ru−CH	154.8(2)	161.7(2)	163.3(1)
N1−Ru−CH_2	168.8(2)	162.1(2)	161.0(1)
CH-Ru-CH_2	36.4(2)	36.2(2)	35.3(1)
C7−N9−C10−C11	93.2(6)	−91.4(4)	88.2(4)
C7−N9−C10−C15	−86.4(6)	89.6(4)	−92.4(4)

[a] Bond lengths are given in Å and angles in deg. [b] There are two molecules per unit cell; data are given for molecule A. In molecule B C26−C28 is disordered.

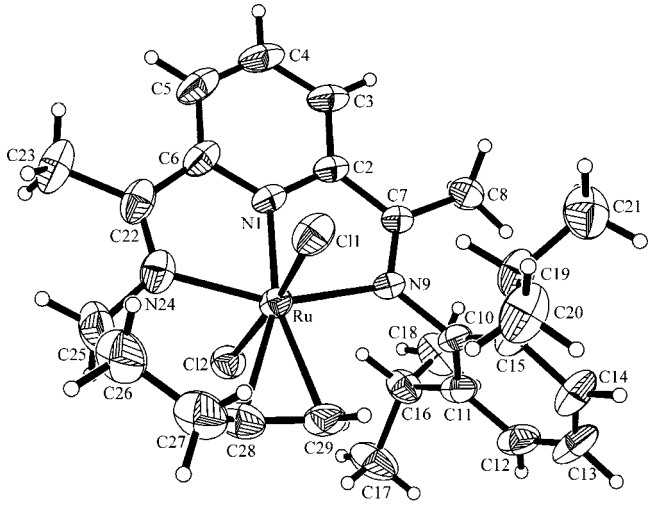

Figure 4. Molecular structure of complex **7c**.

The η^2-pentenyl Ru complex **7c** shows a very similar core (see Figure 4 and Table 2). The κ^3N,N',N''-chelate ligand and the trans pair of chloride ligands occupy five coordination sites of the distorted-octahedral framework. The sixth place is taken by the η^2-alkenyl ligand. Again, the C=C bond of the coordinated olefin is markedly elongated (see Table 2). The longer trimethylene tether now allows the C−C vector of the coordinated olefin to lie in the meridional plane of the molecule. The half-chair-like conformation of the connecting $-CH_2CH_2CH_2-$ unit has caused a pronounced distinction between the faces of the central chelate ligand.

The molecular structure of complex **7d** is similar (see Figure 5 and Table 2). The overall conformational arrangement of the $(N(CH_2)_4$-η^2-CH=$CH_2)$Ru unit resembles a boatlike medium-sized-ring arrangement. We note that a trend is continued to have the terminal (η^2-alkene) CH_2−Ru become increasingly shorter and, consequently, the internal CH−Ru bond to open up on going from **7b** to **7c** to **7d** (see Table 2). This seems to be a structural response to the conformational characteristics of this secondary chelate ring.

The complexes seem to adopt similar structures in solution. This is supported by a variety of characteristic NMR features. In the η^2-alkene complexes **7** the internal π-olefin coordination has resulted in a marked shift of the ^{13}C NMR resonances of

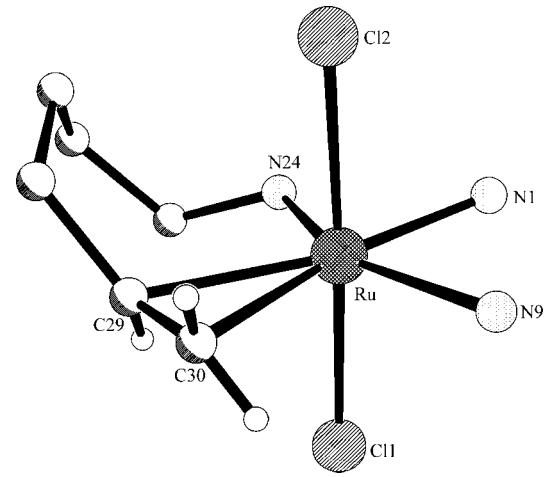

Figure 5. View of the conformational arrangement of the secondary $(N(CH_2)_4$-η^2-CH=$CH_2)$Ru chelate ring in complex **7d**.

Table 3. Selected NMR Data of the Ruthenium Phosphine Complexes 6a and 8c,d[a]

	6a	8c	8d
ligand[b]	cis-PPh_3	trans-PMe_3	trans-PMe_3
$\delta(^{31}P)$	38.1	−9.0	−8.9
$\delta(^1H)$ (−*CH*=)	6.06	5.85	5.83
$\delta(^{13}C)$ (−*C*H=)	134.9	137.9	138.9
^3J(cis)	10.2	10.2	10.3
^3J(trans)	17.6	17.1	17.1
^2J(gem)	n.o.	1.7	n.o.
$\delta(^1H)$ (=*CH*$_2$)	4.93	5.07	5.04
	4.82	5.00	4.97
$\delta(^{13}C)$ (=*C*H_2)	115.8	115.7	114.9
$\delta(^{13}C)$ (C(22)=N^{alk})	173.0	171.2	171.0
$\delta(^{13}C)$ (C(7)=N^{aryl})	175.1	173.3	173.2

[a] in CD_2Cl_2 solution, with coupling constants in Hz. [b] Cis and trans phosphine assignments are relative to the pyridine nitrogen atom.

both the −CH= and the =CH_2 carbon atoms to smaller δ values as compared to those of the uncomplexed olefinic moieties (as found in their PMe_3 substitution products **8**). For the example of the **7c/8c** pair we have monitored $\Delta\delta$ values of 43.5 for the coordination shift of the −CH= signal and 37.6 ppm for the =CH_2 resonance, respectively (see Tables 3 and 4).[13] Also, the difference in the ^{13}C NMR −CH= and =CH_2 shifts becomes markedly smaller upon coordination (e.g. $\Delta\delta$(−CH=/=CH_2) = 24.5 (**5c**),[7] 22.2 (**8c**), 16.3 (**7c**)). In addition, we monitor a pronounced decrease of the ^3J(cis) and ^3J(trans) H,H-coupling constants in the respective ^{1}H NMR spectra arising from internal olefin coordination to the ruthenium center. It appears that the complexation does not affect the electronic features of the distal −C(Me)=N−(2,6-diisopropylphenyl) imino group−their ^{13}C NMR resonances remain practically unchanged. However, the proximal −C(Me)=N alkenylimino moiety seems to recognize a change caused by internal alkenyl complexation by responding with shifting the heterocarbonyl ^{13}C NMR resonances to lower δ values by $\Delta\delta \approx 1-5$ ppm (see Tables 3 and 4).

