Ruthenium Carbene Complexes Featuring a Tridentate Pincer-type Ligand

Julia-Christina Wasilke,[†,‡] Guang Wu,[†,§] Xianhui Bu,[†,§] Gerald Kehr,[‡] and Gerhard Erker*[,‡]

Department of Chemistry and Biochemistry, Institute for Polymers and Organic Solids, University of California, Santa Barbara, California 93106, and Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

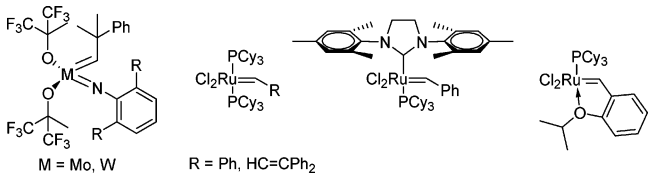
Received March 10, 2005

Ruthenium carbene complexes featuring the bulky tridentate *N*,*N*′-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido pincer-type ligand and different stabilizing phosphine ligands were synthesized and characterized. Preliminary results for the application to ring-closing metathesis show low activity for the cyclization of 1,7-octadiene with benzylidene(triphenylphosphine)[*N*,*N*′-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3*O*,*N*,*O*/*O*,*N*,*N*]-ruthenium(II) (**4a,b**). Benzylidene(tricyclohexylphosphine)[*N*,*N*′-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3*O*,*N*,*O*]ruthenium(II) (**5**) successfully transformed 1,7-octadiene to cyclohexene and ethylene in good yields at room temperature or 80 °C.

Introduction

Olefin metathesis catalyzed by middle-[1] and late-transition-metal[2] carbene complexes has become an important tool in organic synthesis as well as polymer chemistry.[3] Various catalyst modifications have been made improving catalyst activity and sensitivity, reaction conditions, and range of tolerance toward functional groups (Chart 1).[4] One or both phosphine ligands have been replaced by other ligands, such as N-heterocyclic carbenes,[5] showing increased reactivities with various olefinic substrates. Catalyst immobilization has led to recyclable systems.[6]

Chart 1. Catalysts for Olefin Metathesis



Recent development of the [Ru]=CHR type catalysts include structures that contain various connections between the supporting N-heterocyclic carbene ligand and the active alkylidene group at ruthenium[7] as well as variations of donor groups and functionalities at the =CHR end of the Ru−carbene complex.[8] Halide-free systems have found an increasing interest,[9] and the use of small chelate phosphine ligands has sometimes been

* To whom correspondence should be addressed. E-mail: erker@uni-muenster.de.
† University of California.
‡ Universität Münster.
§ X-ray crystal structure determinations.

(1) (a) Feldman, J.; Murdzek, J. S.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2260−2265. (b) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbinson, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875−3886. (c) Sinha, A.; Schrock, R. R. *Organometallics* **2004**, *23*(8), 1643−1645.

(2) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975. (b) Morken, J. P.; Didiuk, M. T.; Visser, M. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1994**, *116*, 3123−3124. (c) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem.* **1995**, *107*, 2179−2181; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041. (d) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110. (e) Morgan, J. P.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 3153−3155. (f) Tsang, W. C. P.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2001**, *20*(26), 5658−5669.

(3) Recent reviews: Connon, S. J.; Blechert, S. *Angew. Chem.* **2003**, *115*, 1944−1968; *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 1900−1923. Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29. Schrock, R. R.; Hoveyda, A. H. *Angew. Chem.* **2003**, *115*, 4740−4782; *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 4592−4633. Mol, J. C. *J. Mol. Catal. A: Chem.* **2004**, *213*, 39−45. Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**. *104*, 1317−1382. *Handbook of Metathesis*; Grubbs, R. H., Ed.; VCH-Wiley: Weinheim, Germany, 2003. Connon, S. J.; Blechert, S. *Top. Organomet. Chem.* **2004**, *11*, 93−124. Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117−7140.

(4) (a) Fürstner, A. *Angew. Chem.* **2000**, *112*, 3140−3171; *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3012−3043. (b) Louie, J.; Bielawski, C.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 11312−11313. (c) Seiders, T. J.; Ward, R. H.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225−3228. (d) Fuerstner, A.; Guth, O.; Düffels, A.; Seidel, G.; Liebl, M.; Gabor, B.; Mynott, R. *Chem. Eur. J.* **2001**, *7*, 4811−4820. (e) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236−3253. (f) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546−2558.

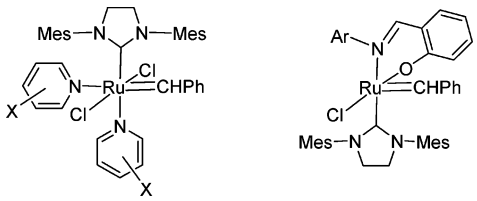
(5) (a) Westkamp, T.; Schattermann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem.* **1998**, *110*, 2631−2634; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*(18), 2490−2493. (b) Huang, J.; Stevens, E. D.; Nolan, S. P.; Peterson, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674−2678. (c) Ackermann, L.; Fürstner, A.; Westkamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787−4790. (d) Westkamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem.* **1999**, *111*, 2573−1576; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2416−2419. (e) Jafapour, L.; Huang, J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 3760−3763. (f) Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783−3784. (g) Choi, T.-L.; Lee, C. W.; Chatterjee, A. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 10417−10418. (h) Choi, T.-L.; Chatterjee, A. K.; Grubbs, R. H. *Angew. Chem.* **2001**, *113*, 1317−1319; *Angew. Chem., Int. Ed.* **2001**, *40*, 1277−1279.

(6) (a) Kobayashi, S.; Akiyama, R. *Angew. Chem.* **2002**, *114*, 2714−2716. (b) Jafarpour, L.; Heck, M.-P.; Baylon, C.; Lee, H. M.; Mioskowski, C.; Nolan, S. P. *Organometallics* **2002**, *21*, 671−679. (c) Yao, Q.; Rodriguez Motta, A. *Tetrahedron Lett.* **2004**, *45*, 2447−2451.

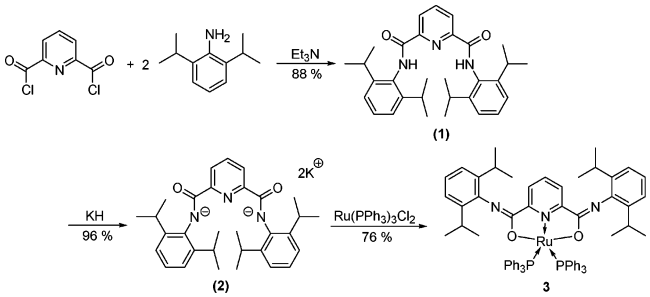
(7) (a) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, 124, 4954−4955. (b) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *J. Am. Chem. Soc*. **2003**, 125, 8424−8425. (c) Van Veldhuizen, J. J.; Gillingham, D. G.; Garber, S. B.; Kataoka, O.; Hoveyda, A. H. *J. Am. Chem. Soc*. **2003**, 125, 12502−12508. (d) Gallivan, J. P.; Jordan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **2005**, *46,* 2577−2580. (e) Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 4510−4517.

10.1021/om0501780 CCC: $30.25
Publication on Web 07/15/2005

Chart 2. Ru Metathesis Catalysts with N-Donor Ligands



Scheme 1



advantageous.[10] Replacement of the labile phosphine at ruthenium by pyridine or pyridine derivates (see Chart 2) has led to very reactive olefin metathesis catalysts.[11] Similarly, the attachment of monoanionic salicylaldimine-type chelate ligands (see Chart 2) has sometimes resulted in improved catalytic features.[12] We want to present the first examples of a new ligand and catalyst development where we have combined the essential features of the latter systems and attached a dianionic tridentate 2,6-disubstituted pyridine pincer-type ligand to [Ru]=CHR to form a new halide-free [(lig)(PR_3)Ru=CHR] olefin metathesis catalyst system.

Results and Discussion

Synthesis of the Ligand System and Ru Complexes. The new carbene complexes were derived from the tridentate ligand **1**, which is easily synthesized from 2,6-pyridinedicarboxylic acid chloride and 2,6-diisopropylaniline (Scheme 1). Deprotonation proceeded most reliably and reproducibly with KH in THF to yield the potassium salt **2**. To obtain the ruthenium precursor material for the carbene complex synthesis, tris(triphenylphosphine)ruthenium dichloride was reacted with **2** to give [*N*,*N*′-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3*O*,*O*,*N*]bis(triphenylphosphine)ruthenium-(II) (**3**; (lig)Ru(PPh_3)$_2$) as a red crystalline material (Scheme 1). The compound was fully characterized by elemental analysis and NMR spectroscopy. The ^{1}H NMR spectrum shows one septet for the isopropyl CH groups and two broad singlets for the methyl groups, indicating that the coordination modes of both sides of the metal are the same and one isomer is formed. This is supported by the ^{31}P NMR spectrum of **3**, showing one peak at δ 60.2 ppm.

