$RuCl_2[(2,6\text{-}Me_2C_6H_3)PPh_2]_2$: A New Precursor for Cyclometalated Ruthenium(II) Complexes

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Received July 30, 2004

The five-coordinate complex $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)(L^*)$ (**2**; $L^* = (2,6\text{-}Me_2C_6H_3)PPh_2$) was prepared in high yield by reaction of the 14-electron complex $RuCl_2(L^*)_2$ (**1**) with formaldehyde in the presence of NEt_3 via cyclometalation of an ortho methyl group and aldehyde decarbonylation. Alternatively, **2** can be obtained from $RuCl_3$ hydrate, L^*, H_2CO, and amine in a one-pot reaction. Treatment of **2** with CO affords the *cis*-dicarbonyl derivative $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)_2(L^*)$ (**3**), whereas reaction with phosphines leads to the five- and six-coordinate complexes $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)(L)_n$ ($n = 1$, $L = PCy_3$ (**4**), $Ph_2P(CH_2)_3PPh_2$ (**6**); $n = 2$, $L = PMePh_2$ (**5**)) by displacement of L^*, according to the steric requirement of the incoming ligand. Similarly, complex **2** reacts with the bidentate nitrogen ligands 2-(aminomethyl)pyridine and ethylenediamine, affording the six-coordinate derivatives $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)(L)$ (L = 2-(aminomethyl)pyridine (**7**), ethylenediamine (**8**)) in high yield. The related iodide derivative $RuI\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)(L^*)$ (**9**) has been prepared from **2** and NaI by chloride displacement. Treatment of **2** with $Na[BAr^f_4]$ in the presence of 2,2′-bipyridine or 2-(aminomethyl)pyridine gives the cationic complexes $[Ru\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)(L^*)(L)][BAr^f_4]$ (L = 2,2′-bipyridine (**10**), 2-(aminomethyl)pyridine (**11**)), while with 3 equiv of pyridine the derivative $[Ru\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)(Py)_3][BAr^f_4]$ (**12**) is obtained. The structure of the δ-agostic complex **2** has been established through an X-ray crystal study, whereas the structure for **7** is supported by 2D NMR experiments in solution. Complexes **7** and **8** are active catalysts for transfer hydrogenation of ketones in 2-propanol, displaying TOF values up to 63 000 h^{-1}.

Introduction

During the past decade the synthesis and reactivity of transition-metal complexes containing bidentate PC or terdentate PCP phosphine ligands have been the subject of increasing research.[1] The formation of five-membered metallacycles represents a prerequisite for obtaining electron-rich metal centers displaying a stable metal−carbon σ bond. In particular, terdentate PCP pincer complexes of Ru, Rh, Ir, Ni, Pd, and Pt have been used as highly efficient reagents and catalysts for a variety of organic transformations, such as allylation of aldehydes, atom-transfer radical polymerization (ATRP), dehydrogenation of alkanes, Heck olefin arylation, and Suzuki coupling of aryl boronic acids with aryl bromides.[1,2] Thus, PCP ruthenium complexes[3] have been found to efficiently catalyze the reduction of ketones via transfer hydrogenation, as reported by van Koten and co-workers.[4] On the other hand, although a large number of transition-metal bidentate PC phosphine complexes have been described,[5] only a few systems have found application in catalysis, the cyclometalated palladium complexes being the well-known efficient catalysts for the Heck reaction.[6] Despite the fact that ruthenium has been widely employed in homogeneous catalysis,[7] and its importance for organic

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(1) (a) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (b) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837. (c) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

(2) (a) Motoyama, Y.; Narusawa, H.; Nishiyama, H. *Chem. Commun.* **1999**, 131. (b) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840. (c) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086. (d) Grove, D. M.; Verschuuren, A. H. M.; van Koten, G.; van Beek, J. A. M. *J. Organomet. Chem.* **1989**, *372*, C1. (e) Granel, C.; Dubois, P.; Jérôme, R.; Teyssié, P. *Macromolecules* **1996**, *29*, 8576. (f) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687. (g) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379. (h) Gruber, A. S.; Zim. D.; Ebeling, G.; Monteiro, A. L.; Dupont, J. *Org. Lett.* **2000**, *2*, 1287. (i) Gibson, S.; Foster, D. F.; Eastham, G. R.; Tooze, R. P.; Cole-Hamilton, D. J. *Chem. Commun.* **2001**, 779. (j) Bedford, R. B.; Draper, S. M.; Scully, P. N.; Welch, S. L. *New J. Chem.* **2000**, *24*, 745.