The internal alkenyl coordination has introduced a new element of asymmetry to the chelate complexes. Therefore, the

(13) See for a comparison: (a) Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867–5868. (b) Carpentier, J.-F.; Wu, Z.; Lee, C. W.; Strömberg, S.; Christopher, J. N.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7750–7767. (c) Casey, C. P.; Klein, J. F.; Fagan, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 4320–4330. (d) Carpentier, J.-F.; Maryin, V. P.; Luci, J.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 898–909. (e) Brandow, C. G.; Mendiratta, A.; Bercaw, J. E. *Organometallics* **2001**, *20*, 4253–4261. (f) Martínez, G.; Royo, P. *Organometallics* **2005**, *24*, 4782–4787. (g) Stoebenau, E. J., III; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *128*, 8638–8650, and references cited therein.

Table 4. Selected NMR Data of the Internal Olefin Ru Complexes 7b−d[a]

	7b	7c	7d
n	2	3	4
$\delta(^1H)$ (−C*H*═)	6.17	5.65	5.40
$\delta(^{13}C)$ (−*C*H═)	105.8	94.4	100.2
^3J(cis)	9.3	8.9	9.7
^3J(trans)[b]	14.8	13.8	13.5
$\delta(^1H)$ (═CH_2)	4.54	4.34	4.35
	4.10	4.05	4.28
$\delta(^{13}C)$ (═*C*H_2)	77.2	78.1	82.1
$\delta(^{13}C)$ (C(22)═N^{alk})	167.9	170.0	170.0
$\delta(^{13}C)$ (C(7)═N^{aryl})	174.3	174.3	174.2

[a] In CD_2Cl_2 solution, with coupling constants in Hz. [b] ^2J(gem) not observed.

isopropyl groups of the orthogonally oriented bis-2,6-diisopropylphenyl substituents have become differentiated (cis/trans to the carbon substituent at the π-alkenyl unit) *and* their methyl groups are diastereotopic. Therefore, we observed a set of two −C*H*Me$_2$ ^{1}H NMR resonances and a total of four isopropyl methyl groups for each of the complexes **7**.

Breaking up the internal π-olefin coordination in the complexes **7** by treatment with PMe_3 (to give **8c**,**d**) removes the inherent element of chirality from the system. The resulting complexes **8** are achiral in solution, but the perpendicular arrangement of the 2,6-diisopropylphenyl substituent at the "right" imino nitrogen atom relative to the pyridine plane leaves an element of axial prochirality in the complexes **8**.[14] Consequently, for each of the complexes **8c**,**d** we observe a single ^{1}H NMR −C*H*Me$_2$ isopropyl septet and a pair of corresponding −CH(C*H*$_3$)$_2$ signals of the adjacent diastereotopic isopropyl methyl groups (for further details see the Experimental Section and the Supporting Information, where representative NMR spectra of these complexes are depicted).

Complex **6a** shows spectroscopic behavior different from that of the systems **8** due to the cis coordination of the PPh_3 ligand relative to the pyridine nitrogen atom.[15] This leads to the observation of two −C*H*Me$_2$ ^{1}H NMR septets and a total of four −CH(C*H*$_3$)$_2$ methyl group signals. One of these methyl ^{1}H NMR resonances is found at negative δ values (δ −0.60 in dichloromethane), probably caused by closing of this substituent into the anisotropy cone of an adjacent PPh_3 phenyl group.

Conclusions

The unsymmetrically substituted bis(2,6-iminoethyl)pyridine ligands **5** that bear pendant alkenyl groups with tethers of varying lengths at one imino nitrogen atom and the bulky ubiquitous 2,6-diisopropylphenyl substituent at the other readily form very stable κ^3N,N',N''-chelate complexes upon treatment with suitable $RuCl_2$ complex precursors. With the exception of the allyl-substituted system (**5a**), where the tether might be too small, all the other systems seem to favor the formation of internally coordinated η^2-alkenyl $RuCl_2$ complexes (**7b**−**d**). A comparison of the structural parameters of the π-(−CH═CH$_2$)Ru units of the series of complexes **7b**−**d** reveals some influence of the lengths of the tether on the structural details. We see that the Ru to terminal CH_2 linkage of the Ru(η^2-CH═CH$_2$) units gets shorter with increasing length of the tether, while the internal Ru to CH linkage progressively becomes longer. It seems that we have encountered a specifically favorable secondary [(NCH$_2$CH$_2$-η^2-CH═CH$_2$)Ru] chelate situation for the *n*-butenyl-substituted complex **7b**, which has proven resistant to replacement of the internal π-alkenyl coordination by PMe_3, even under enforced reaction conditions. The complexes **7c**,**d** form PMe_3 substitution products, albeit at elevated temperatures. Here the conformational situation of the tether might be slightly less favorable than it is for **7b**.

This study has shown that our new ligands **5** seem to have a tendency to form internal alkene π-complexes with ruthenium, although this internal coordination appears to follow specific rules. The (chelate ligand)$RuCl_2$ complexes (**6**−**8**), as expected, did not give active catalysts upon treatment with, for example, the MAO activator.[9] The easy formation of the (π-alkenyl)Ru systems, however, might be taken as an indication of the alleged involvement of the pendant alkenyl groups in the respective iron or cobalt systems at their active catalyst stage, as was suggested from the special behavior that was observed for the homogeneous Ziegler−Natta catalyst systems derived from the reaction of the chelate ligand **5** with $FeCl_2$ and $CoCl_2$, respectively.[7]

Experimental Section

General Procedures. Reactions with air- and water-sensitive compounds were carried out under argon using Schlenk-type glassware or in a glovebox. Solid compounds were collected on sintered-glass frits and washed with appropriate solvents before being dried under vacuum. Solvents were dried and distilled under argon prior to use. The unsymmetrically substituted bis(2,6-iminoethyl)pyridine ligands **5**[7] and [$RuCl_2$(*p*-cymene)]$_2$[12] were prepared analogously as described in the literature. The ruthenium precursor $Ru(PPh_3)_3Cl_2$ was used as purchased from commercial suppliers.