Reaction of **3** with phenyldiazomethane in dichloromethane at −35 °C led to replacement of one PPh_3 ligand to yield the product **4** as a mixture of two isomers in an overall yield of 91% (Scheme 2). The metal center can be coordinated by the ligand in an O∧N∧O or O∧N∧N fashion (ratio ∼4:7). Each isomer could be isolated from the red-brown solid. Crystallization from dichloromethane by pentane diffusion at −35 °C gave the O∧N∧O isomer **4a** as dark red crystals suitable for X-ray diffraction. Crystallization from toluene by pentane diffusion at room temperature gave the O∧N∧N isomer **4b** as a red crystalline material. ^{1}H NMR data confirmed the installation of the carbene moiety at δ 18.21 (**4a**) and δ 18.24 (**4b**) for the two isomers, respectively. Due to the electronic influences of the different ligand coordination environments, the ^{31}P NMR spectra display two distinct signals at δ 49.2 (**4a**) and δ 38.2 (**4b**) for the two isomers, respectively.

Attempts were directed toward the replacement of the triphenylphosphine ligand of the compounds **4** with tricyclohexylphosphine. Prolonged reaction with tricyclohexylphosphine, as previously reported for other compounds,[13] did not result in phosphine exchange. Therefore, we reacted the dianionic ligand **2** with benzylidenebis(tricyclohexylphosphine)ruthenium (II) dichloride in dichloromethane at room temperature overnight (Scheme 3). After purification the product **5** was isolated as a brown powder in 93% yield. Single crystals could not be obtained, but NMR spectroscopy indicates only O∧N∧N coordination of the ligand in comparison to the triphenylphosphine derivatives.

Nickel Complexes. The system was carried forward to nickel compounds, since only a limited number of nickel carbene complexes are known.[14] To obtain the nickel precursor material for the carbene compound synthesis, (dimethoxyethane)nickel dichloride was reacted with **2**. At room temperature over 3 h, potassium [*N*,*N*′-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxa-

(8) (a) Fürstner, A.; Thiel, O. R.; Lehmann, C. W. *Organometallics* **2002**, *21,* 331−335. (b) Wakamatsu, H.; Blechert, S. *Angew. Chem.* **2002**, *114*, 832−834; *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 794−796. (c) Michrowska, A.; Bujok, R.; Harutyunyan, S.; Sashuk, V.; Dolgonos, G.; Grela, K. *J. Am. Chem. Soc.* **2004**, *126*, 9318−9325. (d) Williams, J. E.; Harner, M. J.; Sponsler, M. B. *Organometallics* **2005**, *24,* 2013−2015. (e) Matsugi, M.; Curran, D. P. *J. Org. Chem.* **2005**, *70*, 1636−1642.

(9) (a) Conrad, J. C.; Amoroso, D.; Czechura, P.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2003**, *22,* 3634−3636. (b) Krause, J. O.; Nuyken, O.; Wurst, K.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 777−784.

(10) (a) Hansen, S. M.; Volland, M. A. O.; Rominger, F.; Eisenträger, F.; Hofmann, P. *Angew. Chem.* **1999**, *111,* 1360−1364. (b) Gatard, S.; Kahlal, S.; Méry, D.; Nlate, S.; Cloutet, E.; Saillard, J.-Y.; Astruc, D. *Organometallics* **2004**, *23,* 1313−1324. (c) Volland, M. A. O.; Hansen, S. M.; Rominger, F.; Hofmann, P. *Organometallics* **2004**, *23,* 800−816.

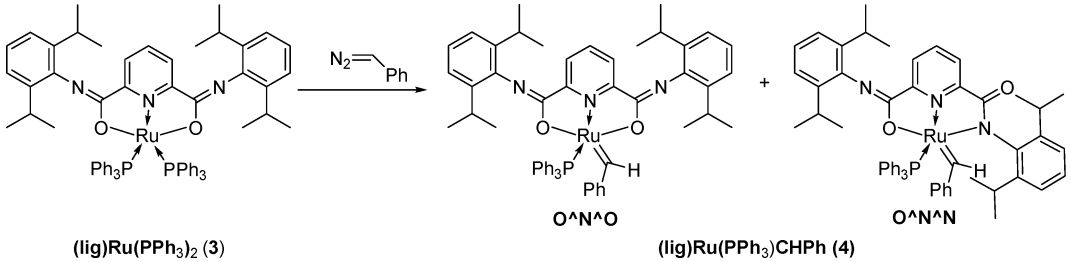
(11) (a) Hill, A. F.; Hulkes, A. G.; White, A. J. P.; Williams, D. J. *Organometallics* **2000**, *19*, 371−373. (b) Katayama, H.; Wada, C.; Taniguchi, K.; Ozawa, F. *Organometallics* **2002**, *21*, 3285−3291. (c) Choi, T.-L.; Grubbs, R. H. *Angew. Chem.* **2003**, *115*, 1785−1788; *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 1743−1746. (d) Ung, T.; Hejl, A.; Grubbs, R. H.; Schrodi, Y. *Organometallics* **2004**, *23,* 5399−5401. (e) Williams, J. E.; Harner, M. J.; Sponsler, M. B. *Organometallics* **2005**, *24,* 2013−2015.

(12) (a) De Clercq, B.; Verpoort, F. *Tetrahedron Lett.* **2002**, *43,* 9101−9104. (b) Opstal, T.; Verpoort, F. *Angew. Chem.* **2003**, *115*, 2982−2985; *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 2876−2879.

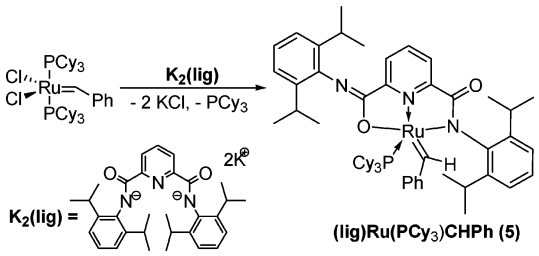
(13) (a) Retbøll, M.; Edwards, A. J.; Rae, A. D.; Willis, A. C.; Bennett, M. A.; Wenger, E. *J. Am. Chem. Soc.* **2002**, *124*, 8348−8360. (b) Hejl, A.; Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Chem. Commun.* **2002**, 2524−2525. (c) Groux, L. F.; Zargaruan, D. *Organometallics* **2003**, *22*, 4759−4769.

(14) (a) Miki, K.; Taniguchi, H.; Kai, Y.; Kasai, N.; Nishiwaki, K.; Wada, M. *J. Chem. Soc., Chem. Commun.* **1982**, *20*, 1178−1180. (b) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*(10), 4391−4394. (c) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*(34), 9976−9977. (d) McGuinness, D. S.; Mueller, W.; Wasserscheid, P.; Cavell, K. J.; Skelton, B. W.; White, A. H.; Englert, U. *Organometallics* **2002**, *21*(1), 17−181. (e) Hou, H.; Gantzler, P. K.; Kubiak, P. C. *J. Am. Chem. Soc.* **2003**, *125*(32), 9564−9565. (f) Hou, H.; Gantzel, P. K.; Kubiak, C. P. *Organometallics* **2003**, *22*(14), 2817−2819. (g) Kuhl, S.; Schneider, R.; Fort, Y. *Adv. Synth. Catal.* **2003**, *345*(3), 341−344. (h) Wang, X.; Liu, S.; Jin, G.-X. *Organometallics* **2004**, *23*, 6002−6007.

Scheme 2



Scheme 3



mido-κ^3N,N,N]nickel(II) chloride (**6**) was obtained as a polymeric material with loss of 1 equiv of potassium chloride. Reaction at 80 °C over 5 days yielded [*N*,*N*′-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3N,N,N]nickel(II) as a poorly soluble orange powder. Crystallization from polar solvents provided X-ray structures of the solvent adducts **7** and **8**. The reaction was repeated in the presence of trimethylphosphine to give [*N*,*N*′-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3O,N,N'](trimethylphosphine)nickel(II) (**9**; (lig)NiPMe$_3$) as a red crystalline material after workup (Scheme 4). Compound **9** is more soluble than compounds **7** and **8** and was characterized by elemental analysis, NMR spectroscopy, and X-ray diffraction.

Reaction of (lig)NiPMe$_3$ (**9**) with phenyldiazomethane in dichloromethane at −35 °C gave an orange powder after workup. Two isomers were observed by ^{1}H NMR spectroscopy, both containing a signal at low field for the carbene proton, but the compounds were otherwise ill defined. Comparison of the ^{1}H NMR spectrum (for details see the Experimental Section) with the ruthenium derivatives suggests O∧N∧O and O∧N∧N coordination at nickel in a 3:7 ratio.