(3) (a) Karlen, T.; Dani, P.; Grove, D. M.; Steenwinkel, P.; van Koten, G. *Organometallics* **1996**, *15*, 5687. (b) Jia, G.; Lee, H. M.; Xia, H. P.; Williams, I. D. *Organometallics* **1996**, *15*, 5453. (c) van der Boom, M. E.; Kraatz, H. B.; Hassner, L.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 3873. (d) Gusev, D. G.; Madott, M.; Dolgushin, F. M.; Lyssenko, K. A.; Antipin, M. Y. *Organometallics* **2000**, *19*, 1734.

(4) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 743.

(5) (a) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (b) Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235.

10.1021/om049408l CCC: $27.50
Publication on Web 11/16/2004

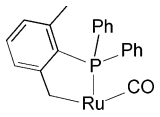


Figure 1.

synthesis has now been elevated to the same level as palladium, only a few examples of application of ruthenium PC phosphine derivatives in catalysis have been reported: i.e. olefin hydrogenation.[8] It is noteworthy that cyclometalated NC ruthenium complexes have been found to catalyze dihydrogen reduction and reductive N-carbonylation of nitroaromatics[9] and to mediate electron-transfer reactions,[10] whereas ortho-metalated OC ruthenium compounds are regarded as key species for the coupling of olefins to functional arenes (Murai's reaction).[11] Therefore, the search for new cyclometalated ruthenium complexes capable of efficiently promoting catalytic reactions is a target of primary importance.

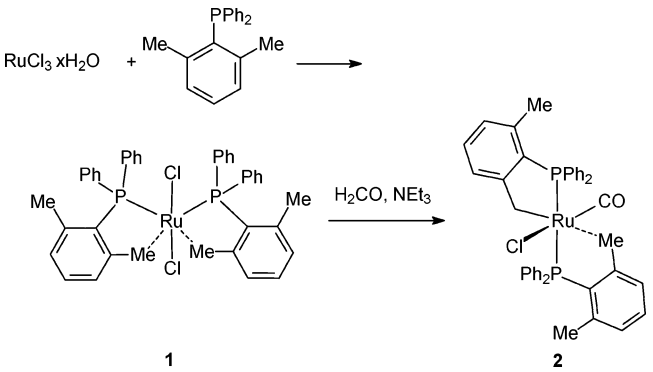
We have been recently interested in the coordination chemistry of complexes containing arylphosphines with methyl groups in the ortho position, and we pointed out that (2,6-$Me_2C_6H_3$)PPh_2 (L*) is a suitable ligand for the isolation of a rare example of the 14-electron ruthenium compound $RuCl_2(L^*)_2$ (**1**),[12a] stabilized by two nonclassical (M···η^3-H_2C) agostic interactions[12b] of the *o*-methyl groups. Since *o*-methylated phosphines of this type easily afford cyclometalation with formation of strong M−C σ-bond complexes,[13] we decided to investigate the use of **1** as a starting material for the preparation of cyclometalated ruthenium complexes. As an extension of a previous communication,[14] we describe herein the synthesis and characterization of a new class of PC ruthenium complexes of the general formula $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)(L)_n$ (n = 1, 2; L = ligands with phosphorus or nitrogen donor atoms), characterized by the robust basic structural unit reported in Figure 1.

Among these derivatives, those containing bidentate nitrogen ligands have been found to be highly efficient catalysts for transfer hydrogenation of ketones,[15] showing TOF values up to 63 000 h^{-1}.[14]

Results and Discussion

It is well-known that arylphosphines containing methyl groups in an ortho position can give C−H activation under mild conditions with formation of a stable five-membered cycle. This process can be facilitated by the presence of hydrido or alkyl ligands at the metal center or using metal halogenide precursors with addition of a base.

Scheme 1



The 14-electron complex **1**, obtained from ruthenium trichloride hydrate and the phosphine L*, reacts in ethanol with formaldehyde and NEt_3 to give the five-coordinate complex **2** (Scheme 1).