The following instruments were used for physical characterization of the compounds. Melting points: DSC 2010 TA instruments. Elemental analyses: Foss-Heraeus CHNO-Rapid. ESI-MS analysis: Quattro LCZ (Waters Micromass, Manchester, U.K.) equipped with a nano spray inlet. NMR: Bruker AC 200 P (^{1}H, 200 MHz; ^{31}P, 81 MHz), Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{31}P, 243 MHz). Assignments of the resonances were supported by 2D experiments.

X-ray Crystal Structure Analyses. Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius BV, 1998), data reduction Denzo-SMN (Otwinowski, Z.; Minor, W. Methods Enzymol. 1997, 276, 307−326), absorption correction SORTAV (Blessing, R. H. Acta Crystallogr. 1995, A51, 33−37; Blessing, R. H. J. Appl. Crystallogr. 1997, 30, 421−426) and Denzo (Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. Acta Crystallogr. 2003, A59, 228−234), structure solution SHELXS-97 (Sheldrick, G. M. Acta Crystallogr. 1990, A46, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112−122), graphics XP (BrukerAXS, 2000) and SCHAKAL (E. Keller, Universität Freiburg, 1997).

Preparation of Complex 6a. A solution of the bis(2,6-iminoethyl)pyridine ligand **5a** (1.24 g, 3.43 mmol, 1.1 equiv) and $Ru(PPh_3)_3Cl_2$ (3.00 g, 3.13 mmol) in 100 mL of dichloromethane was stirred overnight and refluxed under argon for 4 h. Subsequently the volume of the solvent was reduced in vacuo until a purple solid began to form. The precipitation was completed by addition of 80 mL of pentane, and the solid was collected by filtration, washed with pentane until the solvent was colorless, and dried in vacuo to give the purple product (84%, 2.31 g, 2.62 mmol). Slow evaporation from a saturated chloroform solution gave single crystals of **6a** for the X-ray crystal structure analysis. Mp (DSC): 272 °C dec. MS-ESI ($CHCl_3$, ES$^+$): *m*/*z* 760.5 ([M − Cl])$^+$. Anal. Calcd for $C_{42}H_{46}Cl_2N_3PRu \cdot CH_2Cl_2$ (880.73): C, 58.64; H, 5.49; N, 4.77. Found: C, 58.43; H, 5.37; N, 4.65. ^{1}H NMR (d_2-dichloromethane,

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(15) Bianchini, C.; Lee, H. M. *Organometallics* **2000**, *19*, 1833–1840.

600 MHz, 298 K): $\delta(^1H)$ 8.04 (dd, $^3J = 7.8$ Hz, $^4J = 1.0$ Hz, 1H, 3-H^{py}), 7.77 (t, $^3J = 7.8$ Hz, 1H, 4-H^{py}), 7.69 (dd, $^3J = 7.8$ Hz, $^4J = 1.0$ Hz, 1H, 5-H^{py}), 7.46 (dd, $^3J = 7.8$ Hz, $^4J = 1.4$ Hz, 1H, 3-H^{aryl}), 7.30 (t, $^3J = 7.8$ Hz, 1H, 4-H^{aryl}), 7.24 (br, 3H, Ph$_p$), 7.12 (br, 6H, Ph$_o$), 7.02 (br, 6H, Ph$_m$), 6.83 (d, $^3J = 7.8$ Hz, $^4J = 1.4$ Hz, 1H, 5-H^{aryl}), 6.06 (dddd, $^3J = 17.6$ Hz, $^3J = 10.2$ Hz, $^3J = 9.4$ Hz, $^3J = 3.5$ Hz, 1H, −CH═), 4.93 (dm, $^3J = 10.2$ Hz, 1H, ═CH$_2^E$), 4.82 (dm, $^3J = 17.6$ Hz, 1H, ═CH$_2^Z$), 4.72 (sept, $^3J = 6.8$ Hz, 1H, −C*H*^{B}(CH$_3$)$_2$), 4.31 (dm, $^2J = 13.4$ Hz, 1H, ═NCH$_2^A$−), 2.54 (s, 3H, −CH$_3^{aryl}$), 2.51 (dd, $^2J = 13.4$ Hz, $^3J = 9.4$ Hz, 1H, ═NCH$_2^B$−), 2.34 (s, 3H, −CH$_3^{alk}$), 2.09 (sept, $^3J = 6.8$ Hz, 1H, −C*H*^{A}(CH$_3$)$_2$), 1.48 (d, $^3J = 6.8$ Hz, 3H, −CH^B(C*H*$_3^A$CH$_3^B$)), 0.93 (d, $^3J = 6.8$ Hz, 3H, −CH^B(CH$_3^A$C*H*$_3^B$)), 0.82 (d, $^3J = 6.8$ Hz, 3H, −CH^A(C*H*$_3^A$CH$_3^B$)), −0.60 (d, $^3J = 6.8$ Hz, 3H, −CH^A-(CH$_3^A$C*H*$_3^B$)). $^{13}C\{^1H\}$ NMR (d_2-dichloromethane, 150 MHz, 298 K): $\delta(^{13}C)$ 175.1 (C═N^{aryl}), 173.0 (d, $\sum^3J_{P,C} + {}^4J_{P,C} = 1.3$ Hz, C═N^{alk}), n.o. (Ph$_i$), 164.7 (C-6^{py}), 164.5 (d, $\sum^3J_{P,C} + {}^4J_{P,C} = 1.3$ Hz, C-2^{py}), 147.4 (C-1^{aryl}), 145.3 (C-2^{aryl}), 140.1 (C-6^{aryl}), 134.9 (−CH═), 129.9 (Ph$_p$), 128.9 (C-4^{py}), n.o. (Ph$_o$), 127.5 (Ph$_m$), 127.4 (C-4^{aryl}), 126.3 (C-3^{py}), 125.1 (C-3^{aryl}), 124.7 (C-5^{aryl}), 124.4 (C-5^{py}), 115.8 (═CH$_2$), 56.7 (═NCH$_2$−), 28.4 (−CH^B(CH$_3$)$_2$), 27.9 (−C*H*^{A}(CH$_3$)$_2$), 26.2 (−CH^B(CH$_3^A$C*H*$_3^B$)), 24.8 (−CH^A(C*H*$_3^A$-CH$_3^B$)), 23.9 (−CH^B(C*H*$_3^A$CH$_3^B$)), 22.8 (−CH^A(CH$_3^A$C*H*$_3^B$)), 22.0 (−CH$_3^{aryl}$), 16.8 (−CH$_3^{alk}$). $^{31}P\{^1H\}$ NMR (d_2-dichloromethane, 121 MHz, 298 K): $\delta(^{31}P)$ 38.1 (s).