X-ray Crystal Structure Analyses. Some of the compounds synthesized in the course of this study were characterized by X-ray diffraction. First, we investigated the free ligand system **1** by an X-ray crystal structure analysis (Figure 1). Suitable single crystals were grown from a methanol solution by evaporation in air. A conformation is found where all three nitrogens are oriented toward the "inside" of the chelate framework.

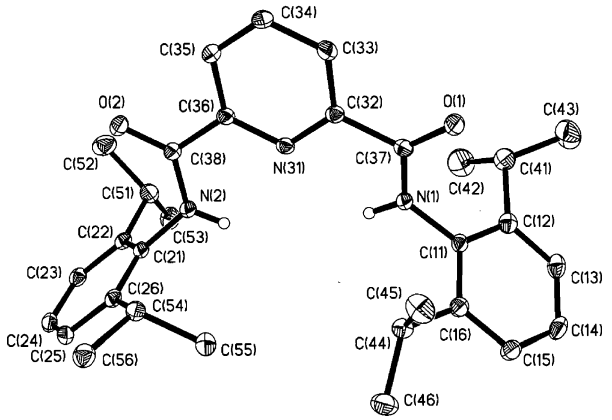
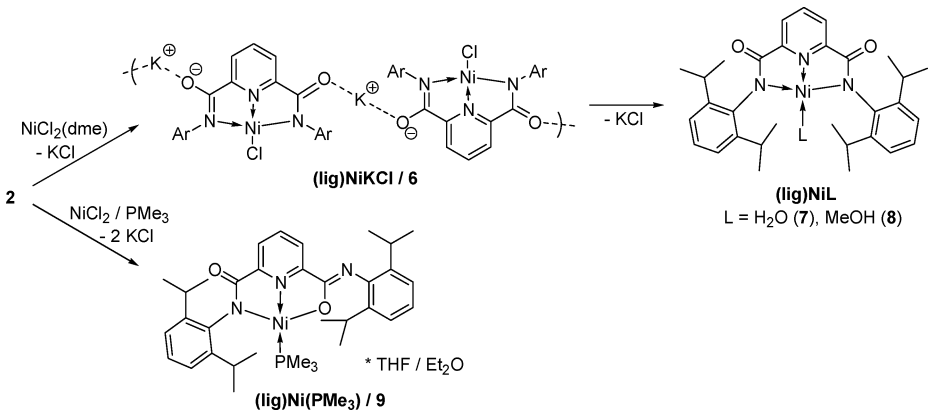


Figure 1. Molecular structure of the ligand system **1**. Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms have been omitted for clarity.

Single crystals of the potassium salt **2** were grown from hot THF. The compound revealed a complex crystallization pattern. The ratio of potassium to ligand is 2:1, q.e.d. Two ligands are facing each other, and the four oxygen and the two pyridine nitrogen centers are coordinating three potassium atoms. The central potassium is further coordinated by two molecules of THF. Each dimeric set of ligands is connected via a fourth potassium binding a nitrogen from each set in such a way that the individual dimers are shifted against each other (Figure 2).

Pentane diffusion into a solution of the compound **3** in toluene at room temperature gave a red crystalline material suitable for X-ray crystal structure analysis

Scheme 4



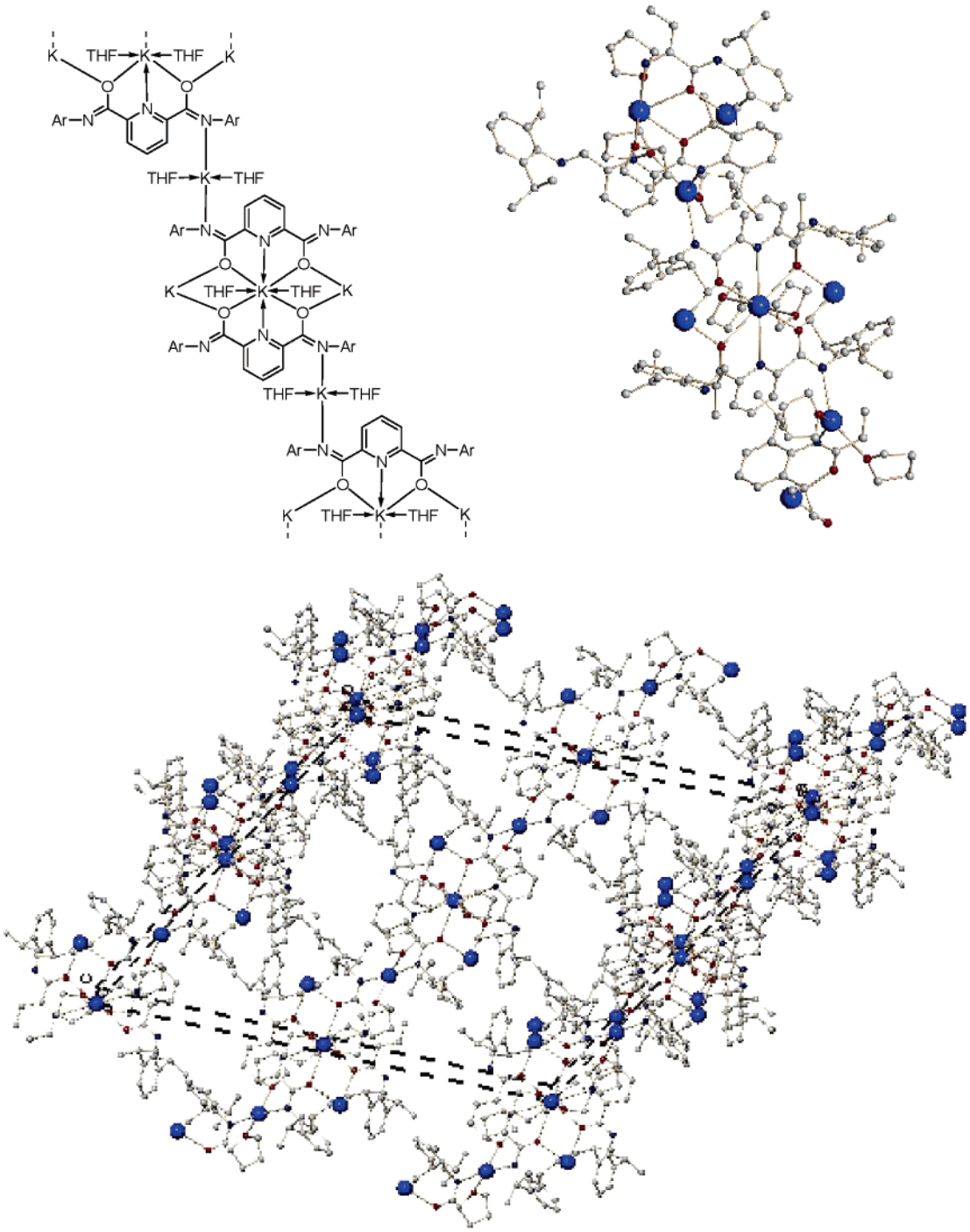


Figure 2. Drawing and X-ray structure of the ligand potassium salt **2**.

(Figure 3). The structure reveals O∧N∧O coordination of the ligand. The ruthenium is surrounded by its ligands in a distorted-square-pyramidal fashion with the two phosphines and the coordinating oxygen atoms in the plane and the coordinating pyridine ring perpendicular to it.

Crystallographic analysis of compounds **4a**,**b** show a square-pyramidal arrangement of the ligand coordinating to the metal center for both isomers (Figure 4). In each case the tridentate ligand and phosphine form a square-planar arrangement around the metal center while the carbene carbon builds the tip of the pyramid. In the triclinic O∧N∧O isomer (**4a**) the ruthenium atom is slightly pushed out of the plane toward the carbene carbon and the metal center is less sterically hindered than in the monoclinic O∧N∧N isomer (**4b**). The nitrogen coordination by one of the amidate functionalities renders the isopropyl groups of the amide in closer proximity to the ruthenium−carbene carbon bond. The coordinating oxygen is slightly distorted out of the plane away from the carbene carbon, and ruthenium is equally pushed out of the plane toward the carbene carbon.