In this reaction one δ-agostic *o*-methyl group in **1** easily undergoes cyclometalation via elimination of HCl promoted by triethylamine, whereas a CO ligand is formed from formaldehyde through dihydrogen extrusion. A straightforward one-pot synthesis of **2** can be achieved through in situ formation of **1** from $RuCl_3$ hydrate and phosphine, according to Scheme 1. It is noteworthy that the monocarbonyl derivative $RuHCl(CO)(P^iPr_3)_2$ can be obtained from $[RuHCl(P^iPr_3)_2]_2$ via decarbonylation of aldehydes, as reported by Caulton and co-workers.[16] The thermally stable complex **2** can be kept in air for long periods without appreciable decomposition, but it is relatively air sensitive in solution. The IR spectrum of **2** displays a ν_{CO} stretching band at 1923 cm^{-1}, in the range of related ruthenium(II) carbonyl derivatives.[17] In the ^1H NMR spectrum the doublet at δ 3.48 and the doublet of doublets at 3.29 (J(HH) = 13.4 Hz and J(HP) = 5.4 Hz) are for the nonequivalent geminal CH_2 protons. The variable-temperature NMR spectra in the range from 20 to −90 °C show a single resonance at δ 1.60 (in CD_2Cl_2) for two *o*-methyl groups. Unlike **1**, which shows two signals at room temperature with a coalescence temperature of 35 °C ($CDCl_3$),[12b] complex **2** reveals a low barrier of rotation for the xylyl group along the P−C bond, which can be ascribed to the high trans influence of the alkyl group. As for **1**[12] and other related T-shaped 14-electron platinum(II) complexes $[Pt(P-C)\{(2,6\text{-}Me_2C_6H_3)PR_2\}]^+$ (P−C = $(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PR_2$; R = Ph, Cy),[13c] the

(6) (a) Böhm, V. P. W.; Herrmann, W. A. *Chem. Eur. J.* **2001**, *7*, 4191. (b) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917. (c) Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23. (d) Herrmann, W. A.; Brossmer, C.; Reisinger, C.-P.; Riermeier, T. H.; Öfele, K.; Beller, M. *Chem. Eur. J.* **1997**, *3*, 1357.
(7) Naota, T.; Takaya, H.; Murahashi, S.-I. *Chem. Rev.* **1998**, *98*, 2599.
(8) (a) Lewis, L. N. *J. Am. Chem. Soc.* **1986**, *108*, 743. (b) Lewis, L. N.; Smith, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 2728.
(9) (a) Mukherjee, D. K.; Palit, B. K.; Saha, C. R. *J. Mol. Catal.* **1994**, *88*, 57. (b) Mukherjee, D. K.; Palit, B. K.; Saha, C. R. *J. Mol. Catal.* **1994**, *91*, 19.
(10) Ryabov, A. D.; Sukharev, V. S.; Alexandrova, L.; Le Lagadec, R. Pfeffer, M. *Inorg. Chem.* **2001**, *40*, 6529.
(11) (a) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529. (b) Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N.; Murai, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62. (c) Hiraki, K.; Ishimoto, T.; Kawano, H. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2099.
(12) (a) Baratta, W.; Herdtweck, E.; Rigo, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1629. (b) Baratta, W.; Mealli, C.; Herdtweck, E.; Ienco, A.; Mason, S. A.; Rigo, P. *J. Am. Chem. Soc.* **2004**, *126*, 5549.
(13) (a) Baratta, W.; Del Zotto, A.; Herdtweck, E.; Vuano, S.; Rigo, P. *J. Organomet. Chem.* **2001**, *617*−*618*, 511. (b) Baratta, W.; Herdtweck, E.; Martinuzzi, P.; Rigo, P. *Organometallics* **2001**, *20*, 305. (c) Baratta, W.; Stoccoro, S.; Doppiu, A.; Herdtweck, E.; Zucca, A.; Rigo, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 105.
(14) Baratta, W.; Da Ros, P.; Del Zotto, A.; Sechi, A.; Zangrando, E.; Rigo, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3584.
(15) (a) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97. (c) Bäckvall, J. E. *J. Organomet. Chem.* **2002**, *652*, 105. (d) Gladiali, S.; Mestroni G. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, p 97.
(16) Coalter, J. N., III; Huffman, J. C.; Caulton, K. G. *Organometallics* **2000**, *19*, 3569.
(17) Seddon, E. A.; Seddon, K. R. In *The Chemistry of Ruthenium*; Clark, R. J. H., Ed.; Elsevier: Amsterdam, 1984; Chapter 9.