X-ray crystal structure analysis of **6a**: formula $C_{42}H_{46}Cl_2N_3PRu \cdot CH_2Cl_2$, $M_r = 880.68$, red crystal, 0.35 × 0.35 × 0.03 mm, $a = 9.688(1)$ Å, $b = 11.853(1)$ Å, $c = 36.224(1)$ Å, $\beta = 93.24(1)°$, $V = 4153.0(6)$ Å^3, $\rho_{calcd} = 1.409$ g cm^{-3}, $\mu = 0.707$ mm^{-1}, empirical absorption correction ($0.790 \le T \le 0.979$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 42 153 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.67$ Å^{-1}, 10 013 independent ($R_{int} = 0.051$) and 8176 observed reflections ($I \ge 2\sigma(I)$), 491 refined parameters, R1 = 0.046, wR2 = 0.135, maximum (minimum) residual electron density 2.30 (−0.82) e Å^{-3} close to the disordered solvent molecule, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 7b. A solution of the bis(2,6-iminoethyl)pyridine ligand **5b** (613 mg, 1.63 mmol, 2 equiv) and [RuCl$_2$(*p*-cymene)]$_2$ (503 mg, 0.82 mmol) in 60 mL of ethanol was refluxed under argon for 16 h. Subsequently the volume of the solvent was reduced in vacuo until a purple solid began to form. The precipitation was completed by addition of pentane, and the solid was collected by filtration, washed with pentane until the solvent was colorless, and dried in vacuo to give the air-stable product (61%, 549 mg, 1.00 mmol). Slow evaporation from a saturated dichloromethane solution gave single crystals of **7b** for the X-ray crystal structure analysis. Mp (DSC): >350 °C. MS-ESI (MeOH/CHCl$_3$, ES$^+$): *m*/*z* 512.3 ([M − Cl]$^+$. Anal. Calcd for $C_{25}H_{33}Cl_2N_3Ru$ (547.53): C, 54.84; H, 6.08; N, 7.67. Found: C, 54.81; H, 5.91; N, 7.44. ^1H NMR (d_2-dichloromethane, 600 MHz, 298 K): $\delta(^1H)$ 7.92 (dd, $^3J = 7.8$ Hz, $^4J = 0.8$ Hz, 1H, 3-H^{py}), 7.86 (t, $^3J = 7.8$ Hz, 1H, 4-H^{py}), 7.80 (dd, $^3J = 7.8$ Hz, $^4J = 0.8$ Hz, 1H, 5-H^{py}), 7.29 (m, 1H, 5-H^{aryl}), 7.29 (m, 1H, 4-H^{aryl}), 7.24 (m, 1H, 3-H^{aryl}), 6.17 (m, 1H, −CH═), 4.54 (d, $^3J = 14.8$ Hz, 1H, ═CH$_2^Z$), 4.47 (dd, $^2J = 15.3$ Hz, $^3J = 6.0$ Hz, 1H, ═NC*H*$_2^A$−), 4.35 (m, 1H, ═NC*H*$_2^B$−), 4.10 (d, $^3J = 9.3$ Hz, 1H, ═CH$_2^E$), 3.41 (sept, $^3J = 6.8$ Hz, 1H, −C*H*^{A}(CH$_3$)$_2$), 3.03 (sept, $^3J = 6.8$ Hz, 1H, −C*H*^{B}(CH$_3$)$_2$), 2.99 (m, 1H, ═NCH$_2$C*H*$_2^A$−), 2.83 (s, 3H, −CH$_3^{alk}$), 2.61 (s, 3H, −CH$_3^{aryl}$), 2.53 (dq, $^2J = 12.3$ Hz, $^3J = {}^3J = 6.4$ Hz, 1H, ═NCH$_2$C*H*$_2^B$−), 1.14 (d, $^3J = 6.8$ Hz, 3H, −CH^A(C*H*$_3^A$CH$_3^B$)), 1.01 (d, $^3J = 6.8$ Hz, 3H, −CH^A(CH$_3^A$C*H*$_3^B$)), 0.96 (d, $^3J = 6.8$ Hz, 3H, −CH^B(C*H*$_3^A$CH$_3^B$)), 0.94 (d, $^3J = 6.8$ Hz, 3H, −CH^B(CH$_3^A$C*H*$_3^B$)). $^{13}C\{^1H\}$ NMR (d_2-dichloromethane, 150 MHz, 298 K): $\delta(^{13}C)$ 174.3 (C═N^{aryl}), 167.9 (C═N^{alk}), 160.0 (C-6^{py}), 157.5 (C-2^{py}), 146.1 (C-1^{aryl}), 141.1 (C-6^{aryl}), 140.9 (C-2^{aryl}), 133.4 (C-4^{py}), 127.0 (C-4^{aryl}), 124.9 (C-5^{aryl}), 124.6 (C-3^{aryl}), 123.5 (C-3^{py}), 122.9 (C-5^{py}), 105.8 (−CH═), 77.2 (═CH$_2$), 65.1 (═NCH$_2$−), 35.8 (═NCH$_2$C*H*$_2$−), 27.9 (−C*H*^{A}(CH$_3$)$_2$), 27.7 (−C*H*-^{B}(CH$_3$)$_2$), 25.7 (−CH^A(C*H*$_3^A$CH$_3^B$)), 25.5 (−CH^B(C*H*$_3^A$CH$_3^B$)), 25.3 (−CH^A(CH$_3^A$C*H*$_3^B$)), 25.1 (−CH^B(CH$_3^A$C*H*$_3^B$)), 20.1 (−CH$_3^{aryl}$), 17.3 (−CH$_3^{alk}$).