Selected bond lengths for both isomers are shown in Table 1. The C(7)−N(1) bonds (**4a**, 1.275(4) Å; **4b**, 1.269(5) Å) show double-bond character, and the C(7)−O(1) bonds (1.329(3), 1.326(4) Å) show single-bond character in both isomers, as expected. The C(13)−N(3) bonds (1.283(4), 1.359(5) Å) show double-bond character in the

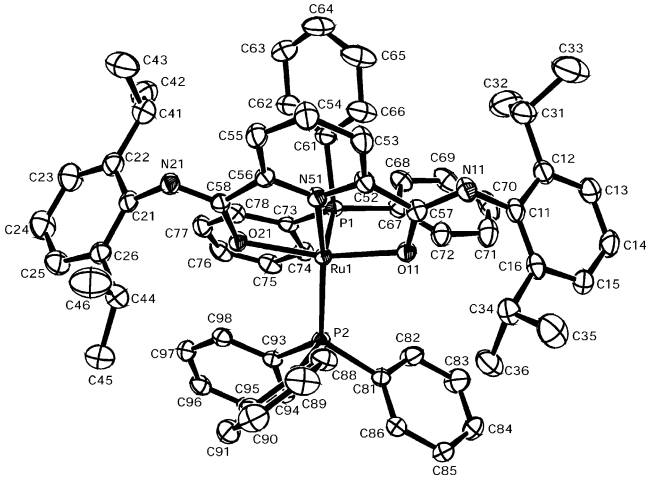


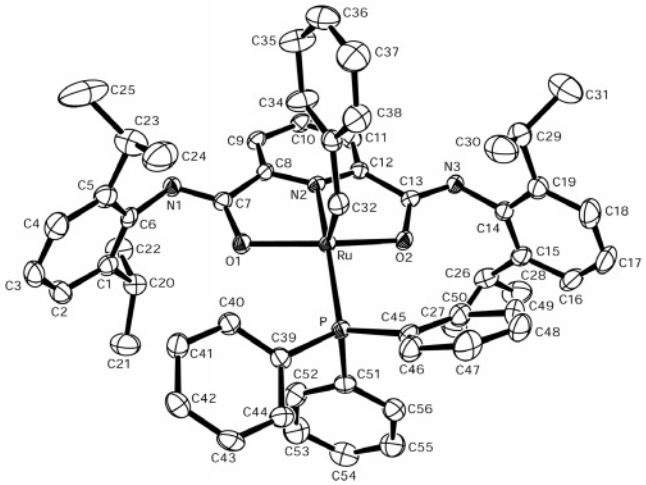
Figure 3. View of the molecular structure of (lig)Ru(PPh$_3$)$_2$ (**3**). Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms have been omitted for clarity.

O∧N∧O isomer (**4a**) and single-bond character in the O∧N∧N isomer, while the C(13)−O(2) bond of **4a** shows single-bond character (1.324(4) Å) and that of **4b** double-bond character (1.230(4) Å). The C(32)−Ru bonds (**4a**, 1.853(3) Å; **4b**, 1.846(4) Å) show the expected bond lengths for a ruthenium−carbene bond (1.77−1.90 Å).[15] Bond angles are similar in both isomers. The C(32)−Ru−N(2) (105.71(12), 102.23(14)°), −O(2) (102.89(11)°), −N(3) (103.37(14)°), and −O(1) (102.70(11), 98.19(14)°) angles exceed a perpendicular arrangement, while the C(32)−Ru−P (88.43(10), 90.74(12)°) angles match a perpendicular alignment. The angles formed by the tridentate ligand with the ruthenium center fall short of 90° angles, while the bond angles formed by the tridentate ligand, ruthenium, and the phosphine ligand exceed perpendicular alignment (see Table 1).

Single crystals of the nickel complex **6** were obtained from hot THF, and the structure incorporates three additional molecules of THF (Figure 5). The nickel center is surrounded by the N∧N∧N-coordinating tridentate ligand and chloride in a square-planar arrangement. Potassium coordinates to oxygen and one phenyl ring in an η^6 fashion. The structure is polymeric, forming a chain with potassium linking the monomeric subunits (K(1)−O(11) = 2.716(4) Å; e.g. K(1)−C(13) = 3.255(6) Å). As expected, the carboxamido C−N bonds are rather long (N(11)−C(57) = 1.354(7) Å, N(21)−C(58) = 1.352(7) Å), whereas the adjacent C=O bonds are short (O(11)−C(57) = 1.241(6) Å, O(21)−C(58) = 1.230(6) Å).

Single crystals of compound **7** were obtained from wet hexane (Figure 6). The structure reveals N∧N∧N coordination of the ligand to the metal center. Crystallization from methanol gives the according structure where the water ligand is replaced by methanol (**8**) (for details see the Supporting Information).

Single crystals of compound **9** were grown from THF or from toluene by pentane diffusion at −35 °C (Figure 7). The nickel center is surrounded by the O∧N∧N-



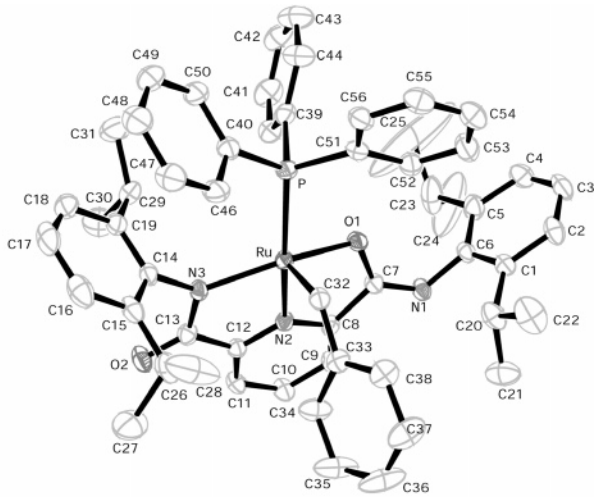


Figure 4. ORTEP drawings of (lig)Ru(PPh$_3$)CHPh (**4a**) (O∧N∧O) (left) and (lig)Ru(PPh$_3$)CHPh (**4b**) (O∧N∧N) (right). Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths for Both Isomers of (lig)Ru(PPh$_3$)CHPh (4)

bond length (Å)	O∧N∧O (**4a**)	O∧N∧N (**4b**)	bond angle (deg)	O∧N∧O (**4a**)	O∧N∧N (**4b**)
C(6)−N(1)	1.425(4)	1.426(4)	C(33)−C(32)−Ru	131.9(2)	132.3(3)
C(7)−N(1)	1.275(4)	1.269(5)	C(32)−Ru−N(2)	105.71(12)	102.23(14)
C(7)−O(1)	1.329(3)	1.326(4)	C(32)−Ru−O(2)	102.89(11)	
C(13)−N(3)	1.283(4)	1.359(5)	N(2)−Ru−O(2)	78.29(9)	
C(13)−O(2)	1.324(4)	1.230(4)	C(32)−Ru−N(3)		103.37(14)
C(14)−N(3)	1.430(4)	1.451(5)	N(2)−Ru−N(3)		77.55(12)
C(32)−C(33)	1.469(4)	1.450(5)	C(32)−Ru−(O1)	102.70(11)	98.19(14)
C(32)−Ru	1.853(3)	1.846(4)	N(2)−Ru−O(1)	78.64(9)	78.23(11)
N(2)−Ru	2.029(2)	2.009(3)	C(32)−Ru−P	88.43(10)	90.74(12)
O(1)−Ru	2.0369(19)	2.060(3)	O(2)−Ru−P	97.10(6)	
O(2)−Ru	2.037(2)		N(2)−Ru−P	165.75(7)	164.76(9)
N(3)−Ru		2.077(3)	O(1)−Ru−P	100.32(6)	92.16(7)
P−Ru	2.2975(8)	2.3273(10)			

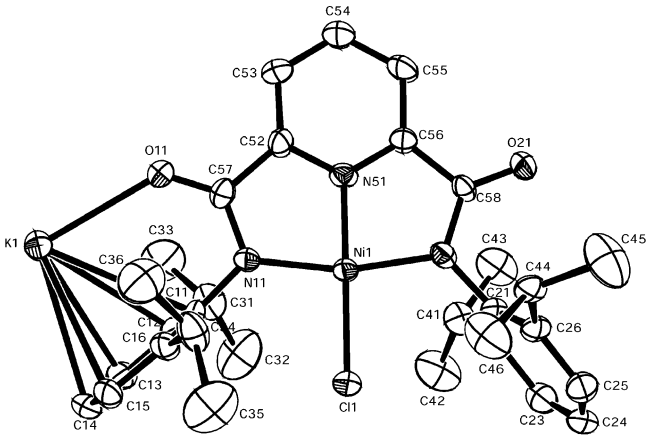


Figure 5. X-ray structure analysis of (lig)NiKCl (**6**): view of the repetitive unit in the coordination polymer. Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms have been omitted for clarity.

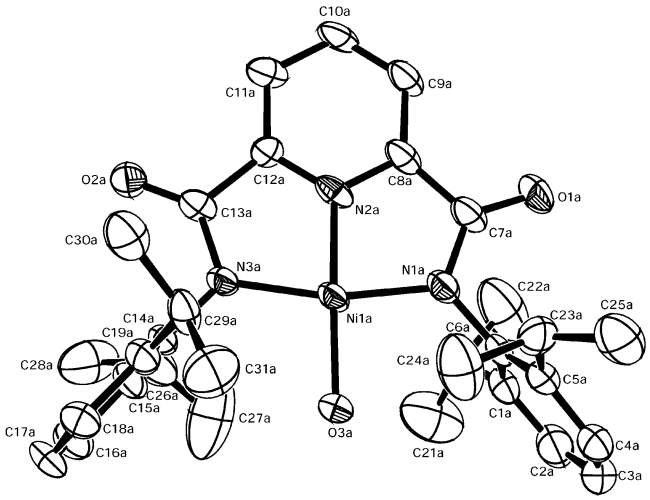


Figure 6. X-ray structure analysis of (lig)Ni(H_2O) (**7**). Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms have been omitted for clarity.