Table 1. Crystallographic Data for 2

chem formula	$C_{41}H_{37}ClOP_2Ru$
fw	744.17
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
a (Å)	9.502(3)
b (Å)	9.974(3)
c (Å)	19.771(6)
β (deg)	111.98(2)
V (Å^3)	1737.5(9)
Z	2
T (K)	150
ρ_{calcd} (g cm^{-3})	1.422
μ (mm^{-1})	0.652
F_{000}	764
θ range (deg)	2.16−29.94
data collcd (h, k, l)	±13, ±13, ±27
no. of rflns collcd	9754
no. of indep rflns/R_{int}	9401/0.0393
no. of obsd rflns ($I > 2\sigma(I)$)	6481
no. of params refined	412
Flack param	0.30(8)
R1 ($I > 2\sigma(I)$)[a]	0.0497
wR2[a]	0.1454
GOF (obsd)	1.045
max/min $\Delta\rho$ (e Å^{-3})	0.691/ −0.821

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2

Ru−C(1)	1.780(9)	Ru−P(2)	2.349(3)
Ru−C(2)	2.043(8)	Ru−Cl(1)	2.525(4)
Ru−P(1)	2.351(3)	Ru−C(10)	2.765(10)
C(1)−Ru−C(2)	90.2(4)	C(2)−Ru−C(10)	168.7(3)
C(1)−Ru−P(1)	87.0(2)	P(1)−Ru−P(2)	179.83(15)
C(1)−Ru−P(2)	93.0(2)	P(1)−Ru−Cl(1)	89.41(11)
C(1)−Ru−Cl(1)	176.1(3)	P(1)−Ru−C(10)	73.9(3)
C(1)−Ru−C(10)	87.2(4)	P(2)−Ru−Cl(1)	90.62(12)
C(2)−Ru−P(1)	95.1(2)	P(2)−Ru−C(10)	106.3(3)
C(2)−Ru−P(2)	84.8(2)	Cl(1)−Ru−C(10)	90.34(3)
C(2)−Ru−Cl(1)	91.7(3)	Ru−C(10)−C(11)	111.0(6)

$^{13}C\{^1H\}$ NMR signal for the *o*-methyl groups of **2** is shifted upfield (δ 18.4) compared to free phosphine (δ 23.0), in agreement with a time-averaged agostic interaction.

The molecular structure of **2** was confirmed by X-ray analysis carried out on a single crystal. Crystallographic data are summarized in Table 1, and selected bond distances and angles are reported in Table 2. Figure 2 shows an ORTEP plot of the molecular structure of **2**. The ruthenium complex displays a distorted-octahedral geometry with two trans phosphorus atoms, whereas the chloride and the carbonyl group are cis to the alkyl ligand, which shows a rather short Ru−C2 bond length (2.043(8) Å). The sixth coordination site is completed by a xylyl methyl group, with the C10 atom at 2.765(10) Å from the metal, a distance slightly longer compared to that of **1** (mean value 2.651(1) Å). The deviation of C10 from the Ru,P1,C2,P2 plane is small ($\Delta = 0.10(2)$ Å), whereas the C2−Ru···C10 angle slightly deviates from linearity (168.7(3)°). Similarly to **1**, in complex **2** the Ru−P1−C12 angle of the xylyl ring (112.1(4)°) is not significantly affected by the δ-agostic interaction and it is close to that of the phenyl substituents (113.3(3), 114.2(4)°). This result strongly differs from that for the cation $[Ru(CO)(P^tBu_2Me)_2(\eta^2\text{-}Me_3SiCH{=}CHC{=}CHSiMe_3)]^+$,[18] where the angle involved in the γ-agostic interaction is as small as 99°. The phosphine arrangement in **2** resembles that of the T-shaped platinum(II) species $[Pt(P-C)\{(2,6\text{-}Me_2C_6H_3)PCy_2\}]^+$, for which a short agostic metal···C distance has been observed.[13c] Note that Ru(Ph)Cl(CO)$(P^tBu_2Me)_2$[19] and Ru(p-tolyl)Cl(CO)$(PPh_3)_2$[20] show a structure similar to **2**, but with no or very weak agostic interactions to the site trans to the Ru−aryl group, and they differ from the distorted-trigonal-bipyramidal arrangement found in Ru(*o*-tolyl)Cl(CO)$(PPh_3)_2$,[20] $Ru(COCH_2CH_3)Cl(CO)(PPh_3)_2$,[21] and Ru[C(=CH^{t}Bu)-C≡C^{t}Bu]Cl(CO)$(PPh_3)_2$.[22]

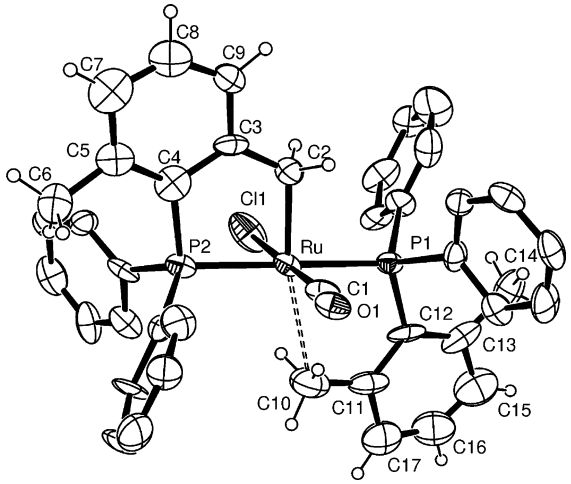


Figure 2. ORTEP drawing of complex **2**, using thermal ellipsoids at the 40% probability level.