X-ray crystal structure analysis of **7b**: formula $C_{25}H_{33}Cl_2N_3Ru$, $M_r = 547.51$, black crystal, 0.30 × 0.20 × 0.10 mm, $a = 15.651(1)$ Å, $b = 10.898(1)$ Å, $c = 30.092(1)$ Å, $\beta = 91.90(1)°$, $V = 5129.8(6)$ Å^3, $\rho_{calcd} = 1.418$ g cm^{-3}, $\mu = 0.836$ mm^{-1}, empirical absorption correction ($0.788 \le T \le 0.921$), $Z = 8$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 18 264 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.62$ Å^{-1}, 10 141 independent ($R_{int} = 0.053$) and 6661 observed reflections ($I \ge 2\sigma(I)$), 599 refined parameters, R1 = 0.056, wR2 = 0.141, maximum (minimum) residual electron density 1.61 (−0.64) e Å^{-3} close to the metal centers, two almost identical molecules, one with disorder in the chain (C26−C27−C28) refined with split positions, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 7c. A solution of the bis(2,6-iminoethyl)pyridine ligand **5c** (1.39 g, 3.56 mmol, 2 equiv) and [RuCl$_2$(*p*-cymene)]$_2$ (1.10 g, 1.78 mmol) in 60 mL of ethanol was refluxed under argon for 16 h. Subsequently the volume of the solvent was reduced in vacuo until a purple solid began to form. The precipitation was completed by addition of 60 mL of pentane and the solid was collected by filtration, washed with pentane until the solvent was colorless, and dried in vacuo to give the air-stable product (69%, 1.49 g, 2.47 mmol). Slow evaporation from a saturated dichloromethane solution gave single crystals of **7c** for the X-ray crystal structure analysis. Mp (DSC): 288 °C dec. MS-ESI (MeOH/CHCl$_3$, ES$^+$): *m*/*z* 526.1 ([M − Cl])$^+$, 490.2 ([M − 2 Cl])$^+$. Anal. Calcd for $C_{26}H_{35}Cl_2N_3Ru \cdot 0.5CH_2Cl_2$ (604.03): C, 52.69; H, 6.01; N, 6.96. Found: C, 53.38; H, 6.36; N, 6.96. ^1H NMR (d_2-dichloromethane, 600 MHz, 298 K): $\delta(^1H)$ 7.98 (m, 2H, 3-H^{py}, 5-H^{py}), 7.89 (m, 1H, 4 H^{py}), 7.32 (m, 1H, 4-H^{aryl}), 7.29 (m, 1H, 5-H^{aryl}), 7.25 (m, 1H, 3-H^{aryl}), 5.65 (m, 1H, −CH═), 4.34 (d, $^3J = 13.8$ Hz, 1H, ═CH$_2^Z$), 4.05 (d, $^3J = 8.9$ Hz, 1H, ═CH$_2^E$), 4.02 (dm, $^2J = 13.2$ Hz, 1H, ═NC*H*$_2^A$−), 3.97 (dm, $^2J = 13.2$ Hz, 1H, ═NC*H*$_2^B$−), 3.23 (sept, $^3J = 6.6$ Hz, 1H, −C*H*^{A}(CH$_3$)$_2$), 2.96 (m, 1H, ═NCH$_2$CH$_2$C*H*$_2^A$−), 2.94 (sept, $^3J = 6.6$ Hz, 1H, −C*H*^{B}(CH$_3$)$_2$), 2.93 (s, 3H, −CH$_3^{alk}$), 2.67 (s, 3H, −CH$_3^{aryl}$), 2.26 (m, 1H, ═NCH$_2$CH$_2$C*H*$_2^B$−), 2.07 (m, 1H, ═NCH$_2$C*H*$_2^A$−), 1.95 (m, 1H, ═NCH$_2$C*H*$_2^B$−), 1.11 (d, $^3J = 6.6$ Hz, 3H, −CH^A-(C*H*$_3^A$CH$_3^B$)), 0.98 (d, $^3J = 6.6$ Hz, 6H, −CH^A(CH$_3^A$C*H*$_3^B$), −CH^B(C*H*$_3^A$CH$_3^B$)), 0.93 (d, $^3J = 6.6$ Hz, 3H, −CH^B(CH$_3^A$C*H*$_3^B$)). $^{13}C\{^1H\}$ NMR (d_2-dichloromethane, 150 MHz, 298 K): $\delta(^{13}C)$ 174.3 (C═N^{aryl}), 170.0 (C═N^{alk}), 158.0 (C-6^{py}), 157.1 (C-2^{py}), 146.1 (C-1^{aryl}), 141.3 (C-6^{aryl}), 141.3 (C-2^{aryl}), 132.5 (C-4^{py}), 127.3 (C-4^{aryl}), 125.0 (C-5^{aryl}), 124.6 (C-3^{aryl}), 124.2, 123.5 (C-5^{py} o. C-3^{py}), 94.4 (−CH═), 78.1 (═CH$_2$), 52.3 (═NCH$_2$−), 27.8 (−C*H*^{A}(CH$_3$)$_2$), 27.7 (−C*H*^{B}(CH$_3$)$_2$), 26.9 (═NCH$_2$CH$_2$C*H*$_2$−), 25.9 (═NCH$_2$C*H*$_2$−), 25.6 (−CH^A(C*H*$_3^A$CH$_3^B$)), 25.6, 25.4 (−CH^A(CH$_3^A$C*H*$_3^B$), −CH^B(C*H*$_3^A$CH$_3^B$)), 25.3 (−CH^B(CH$_3^A$C*H*$_3^B$)), 20.8 (−CH$_3^{aryl}$), 17.2 (−CH$_3^{alk}$).