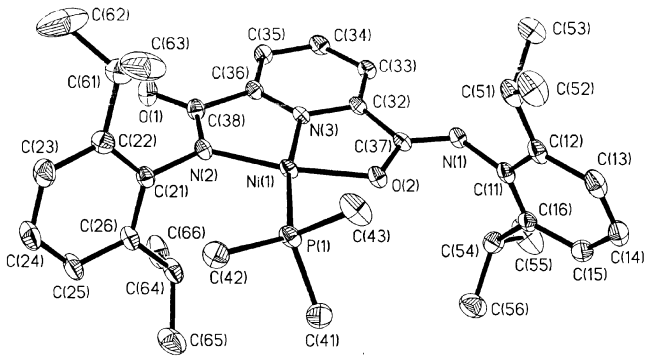
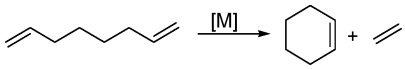


Figure 7. X-ray structure analysis of (lig)NiPMe_3 (**9**). Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms have been omitted for clarity.

coordinating tridentate ligand and trimethylphosphine in a square-planar fashion. It seems that the steric demand of the phosphine is sufficient to change one coordination site of the ligand from N to O coordination.

(15) Ru−C bond compared to: Li, Y.; Huang, J.-S.; Xu, G.-B.; Zhu, N.; Zhou, Z.-Y.; Che, C.-M.; Wong, K.-Y. *Chem. Eur. J.* **2004**, *10*, 3486−3502.

Scheme 5. RCM of 1,7-Octadiene to Cyclohexene and Ethylene



Ring-Closing Metathesis: Preliminary Results. To investigate the activity of the ruthenium and nickel carbene complexes for RCM, 1,7-octadiene was chosen as a simple and straightforward example known from the literature.[16] The main products are expected to be cyclohexene and 1 equiv of ethylene (Scheme 5). Possible side products are mainly double-bond isomers of the diene.

Reactions were run in deuterated benzene inside Young NMR tubes at room temperature or 80 °C and monitored by ^{1}H NMR spectroscopy. Alternatively, reactions were run more dilute in toluene and aliquots were analyzed by GC. Commercially available samples served as reference for the product. Commercially available $Cl_2Ru(PCy_3)_2$=CHPh, $Cl_2Ru(PCy_3)_2$=CHCH=CMe_2, and $Cl_2Ru(PCy_3)$=CH(*o*-$C_6H_4O^iPr$) were tested for comparison. Table 2 summarizes the results.

The triphenylphosphine-stabilized O∧N∧O-coordinated ruthenium carbene complex **4a** displays relatively low conversion of 1,7-octadiene to cyclohexene. After 3 h at 80 °C 76% product is observed, as well as 24% isomers. Prolonged reaction time up to 27 h yields conversion up to 98% product. The presence of the proton source (2*H*-pyrrole)B(C_6F_5)$_3$[17] did not markedly change the catalyst performance. Activation with Lewis acids reduced the product yield drastically along with increased amounts of isomers.[18] Addition of 3 equiv of B(C_6F_5)$_3$ reduced the yield to 40% after 3 days at 80 °C. The N∧N∧O isomer **4b** showed no activity with or without B(C_6F_5)$_3$ activation under the applied reaction conditions.

Replacement of the triphenylphosphine moiety by tricyclohexylphosphine provides a catalyst (**5**) with activities comparable to Grubbs analogues at 80 °C as well as at room temperature. Product yields varied in the range of 83−95% with negligible amounts of isomers. Overall the concentration did not play as significant a role as reported for commonly used ruthenium carbene catalysts. Within the range of 1.6−6 mM catalyst in deuterated benzene or toluene, yields did not vary significantly.

Conclusions

Two ruthenium carbene complexes (**4** and **5**) with a bulky tridentate ligand were synthesized and characterized. NMR spectroscopy and X-ray crystallography allowed for characterization of the coordination mode of the ligand in compound **4**. Compound **5** shows activities comparable to that of previously reported catalysts for RCM of 1,7-octadiene, while the nickel compound has not shown any activity so far. The Ru

(16) For examples see: (a) Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 204−227. (b) Opstal, T.; Verpoort, F. *J. Mol. Catal.* **2003**, *200*, 49−61.

(17) Kleingrewe, N.; Kehr, G.; Roesmann, R.; Fröhlich, R.; Holst, C.; Erker, G. *Eur. J. Inorg. Chem.* **2001**, *2*, 535−538.

(18) (a) Romero, P. E.; Piers, W. E.; McDonald, R. *Angew. Chem.* **2004**, *116*, 6287−6291; *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 6161−6165. (b) Yang, L.; Mayr, M.; Wurst, K.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 5761−5770.

Table 2. [Ru]=CHR-Catalyzed RCM of 1,7-Octadiene

				yield, %	
catalyst	cocatalyst	time	temp	product	isomers
(lig)Ru(PPh_3)=CHPh(O∧N∧O) (**4a**)		3 h	80 °C	76	24
(lig)Ru(PPh_3)=CHPh(O∧N∧O) (**4a**)	$PyrB(C_6F_5)_3$[17]	3 h	80 °C	70	20
(lig)Ru(PPh_3)=CHPh(O∧N∧O) (**4a**)	$B(C_6F_5)_3$	3 d	80 °C	40	12
(lig)Ru(PPh_3)=CHPh(N∧N∧O) (**4b**)	$B(C_6F_5)_3$	9 h	80 °C	21	
(lig)Ru(PPh_3)=CHPh(N∧N∧O) (**4b**)		9 h	80 °C	0	
(lig)Ru(PCy_3)=CHPh (**5**)		1 h	80 °C	95	5
(lig)Ru(PCy_3)=CHPh (**5**)		3 h	room temp	94	6
(lig)Ru(PCy_3)=CHPh (**5**)		5 h	room temp	83	
$Cl_2Ru(PCy_3)_2$=CHPh		1 h	room temp	93	7
$Cl_2Ru(PCy_3)_2$=CHPh		1 h	80 °C	quantitative	minimal
$Cl_2Ru(PCy_3)_2$=CHCH=CMe_2		1 h	room temp	96	4
$Cl_2Ru(PCy_3)_2$=CHCH=CMe_2		1 h	80 °C	quantitative	minimal
$Cl_2Ru(PCy_3)$=CH(*o*-$C_6H_4O^iPr$)		1 h	room temp	95	5
$Cl_2Ru(PCy_3)$=CH(*o*-$C_6H_4O^iPr$)		1 h	80 °C	quantitative	minimal
(lig)Ni(PMe_3)CHPh (**10**)		1 day	80 °C		

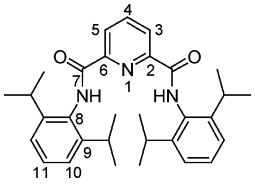
catalyst system **5** proved to be relatively insensitive to changes of concentration and temperature.

Experimental Section

General Procedures. Reactions with organometallic substrates or reagents were carried out in an inert atmosphere using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. NMR spectra were recorded with Varian UNITY INOVA 500 MHz (499.9 MHz) and Varian UNITY INOVA 400 MHz instruments (^{1}H, 399.9 MHz; ^{13}C, 100.6 MHz; ^{31}P, 161.9 MHz). The following instruments were used for additional physical characterization: melting points, DSC 2010 TA instruments; elemental analysis, Leeman Labs Inc. CE440 elemental analyzer or a Control Equipment Corp. 440 elemental analyzer. 2*H*-Pyrrole-*N*-tris(pentafluorophenyl)borane ($PyrB(C_6F_5)_3$) was synthesized according to literature procedures.[17]

For X-ray crystal structure analysis, the single crystal was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART program package (SMART Software Users Guide, Version 5.1, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1999) was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[20] and SADABS[21] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[22] program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Analytical scattering factors[23] for neutral atoms were used throughout the analysis.

***N,N′*-Bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamide (1).** 2,6-Pyridinedicarboxylic acid chloride (500 mg, 2.45



$\times 10^{-3}$ mol) was dissolved in 15−20 mL of dry THF. Diisopropylaniline (924 mL, 4.90×10^{-3} mol) and triethylamine (683 mL, 4.90×10^{-3} mol), dried over molecular sieves (4 Å), were added at 0 °C. The reaction mixture was stirred at room temperature for 2 h. The precipitated $Et_3N{\cdot}HCl$ was filtered off and the solvent of the filtrate removed under vacuum. The crude material was triturated with boiling hexane to provide the product as a white solid, which was dried in DCM over magnesium sulfate. Single crystals were grown from methanol at room temperature through solvent evaporation. Yield: 1.05 g, 88%. Mp: 210 °C. MS-EI (*m/z*): calcd 485.3042, found 485.3050. Anal. Calcd for $C_{31}H_{39}N_3O_2$ (mol wt 485.65): C, 76.66; H, 8.09; N, 8.65. Found: C, 76.56; H, 8.14; N, 8.75. ^{1}H NMR (chloroform-*d*, 298 K): δ 9.05 (br s, 2H, NH), 8.58 (d, 2H, H-3, H-5), 8.20 (t, 1H, H-4), 7.36 (t, 2H, H-11), 7.25 (d, 4H, H-10), 3.16 (s, 4H, $^3J_{H-12,H-13} = 6.87$ Hz, CH), 1.24 (d, 24H, $^3J_{H-12,H-13} = 6.87$ Hz, CH_3). ^{1}H NMR (methanol-d_4, 298 K): δ 9.99 (br s, 2H, NH), 8.46 (d, 2H, H-3, H-5), 8.22 (t, 1H, H-4), 7.28 (t, 2H, H-11), 7.20 (d, 4H, H-10), 3.22 (sep., 2H, $^3J_{H-1,2H-13} = 6.86$ Hz, CH), 1.20 (d, 24H, $^3J_{H-12,H-13} = 6.86$ Hz, CH_3). ^{1}H NMR (benzene-d_6, 298 K): δ 9.12 (br s, 2H, NH), 9.32 (d, 2H, H-3, H-5), 7.23 (t, 1H, H-11), 7.13 (d, 4H, H-10), 7.04 (t, 1H, H-4), 3.28 (s, 2H, $^3J_{H-12,H-13} = 6.94$ Hz, CH), 1.20 (d, 24H, $^3J_{H-12,H-13} = 6.94$ Hz, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6, 298 K): δ 163.0 (C-7), 149.8 (C-2, C-6), 146.9 (C-9), 140.0 (C-4), 132.2 (C-8), 129.1 (C-3, C-5), 126.2 (C-10), 124.3 (C-11), 29.9 (C−CH), 24.1 (C−CH_3).

X-ray crystal structure analysis of **1**: formula $C_{33}H_{47}N_3O_4$, $M_r = 549.74$, colorless crystals, 0.30 × 0.30 × 0.30 mm, $a = 9.510(3)$ Å, $b = 12.530(4)$ Å, $c = 14.021(5)$ Å, $\alpha = 82.479(6)°$, $\beta = 85.019(6)°$, $\gamma = 72.137(6)°$, $V = 1574.6(9)$ Å^3, $\rho_{calcd} = 1.159$ Mg m^{-3}, $\mu = 0.076$ mm^{-1}, $Z = 2$, triclinic, space group $P\bar{1}$, $\lambda = 0.710\,73$ Å, $T = 150$ K, 13 442 reflections collected, 5524 independent ($I > 2\sigma(I)$), 381 refined parameters, R1 = 0.0583, wR2 = 0.1536, hydrogen atoms added to calculated positions.

Dipotassium *N,N′*-Bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamidate (2). *N,N′*-Bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamide (**1**; 500 mg, 1.03×10^{-3} mol) and potassium hydride (83 mg, 2.06×10^{-3} mol) were stirred in THF (60 mL) overnight. A rapid, strong gas development indicates the side product hydrogen. The solvent was reduced to precipitate the product. Single crystals were obtained from hot THF. Yield: 554 mg, 96%. MS-EI (*m/z*): $(m - 2{\cdot}K + H)^-$ in MeOH calcd 484.2964, found 484.2986, Anal. Calcd for $C_{31}H_{37}K_2N_3O_2$ (mol wt 561.83): C, 66.27; H, 6.64; N 7.48. Found: C, 64.76; H, 6.29; N, 7.09. ^{1}H NMR (chloroform-*d*, 298 K): δ 8.57 (d, 2H, H-3, H-5), 8.20 (t, 1H, H-4), 7.37 (t, 2H, H-11), 7.25 (d, 4H, H-10), 3.15 (sep, 4H, $^3J_{H-12,H-13} = 6.96$ Hz, CH), 1.24 (d, 24H, $^3J_{H-12,H-13} = 6.96$ Hz, CH_3). ^{13}C{^{1}H} NMR (chloroform-*d*, 298 K): δ 162.7 (C-7), 149.1 (C-2, C-6), 146.3 (C-9), 139.8 (C-4), 130.7 (C-8), 128.9 (C-3, C-5), 126.1 (C-10), 123.9 (C-11), 29.3 (CH), 24.8 (CH_3).

X-ray crystal structure analysis of **2**: formula $C_{43}H_{61}N_3O_5K_2$, $M_r = 778.15$, colorless crystals, 0.2 × 0.10 × 0.05 mm, $a =$

(19) Analogous to ref 2b,c.

(20) SAINT Software Users Guide, Version 6.0; Bruker Analytical X-ray Systems, Inc., Madison, WI, 1999.

(21) Sheldrick, G. M. SADABS, Version 2.05; Bruker Analytical X-ray Systems, Inc., Madison, WI, 2001.

(22) Sheldrick, G. M. SHELXTL, Version 6.12; Bruker Analytical X-ray Systems, Inc., Madison, WI, 2001.

(23) *International Tables for X-ray Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C.

32.017(3) Å, b = 11.4707(10) Å, c = 26.801(2) Å, α = 90°, β = 119.704(2)°, γ = 90°, V = 8549.6(12) Å^3, ρ_{calcd} = 1.209 g cm^{-3}, μ = 0.267 mm^{-1}, Z = 8, monoclinic, space group $C2/c$, λ = 0.710 73 Å, T = 117(1) K, 20 177 reflections collected, 6780 independent ($I > 2\sigma(I)$), 510 refined parameters, R1 = 0.0587, wR2 = 0.1605, hydrogen atoms added to calculated positions.

[*N,N′*-Bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3*O,O,N*]bis(triphenylphosphine)ruthenium(II) (3; (lig)Ru(PPh$_3$)$_2$). Tris(triphenylphosphine)ruthenium dichloride (500 mg, 5.21 × 10^{-4} mol) in THF (50 mL) was added to dipotassium *N,N′*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamidate (**2**; 293 mg, 5.21 × 10^{-4} mol) in THF (30 mL). The reaction mixture turned dark red and was stirred overnight. All volatiles were removed under vacuum. The dark red crude material was extracted with toluene, filtered, and triturated with pentane. Further purification by dissolving the red powder in toluene and pentane diffusion at room temperature provided dark red crystals, suitable for X-ray crystallography. Yield: 437 mg, 76%. Anal. Calcd for $C_{37}H_{37}N_3O_2P_2Ru$ (mol wt 1109.24): C, 72.54; H, 6.09; N, 3.79. Found: C, 73.14; H, 6.43; N, 3.26. ^{1}H NMR (benzene-d_6, 298 K): δ 8.03 (d, 2H, H Ph), 7.33 (m, 8H, H Ph), 7.21 (m, 11H, H Ph), 6.86 (t, 9H, H−Ph), 6.74 (t, 9H, H Ph), 3.32 (sep., 4H, $^3J_{HH}$ = 6.9 Hz, CH), 1.42 (br s, 12H, CH$_3$), 1.10 (br s, 12H, CH$_3$). ^{31}P{^{1}H} NMR (benzene-d_6, 298 K, relative to H$_3$PO$_4$): δ 60.2 ($\nu_{1/2}$ = 3.6 Hz).

X-ray crystal structure analysis of **3**: formula $C_{67}H_{67}N_3O_2P_2Ru$, M_r = 1109.25, dark red crystals, 0.30 × 0.16 × 0.08 mm, a = 11.724(3) Å, b = 14.298(3) Å, c = 19.268(4) Å, α = 89.156(4)°, β = 80.866(4)°, γ = 77.064(4)°, V = 3107.3(12) Å^3, ρ_{calcd} = 1.186 Mg m^{-3}, μ = 0.347 mm^{-1}, Z = 2, triclinic, space group $P\bar{1}$, λ = 0.710 73 Å, T = 150 K, 28 168 reflections collected, 10 908 independent ($I > 2\sigma(I)$), 689 refined parameters, R1 = 0.0396, wR2 = 0.1192, hydrogen atoms added to calculated positions.