X-ray crystal structure analysis of **7c**: formula $C_{26}H_{35}Cl_2N_3Ru \cdot 0.5CH_2Cl_2$, $M_r = 604.00$, black crystal, 0.60 × 0.40 × 0.30 mm, $a = 25.836(1)$ Å, $b = 10.897(1)$ Å, $c = 19.487(1)$ Å, $\beta = 96.40(1)°$, $V = 5452.1(6)$ Å^3, $\rho_{calcd} = 1.472$ g cm^{-3}, $\mu = 0.889$ mm^{-1}, empirical absorption correction ($0.618 \le T \le 0.776$), $Z = 8$, monoclinic, space group $C2/c$ (No. 15), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 17 326 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.67$ Å^{-1}, 6506 independent ($R_{int} = 0.036$) and 5809 observed reflections ($I \ge 2\sigma(I)$), 309 refined parameters, R1 = 0.054, wR2 = 0.155, maximum (minimum) residual electron density 1.70 (−2.23) e Å^{-3} close to the disordered solvent molecule, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 7d. A solution of the bis(2,6-iminoethyl)pyridine ligand **5d** (500 mg, 1.24 mmol, 2 equiv) and

$[RuCl_2(p\text{-cymene})]_2$ (380 mg, 0.62 mmol) in 50 mL of ethanol was refluxed under argon for 16 h. Subsequently the volume of the solvent was reduced in vacuo until a purple solid began to form. The precipitation was completed by addition of 60 mL of pentane, and the solid was collected by filtration, washed with pentane until the solvent was colorless, and dried in vacuo to give the air-stable product (30%, 230 mg, 0.37 mmol). Slow evaporation from a saturated dichloromethane solution gave single crystals of **7d** for the X-ray crystal structure analysis. Mp (DSC): >350 °C. MS-ESI (MeOH, ES^+): *m/z* 598.1 $([M + Na])^+$, 575.6 $([M + H])^+$, 540.1 $([M - Cl])^+$, 504.2 $([M - 2\ Cl])^+$. Anal. Calcd for $C_{27}H_{37}Cl_2N_3Ru \cdot 0.5CH_2Cl_2$ (618.05): C, 53.44; H, 6.20; N, 6.80. Found: C, 53.97; H, 6.17; N, 6.93. ^{1}H NMR (d_2-dichloromethane, 600 MHz, 298 K): $\delta(^1H)$ 8.01 (d, $^3J = 7.7$ Hz, 1H, 3-H^{py}), 7.97 (d, $^3J = 7.7$ Hz, 1H, 5-H^{py}), 7.90 (t, $^3J = 7.7$ Hz, 1H, 4-H^{py}), 7.32 (t, $^3J = 7.5$ Hz, 1H, 4-H^{aryl}), 7.27 (d, $^3J = 7.5$ Hz, 1H, 3-H^{aryl}), 7.25 (d, $^3J = 7.5$ Hz, 1H, 5-H^{aryl}), 5.40 (m, 1H, −CH═), 4.52 (m, 1H, ═NCH_2^A-), 4.35 (d, $^3J = 9.7$ Hz, 1H, ═CH_2^E), 4.28 (d, $^3J = 13.5$ Hz, 1H, ═CH_2^Z), 4.16 (m, 1H, ═NCH_2^B-), 3.09 (sept, $^3J = 6.7$ Hz, 1H, −C$H^B(CH_3^ACH_3^B)$), 3.00 (sept, $^3J = 6.7$ Hz, 1H, −C$H^A(CH_3^ACH_3^B)$), 2.90 (m, 1H, ═$NCH_2CH_2CH_2CH_2^A$−), 2.89 (s, 3H, $-CH_3^{alk}$), 2.80 (m, 1H, ═$NCH_2CH_2CH_2CH_2^B$−), 2.68 (s, 3H, $-CH_3^{aryl}$), 2.17 (m, 1H, ═$NCH_2CH_2^A$−), 1.91 (m, 1H, ═$NCH_2CH_2CH_2^A$−), 1.81 (m, 1H, ═$NCH_2CH_2CH_2^B$−), 1.72 (m, 1H, ═$NCH_2CH_2^B$−), 1.08 (d, $^3J = 6.7$ Hz, 3H, −$CH^B(CH_3^ACH_3^B)$), 1.04 (d, $^3J = 6.7$ Hz, 3H, −$CH^A(CH_3^ACH_3^B)$), 0.96 (d, $^3J = 6.7$ Hz, 3H, −$CH^A(CH_3^ACH_3^B)$), 0.95 (d, $^3J = 6.7$ Hz, 3H, −$CH^B(CH_3^ACH_3^B)$). ^{13}C{^{1}H} NMR (d_2-dichloromethane, 150 MHz, 298 K): $\delta(^{13}C)$ 174.2 (C═N^{aryl}), 170.0 (C═N^{alk}), 158.5 (C-6^{py}), 157.1 (C-2^{py}), 145.7 (C-1^{aryl}), 141.6 (C-2^{aryl}), 141.5 (C-6^{aryl}), 132.1 (C-4^{py}), 127.3 (C-4^{aryl}), 124.8 (C-3^{aryl}), 124.6 (C-5^{aryl}), 124.2 (C-3^{py}), 123.9 (C-5^{py}), 100.2 (−CH═), 82.1 (═CH_2), 59.2 (═NCH_2-), 33.1 (═$NCH_2CH_2CH_2CH_2$−), 28.3 (═$NCH_2CH_2CH_2$−), 28.0 (═NCH_2CH_2−), 27.8 (−$CH^A(CH_3^ACH_3^B)$), 27.6 (−$CH^B(CH_3^ACH_3^B)$), 25.8 (−$CH^A(CH_3^ACH_3^B)$), 25.4 (−$CH^A(CH_3^ACH_3^B)$), 25.4 (−$CH^B(CH_3^ACH_3^B)$), 25.3 (−$CH^B(CH_3^ACH_3^B)$), 21.1 ($-CH_3^{aryl}$), 17.1 ($-CH_3^{alk}$).

X-ray crystal structure analysis of **7d**: formula $C_{27}H_{37}Cl_2N_3Ru \cdot 0.5CH_2Cl_2$, $M_r = 618.03$, black crystal, 0.55 × 0.45 × 0.06 mm, $a = 25.8516(5)$ Å, $b = 10.8712(2)$ Å, $c = 20.0594(3)$ Å, $\beta = 94.351(1)°$, $V = 5621.2(2)$ Å^3, $\rho_{calcd} = 1.461$ g cm^{-3}, $\mu = 0.864$ mm^{-1}, empirical absorption correction ($0.648 \le T \le 0.950$), $Z = 8$, monoclinic, space group *C*2/*c* (No. 15), $\lambda = 0.710\ 73$ Å, $T = 198$ K, ω and φ scans, 17 305 reflections collected ($\pm h$, $\pm k$, $\pm l$), (sin θ)/$\lambda = 0.67$ Å^{-1}, 6927 independent ($R_{int} = 0.145$) and 5708 observed reflections ($I \ge 2\sigma(I)$), 318 refined parameters, R1 = 0.042, wR2 = 0.100, maximum (minimum) residual electron density 1.21 (−0.82) e Å^{-3} close to the disordered solvent molecule, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 8c. Complex **7c** (150 mg, 0.25 mmol) was dissolved in 15 mL of toluene, and a 1.0 M solution of trimethylphosphine in toluene (1.35 mL, 1.35 mmol, 5.4 equiv) was added in the glovebox. The mixture was refluxed for 4 h, and the crude product was precipitated by addition of 80 mL of pentane at room temperature. The solid was isolated on a Schlenk frit and recrystallized from 15 mL of dichloromethane. The precipitation was completed again by addition of 80 mL of pentane, and the solid was collected by filtration, washed with pentane until the solvent was colorless, and dried in vacuo to give the violet product (72%, 132 mg, 0.18 mmol). Slow evaporation from a saturated dichloromethane solution gave single crystals of **8c** for the X-ray crystal structure analysis. Mp (DSC): 234 °C. MS-ESI (MeOH/$CHCl_3$, ES^+): *m/z* 660.6 $([M + Na])^+$, 602.3 $([M - Cl])^+$, 490.0 $([M - 2\ Cl - PMe_3])^+$. Anal. Calcd for $C_{29}H_{44}Cl_2N_3PRu \cdot CH_2Cl_2$ (722.57): C, 49.87; H, 6.42; N, 5.82. Found: C, 50.13; H, 6.87; N, 5.54. ^{1}H NMR (d_2-dichloromethane, 600 MHz, 298 K): $\delta(^1H)$ 7.90 (dm, $^3J = 7.8$ Hz, 1H, 3-H^{py}), 7.82 (dm, $^3J = 7.8$ Hz, 1H, 5-H^{py}), 7.78 (t, 1H, $^3J = 7.8$ Hz, 4-H^{py}), 7.26 (m, 1H, 4-H^{aryl}), 7.18 (m, 2H, 3-H^{aryl}), 5.85 (ddt, $^3J = 17.1$ Hz, $^3J = 10.2$ Hz, $^3J = 6.7$ Hz, 1H, −CH═), 5.07 (dq, $^3J = 17.1$ Hz, $^4J = {}^2J = 1.7$ Hz, 1H, ═CH_2^Z), 5.00 (dm, $^3J = 10.2$ Hz, 1H, ═CH_2^E), 3.96 (m, 2H, ═NCH_2−), 3.08 (sept, $^3J = 6.8$ Hz, 2H, −C$H(CH_3)_2$), 2.79 (s, 3H, $-CH_3^{alk}$), 2.52 (s, 3H, $-CH_3^{aryl}$), 2.13 (m, 2H, ═$NCH_2CH_2CH_2$−), 1.87 (m, 2H, ═NCH_2CH_2−), 1.26 (d, $^3J_{PH} = 7.9$ Hz, 9H, PMe), 1.07 (d, $^3J = 6.8$ Hz, 6H, −$CH(CH_3^ACH_3^B)$), 0.92 (d, $^3J = 6.8$ Hz, 6H, −$CH(CH_3^ACH_3^B)$). ^{13}C{^{1}H} NMR (d_2-dichloromethane, 150 MHz, 298 K): $\delta(^{13}C)$ 173.3 (d, $\sum^3J_{P,C} + {}^4J_{P,C} = 3.2$ Hz, C═N^{aryl}), 171.2 (d, $\sum^3J_{P,C} + {}^4J_{P,C} = 2.6$ Hz, C═N^{alk}), 160.5 (d, $\sum^3J_{P,C} + {}^4J_{P,C} = 1.3$ Hz, C-6^{py}), 158.9 (d, $\sum^3J_{P,C} + {}^4J_{P,C} = 1.0$ Hz, C-2^{py}), 149.6 (C-1^{aryl}), 141.5 (C-2^{aryl}), 137.9 (−CH═), 130.9 (C-4^{py}), 126.9 (C-4^{aryl}), 125.2 (C-3^{aryl}), 123.3 (C-3^{py}), 122.3 (C-5^{py}), 115.7 (═CH_2), 60.7 (═NCH_2−), 31.9 (═$NCH_2CH_2CH_2$−), 27.8 (═NCH_2CH_2−), 27.6 (−C$H(CH_3)_2$), 25.3 (−$CH(CH_3^ACH_3^B)$), 25.1 (−$CH(CH_3^ACH_3^B)$), 20.4 ($-CH_3^{aryl}$), 16.1 ($-CH_3^{alk}$), 15.9 (d, $^1J_{P,C} = 24.3$ Hz, PMe). ^{31}P{^{1}H} NMR (d_2-dichloromethane, 243 MHz, 298 K): $\delta(^{31}P) = -9.0$ (s).