(Benzylidene)(triphenylphosphine)[*N,N′*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3*O,N,O/O,N,N*]ruthenium(II) (4; (lig)Ru(PPh$_3$)=CHPh).[19] Phenyldiazomethane (107 mg, 9.02 × 10^{-4} mol) in dichloromethane was added to [*N,N′*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3-*O,N,O*]bis(triphenylphosphine)ruthenium(II) (**3**; (lig)Ru(PPh$_3$)$_2$; 500 mg, 4.51 × 10^{-4} mol) in dichloromethane (60 mL) at −35 °C. The reaction mixture turned from brown-red to dark red with vigorous gas development and was stirred for 5 min. All volatiles were removed in vacuo to give a dark red solid, which was washed with pentane. The resulting brown-red solid was dried in vacuo. The crude material consists of two isomers, which coordinate to the ruthenium in an O∧N∧O and O∧N∧N fashion, respectively. The O∧N∧O isomer was isolated by crystallization from a dichloromethane solution by pentane diffusion at −35 °C to yield the product as dark red crystals suitable for X-ray crystallography. The O∧N∧N isomer **4b** was isolated from a toluene solution by pentane diffusion at room temperature. Yield: 382 mg, 91%, Anal. Calcd for $C_{56}H_{58}N_3O_2PRu$ (mol wt 937.09): C, 71.77; H, 6.24; N, 4.49. Found: C, 71.76; H, 5.98; N, 3.89. O∧N∧O isomer: ^{1}H NMR (benzene-d_6, 298 K) δ 18.21 (d, 1H, $^3J_{HP}$ = 27.3 Hz, =HPh), 7.85, 7.53, 7.16, 6.98, 6.86, 6.77 (29H, H Ph), 3.47 (br m, 1H, CH), 3.34 (br m, 2H, CH), 3.01 (br m, 1H, CH), 1.23 (br s, 12H, CH$_3$), 1.12 (br s, 12H, CH$_3$); ^{31}P{^{1}H} NMR (benzene-d_6, 298 K, relative to H$_3$PO$_4$) δ 49.2 ($\nu_{1/2}$ = 11.9 Hz). O∧N∧N isomer: ^{1}H NMR (benzene-d_6, 298 K) δ 18.24 (d, 1H, $^3J_{HP}$ = 28.6 Hz, =*H*Ph), 7.82, 7.80, 7.11, 6.90, 6.86 (29H, H Ph), 3.56 (sep., 1H, $^3J_{HH}$ = 6.8 Hz, CH), 3.26 (br sep, 1H, $^3J_{HH}$ = 6.4 Hz, CH), 2.95 (br sep, 1H, $^3J_{HH}$ = 6.4 Hz, CH), 2.32 (sep, 1H, $^3J_{HH}$ = 6.8 Hz, CH), 1.27 (m, 15H, CH$_3$), 1.08 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH$_3$), 0.51 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH$_3$), 0.15 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH$_3$); ^{31}P{^{1}H} NMR (benzene-d_6, 298 K, relative to H$_3$PO$_4$) δ 38.2 ($\nu_{1/2}$ = 2.4 Hz).

X-ray crystal structure analysis of **4a** (O∧N∧O): formula $C_{61.5}H_{71}ClN_3O_2PRu$, M_r = 1051.70, dark red crystals, 0.18 × 0.15 × 0.08 mm, a = 14.9888(14) Å, b = 16.3811(15) Å, c = 13.3971(12) Å, α = 101.828(2)°, β = 112.436(2)°, γ = 105.383(2)°, V = 2753.0(4) Å^3, ρ_{calcd} = 1.269 g cm^{-3}, μ = 0.407 mm^{-1}, Z = 2, triclinic, space group $P\bar{1}$, λ = 0.710 73 Å, T = 117(1) K, 16 969 reflections collected, 9573 independent (R_{int} = 0.0192) ($I > 2\sigma(I)$), 651 refined parameters, R1 = 0.0464, wR2 = 0.1159, hydrogen atom of the carbene ligand located from the difference map, other hydrogen atoms added to calculated positions.

X-ray crystal structure analysis of **4b** (O∧N∧N): formula $C_{61}H_{70}N_3O_2PRu$, M_r = 1009.24, dark red crystals, 0.2 × 0.2 × 0.1 mm, a = 13.3875(11) Å, b = 29.217(2) Å, c = 14.0010(12) Å, α = 90°, β = 97.765(3)°, γ = 90°, V = 2753.0(4) Å^3, ρ_{calcd} = 1.269 g cm^{-3}, μ = 0.407 mm^{-1}, Z = 2, triclinic, space group $P\bar{1}$, λ = 0.710 73 Å, T = 117(1) K, 35 017 reflections collected, 11 945 independent ($I > 2\sigma(I)$), 639 refined parameters, R1 = 0.0643, wR2 = 0.1420, hydrogen atom of the carbene ligand located from the difference map, other hydrogen atoms added to calculated positions.

(Benzylidene)(tricyclohexylphosphine)[*N,N′*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3*O,N,O*]-ruthenium(II) (5; (lig)Ru(PCy$_3$)=CHPh). Dipotassium *N,N′*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamidate (**2**; 227 mg, 4.05 × 10^{-4} mol) and (benzylidene)bis(tricyclohexylphosphine)ruthenium(II) dichloride (333 mg, 4.05 × 10^{-4} mol) were added in dichloromethane (50 mL) at room temperature and stirred overnight. All volatiles were removed under vacuum, and the residue was dissolved in toluene and filtered over Celite. Toluene was removed under vacuum, and the crude material was triturated with pentane overnight. The product was isolated as a brown powder by filtration and dried under vacuum. Temperature-dependent ^{1}H NMR spectroscopy showed limited reversible isomerization. Yield: 355 mg, 93%. Anal. Calcd for $C_{56}H_{76}N_3O_2PRu$ (mol wt 944.14): C, 71.24; H, 8.11; N, 4.45. Found: C, 70.10; H, 7.96; N, 3.34. ^{1}H NMR (benzene-d_6, 298 K): δ 20.62 (s, 1H, =C*H*Ph), 8.73, 7.80−6.40 (14H, H Ph), 3.8−2.8 (m, 4H, CH), 2.88 (br t, 33H, PCy), 1.97 (d, 3H, $^3J_{HH}$ = 11.8 Hz, CH$_3$), 1.68 (d, 3H, $^3J_{HH}$ = 11.8 Hz, CH$_3$), 1.61 (d, 3H, $^3J_{HH}$ = 11.8 Hz, CH$_3$), 1.57 (d, 3H, $^3J_{HH}$ = 11.8 Hz, CH$_3$), 1.23 (m, 12 H, CH$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 298 K): δ 295.4 (=*C*HPh), 163.1, 153.7, 150.0, 147.5, 146.9, 139.9, 138.6, 132.4, 131.8, 129.7, 129.6, 126.1, 124.2, 36.4, 35.9, 32.8, 32.0, 30.5, 29.9, 29.3, 28.5, 27.3, 25.9, 25.2, 24.5, 24.2, 23.1, 22.7, 14.6. ^{31}P{^{1}H} NMR (benzene-d_6, 298 K, relative to H$_3$PO$_4$): δ 34.6 ($\nu_{1/2}$ = 7 Hz).

Potassium [*N,N′*-Bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3*N,N,N*]nickel(II) Chloride−Tris(tetrahydrofuran) (6; (lig)NiKCl). A slurry of nickel dichloride−dimethoxyethane (39 mg, 1.78 × 10^{-4} mol) in THF (4 mL) was added to dipotassium *N,N′*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamidate (**2**; 100 mg, 1.78 × 10^{-4} mol) in THF (10 mL). The reaction mixture turned red instantaneously and was stirred for 3 h. The product was filtered and dried under vacuum, to give an orange powder. NMR spectroscopic characterization was limited, due to low solubility of the product. Single crystals were obtained by dissolving the product in hot THF and slowly cooling it to room temperature. Yield: 123 mg, 83%. Anal. Calcd for $C_{31}H_{37}ClKN_3NiO_2$ (mol wt 616.87): C, 60.35; H, 6.05; N, 6.81. Found: C, 58.82; H, 5.75; N, 6.06. ^{1}H NMR (benzene-d_6, 298 K): δ 8.05 (t, 1H, $^3J_{HH}$ = 7.7 Hz, Ph−pyr), 7.61 (d, 2H, $^3J_{HH}$ = 7.7 Hz, Ph−pyr), 7.04 (m, 6 H, Ph), 4.16 (sep, 4H, $^3J_{HH}$ = 6.8 Hz, CH), 3.66 (m, 12H, THF), 1.80 (m, 12H, THF), 1.41 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH$_3$), 1.38 (br s, 6H, CH$_3$), 1.17 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH$_3$), 1.10 (br s, 6H, CH$_3$).

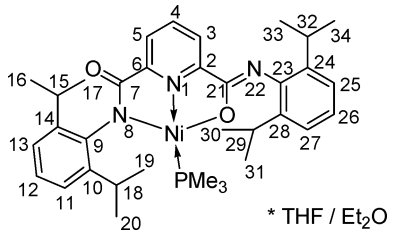
X-ray crystal structure analysis of **6**: formula $C_{43}H_{61}ClKN_3NiO_5$, M_r = 833.21, red crystals, 0.22 × 0.10 × 0.08 mm, a = 21.067(6) Å, b = 11.926(4) Å, c = 19.209(6) Å, α = 90°, β = 115.991(6)°, γ = 90°, V = 4338(2) Å^3, ρ_{calcd} = 1.276 Mg m^{-3}, μ = 0.650 mm^{-1}, Z = 4, monoclinic, space group $P2_1/c$, λ = 0.710 73 Å, T = 150 K, 17 663 reflections collected, 5671

independent (R(int) = 0.0814), 474 refined parameters, R1 = 0.0579, wR2 = 0.1416, hydrogen atoms added to calculated positions.