X-ray crystal structure analysis of **8c**: formula $C_{29}H_{44}Cl_2N_3PRu$, $M = 637.61$, purple-black crystal, 0.60 × 0.25 × 0.02 mm, $a = 15.031(1)$ Å, $b = 10.724(1)$ Å, $c = 19.300(1)$ Å, $\beta = 101.05(1)°$, $V = 3053.3(4)$ Å^3, $\rho_{calcd} = 1.387$ g cm^{-3}, $\mu = 0.763$ mm^{-1}, empirical absorption correction ($0.657 \le T \le 0.985$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\ 73$ Å, $T = 198$ K, ω and φ scans, 17 887 reflections collected ($\pm h$, $\pm k$, $\pm l$), (sin θ)/$\lambda = 0.67$ Å^{-1}, 7264 independent ($R_{int} = 0.037$) and 5762 observed reflections ($I \ge 2\sigma(I)$), 334 refined parameters, R1 = 0.039, wR2 = 0.073, maximum (minimum) residual electron density 0.42 (−0.54) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 8d. Complex **7d** (150 mg, 0.24 mmol) was dissolved in 15 mL of toluene, and a 1.0 M solution of trimethylphosphine in toluene (1.31 mL, 1.31 mmol, 5.4 equiv) was added in the glovebox. The mixture was refluxed for 4 h, and the solvent was reduced in vacuo until a violet solid began to form. The precipitation was completed by addition of 80 mL of pentane, and the solid was collected by filtration, washed with pentane until the solvent was colorless, and dried in vacuo to give the violet product (87%, 136 mg, 0.21 mmol). Slow evaporation from a saturated dichloromethane solution gave single crystals of **8d** for the X-ray crystal structure analysis. Mp (DSC): 267 °C. MS-ESI (MeOH/$CHCl_3$, ES^+): *m/z* 616.2 $([M - Cl])^+$. Anal. Calcd for $C_{30}H_{46}Cl_2N_3PRu$ (651.67): C, 55.29; H, 7.12; N, 6.45. Found: C, 54.33; H, 7.01; N, 6.10. ^{1}H NMR (d_2-dichloromethane, 600 MHz, 298 K): $\delta(^1H)$ 7.90 (d, $^3J = 7.5$ Hz, 1H, 3-H^{py}), 7.82 (d, $^3J = 7.5$ Hz, 1H, 5-H^{py}), 7.78 (t, $^3J = 7.5$ Hz, 1H, H-4^{py}), 7.26 (m, 1H, 4-H^{aryl}), 7.18 (m, 2H, 3-H^{aryl}), 5.83 (ddt, $^3J = 17.1$ Hz, $^3J = 10.3$ Hz, $^3J = 8.4$ Hz, 1H, −CH═), 5.04 (d, $^3J = 17.1$ Hz, 1H, ═CH_2^Z), 4.97 (d, $^3J = 10.3$ Hz, 1H, ═CH_2^E), 3.95 (m, 2H, ═NCH_2−), 3.08 (sept, $^3J = 6.8$ Hz, 2H, −C$H(CH_3)_2$), 2.79 (s, 3H, $-CH_3^{alk}$), 2.53 (s, 3H, $-CH_3^{aryl}$), 2.11 (m, 2H, ═$NCH_2CH_2CH_2CH_2$−), 1.79 (m, 2H, ═NCH_2CH_2−), 1.47 (m, 2H, ═$NCH_2CH_2CH_2$−), 1.27 (d, $^2J_{P,H} = 7.7$ Hz, 9H, PMe), 1.08 (d, $^3J = 6.8$ Hz, 6H, −$CH(CH_3^ACH_3^B)$), 0.92 (d, $^3J = 6.8$ Hz, 6H, −$CH(CH_3^ACH_3^B)$). ^{13}C{^{1}H} NMR (d_2-dichloromethane, 150 MHz, 298 K): $\delta(^{13}C)$ 173.2 (d, $\sum^3J_{P,C} + {}^4J_{P,C} = 2.8$ Hz, C═N^{aryl}), 171.0 (d, $\sum^3J_{P,C} + {}^4J_{P,C} = 2.6$ Hz, C═N^{alk}), 160.4 (C-6^{py}), 158.9 (C-2^{py}), 149.6 (C-1^{aryl}), 141.5 (C-2^{aryl}), 138.9 (−CH═), 130.8 (C-4^{py}), 126.9 (C-4^{aryl}), 125.2 (C 3^{aryl}), 123.2 (C-3^{py}), 122.2 (C-5^{py}), 114.9 (═CH_2), 61.0 (═NCH_2−), 33.8 (═$NCH_2CH_2CH_2CH_2$−), 27.9 (═NCH_2-CH_2−), 27.6 (−C$H(CH_3)_2$), 27.1 (═$NCH_2CH_2CH_2$−), 25.3 (−$CH(CH_3^ACH_3^B)$), 25.1 (−$CH(CH_3^ACH_3^B)$), 20.3 ($-CH_3^{aryl}$), 16.2 ($-CH_3^{alk}$), 15.9 (d, $^1J_{P,C} = 24.0$ Hz, PMe). ^{31}P{^{1}H} NMR (d_2-dichloromethane, 243 MHz, 298 K): $\delta(^{31}P)$ −8.9 (s).

X-ray crystal structure analysis of **8d**: formula $C_{30}H_{46}Cl_2N_3PRu$, $M_r = 651.64$, black crystal, 0.25 × 0.20 × 0.07 mm, $a = 15.6678(4)$ Å, $b = 10.4923(4)$ Å, $c = 19.8860(6)$ Å, $\beta = 102.581(3)°$, $V = 3190.6(2)$ Å^3, $\rho_{calcd} = 1.357$ g cm^{-3}, $\mu = 0.732$ mm^{-1}, empirical absorption correction ($0.838 \leq T \leq 0.951$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 223$ K, ω and φ scans, 27 672 reflections collected ($\pm h$, $\pm k$, $\pm l$), (sin θ)/$\lambda = 0.66$ Å^{-1}, 7569 independent ($R_{int} = 0.073$) and 4628 observed reflections ($I \geq 2\sigma(I)$), 343 refined parameters, R1 = 0.047, wR2 = 0.111, maximum (minimum) residual electron density 0.58 (−0.85) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

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Supporting Information Available: Text and figures giving further experimental and spectroscopic details and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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