[*N,N′*-Bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3*N,N,N*]nickel(II)−Bis(potassium chloride) (L = H_2O (7), MeOH (8); (lig)NiL). Dipotassium *N,N′*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamidate (**2**; 300 mg, 5.34×10^{-4} mol) and nickel dichloride−dimethoxyethane (117 mg, 5.34×10^{-4} mol) were added in THF (40 mL). The reaction mixture turned into a red suspension and was heated to 80 °C for 5 days. The red suspension was isolated by filtration and the solid washed with toluene and pentane and dried under vacuum to give the product as an orange powder. Red single crystals were obtained by crystallization from wet hexane or slow evaporation of methanol. Yield: 334 mg, 91%. Anal. Calcd for $C_{31}H_{37}Cl_2K_2N_3NiO_2 \cdot H_2O$ (mol wt 667.41): C, 52.48; H, 5.54; N, 5.92. Found: C, 52.44; H, 5.41; N, 4.61.

X-ray crystal structure analysis of **7**: formula $C_{67}H_{91}Cl_3N_6Ni_2O_{10}$, M = 1364.23, red crystals 0.2 × 0.15 × 0.06 mm, a = 18.606(4) Å, b = 15.396(3) Å, c = 26.072(6) Å, α = 90°, β = 106.239(4)°, γ = 90°, V = 7170(3) Å^3, ρ_{calcd} = 1.264 Mg m^{-3}, μ = 0.694 mm^{-1}, Z = 4, monoclinic, space group $P2_1/n$, λ = 0.710 73 Å, T = 117(1) K, 23 332 reflections collected, 9645 independent (R(int) = 0.0496), 811 refined parameters, R1 = 0.0868, wR2 = 0.2369, hydrogen atoms added to calculated positions.

[*N,N′*-Bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3*O,N,N′*](trimethylphosphine)nickel(II) (9; (lig)NiPMe$_3$). Dipotassium *N,N′*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamidate (**2**; 500 mg, 1.78×10^{-3} mol), $NiCl_2$ (115 mg, 1.78×10^{-3} mol), and trimethylphosphine (68 mg, 1.78×10^{-3} mol) were added in diethyl ether/THF (1:1) or THF only (100 mL). The yellow suspension turned orange and was stirred for two nights. The suspension was filtered to give a red solution. All volatiles were evaporated under vacuum to give the product as a red powder. A THF/Et_2O solution was cooled to −35 °C to give red crystals overnight, suitable for X-ray crystal structure analysis. Alternatively, monocrystalline material can be obtained from a toluene solution at −35 °C. Yield: 510 mg, 93%. Anal. Calcd for $C_{34}H_{46}N_3NiO_2P$ (mol wt 618.39): C, 66.03; H, 7.50; N, 6.80. Found: C, 64.89; H, 7.51; N, 6.22. ^{1}H NMR (benzene-d_6, 298 K): δ 7.61 (d, 1H, H-5), 7.49 (d, 1H, H-3), 7.22 (d, 1H, Ph-25, Ph-27), 7.13 (m, 1H, Ph-26), 7.05 (m, 1H, Ph-12), 6.97 (d, 2H, Ph-11, Ph-13), 6.84 (dd, 1H, H-4), 3.84 (sept., 2H, $^3J_{iPr}$ = 6.95 Hz, CH-15, CH-18), 3.30 (sept., 2H, $^3J_{iPr}$ = 6.95 Hz, CH-29, CH-32), 1.34 (d, 12H, $^3J_{iPr}$ = 6.95 Hz, CH_3-30, CH_3-31, CH_3-33, CH_3-34), 1.29 (d, 6H, $^3J_{iPr}$ = 6.95 Hz, CH_3-16/19), 1.27 (d, 6H, $^3J_{iPr}$ = 6.95 Hz, CH_3-17/20), 0.27 (d, 9H, $^1J_{HP}$ = 10.53 Hz, PMe_3). ^{13}C{^{1}H} NMR (benzene-d_6, 298 K): δ 153.5 (C-6), 149.1 (C-2), 145.6 (C-23), 145.0, 144.9 (C-10, C-14), 140.2 (C-4), 139.3, 138.3 (C-24, C-28), 125.5 (C Ph-12), 123.6 (C-5), 123.4 (C Ph-11, C Ph-13), 123.1 (C Ph-26), 122.9 (C-3), 122.5 (C Ph-25, C Ph-27), 29.4 (CH-15, CH-18), 29.1 (CH-29, CH-32), 25.6, 24.9 (CH_3-16/17), 23.6 (CH_3-30, CH_3-31, CH_3-33, CH_3-34), 23.1 (CH_3-19/20), 10.0 (d, $P(CH_3)_3$). C-7/9/21 were not identified. Some additional signals may be due to isomers. ^{31}P{^{1}H} NMR (benzene-d_6, 298 K, relative to H_3PO_4): δ −10.0 ($\nu_{1/2}$ = 2.0 Hz).



X-ray crystal structure analysis of **9**: formula $C_{42}H_{64}N_3NiO_4P$, M_r = 764.64, red crystals, 0.32 × 0.24 × 0.20 mm, a = 10.306(2) Å, b = 29.396(6) Å, c = 16.036(4) Å, α = 90°, β = 100.884(4)°, γ = 90°, V = 4770.7(19) Å^3, ρ_{calcd} = 1.065 Mg m^{-3}, μ = 0.477 mm^{-1}, Z = 4, monoclinic, space group $P2_1/n$, λ = 0.717 03 Å, T = 150 K, 19 124 reflections collected, 5841 independent ($I > 2\sigma(I)$), 450 refined parameters, R1 = 0.0960, wR2 = 0.2805, hydrogen atoms added to calculated positions.

(Benzylidene)(trimethylphosphine)[*N,N′*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3*O,N,O/N*]-nickel(II) (10; (lig)Ni(PMe$_3$)=CHPh). *N,N′*-Bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido-κ^3*O,N,N*](trimethylphosphine)nickel(II) (**6**; 86 mg, 1.39×10^{-4} mol) and phenyldiazomethane (33 mg, 2.78×10^{-4} mol) were added in dichloromethane (15 mL) at −35 °C. The red reaction mixture was stirred for 5 min, and all volatiles were removed under vacuum. The crude material was triturated with pentane overnight and the product isolated by filtration as an orange powder, which was dried under vacuum. The product consists of two isomers in a ratio of 3:7. Yield: 91 mg, 92%. ^{1}H NMR (dichloromethane-d_2, 298 K): δ 12.74 (d, 1H, $^3J_{HP}$ = 1.9 Hz, =CHPh), 11.08 (d, 1H, $^3J_{HP}$ = 2.7 Hz, =CHPh), 8.16−6.79 (m, 28 H, H Ph), 4.91 (sep, 1H, $^3J_{HH}$ = 6.8 Hz, CH-b), 3.88 (br sep., 2H, CH-a), 3.66 (sep., 1H, $^3J_{HH}$ = 6.8 Hz, CH-b), 3.55 (sep, 1H, $^3J_{HH}$ = 6.8 Hz, CH-b), 3.07 (sep, 1H, $^3J_{HH}$ = 6.8 Hz, CH-b), 2.95 (br sep, 2H, $^3J_{HH}$ = 6.8 Hz, CH-a), 1.61 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3-b), 1.49 (d, 9H, $^3J_{HH}$ = 13.0 Hz, PMe_3), 1.39 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3-b), 1.16−1.02 (m, 36 H, CH_3-a/-b), 0.94 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3-b), 0.79 (d, 9H, $^3J_{HH}$ = 13.0 Hz, PMe_3), 0.64 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3-b). ^{31}P{^{1}H} NMR (benzene-d_6, 298 K, relative to H_3PO_4): δ 47.2 ($\nu_{1/2}$ = 3.2 Hz), 44.5 ($\nu_{1/2}$ = 2.8 Hz).

Ring-Closing Metathesis: General Procedure. The appropriate catalyst ((4.75−4.90) × 10^{-6} mol) was dissolved in deuterated benzene (800 μL, 6 mM) or toluene (3 mL, 1.6 mM), and 1,7-octadiene (9.50×10^{-5} mol) was added. The reaction mixture was stirred at room temperature or 80 °C and monitored by ^{1}H NMR spectroscopy or GC.

Acknowledgment. Financial support from the DOE (Grant No. DE-FG03098ER 14910) is gratefully acknowledged by J.C.W. We thank Professor Guillermo C. Bazan for his support and for many helpful discussions.

Supporting Information Available: Text giving additional spectroscopic data and details of the catalytic reactions and tables giving additional information about the X-ray crystal structure analyses; X-ray data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0501780