The hydrogen atoms of the agostic methyl have been located by refining the torsion angle that maximizes the electron density of the group. Similarly to the δ-agostic **1** and the cationic T-shaped Pt(II) complexes, two hydrogens lie closer to the metal with two different ruthenium···hydrogen distances (2.31, 2.41 Å) and are off the plane Ru,P1,C2,P2, affording the agostic interaction mode M···η^3-H_2C. Complex **2** presents a Ru···C10−C11 angle of 111.0(6)° with a Ru···C11−C10−H (where H is the closest H to ruthenium) torsion angle of 56.6°, in agreement with other δ-agostic complexes, which significantly differ from β- and γ-agostic ones.[12b] Therefore, the agostic interaction in **2** is better regarded as a nonclassical M···η^3-H_2C mode, instead of dihapto M···η^2-HC bonding.[23] The relatively long agostic Ru···C distance for **2**, associated with the short trans Ru−C2 length, and the low barrier of rotation of the xylyl suggest a weaker δ-agostic interaction for **2**, compared to **1**, according to a trans labilization promoted by the alkyl group.

Neutral Complexes. Compound **2** presents a rich reactivity leading to new cyclometalated ruthenium(II)

(18) Huang, D.; Olivan, M.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 4700.

(19) Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087.

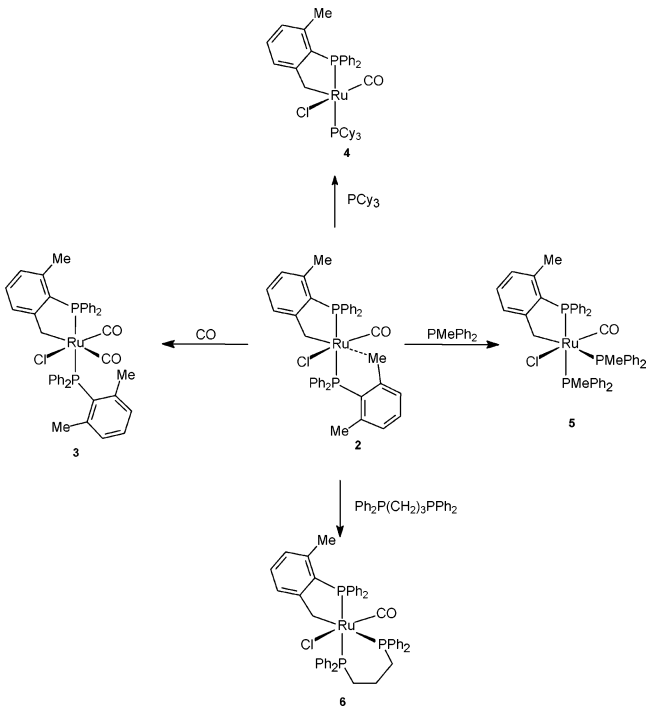
(20) Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1990**, *389*, 375.

(21) Fabre, S.; Kalck, P.; Lavigne, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1092.

(22) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604.

(23) (a) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (c) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (d) Yao, W.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, *254*, 105. (e) Ogasawara, M.; Saburi, M. *Organometallics* **1994**, *13*, 1911.

Scheme 2



complexes by chloride exchange, coordination of ligands to the empty vacant site, or displacement of the bulky phosphine L*, allowing a potential fine-tuning of the reactivity of the complex, including stereochemical information. Thus, reaction of **2** with carbon monoxide (1 atm) at room temperature affords quickly and quantitatively the dicarbonyl derivative **3** (Scheme 2), whereas with monodentate phosphines the substitution of L* leads to the formation of five- or six-coordinate complexes, according to the steric properties of the incoming ligand. With bidentate phosphorus or nitrogen ligands six-coordinate compounds are obtained.

The ^{31}P NMR spectrum of **3** shows two doublets at δ 54.8 and 25.6 with a J(PP) coupling constant of 292 Hz, which is consistent with two trans P phosphorus atoms, whereas the IR spectrum of **3** exhibits two carbonyl stretching bands at 2020 and 1957 cm^{-1} attributable to two cis CO ligands.

Displacement of L* in **2** occurs easily with phosphines displaying higher basicity or smaller cone angle than L*, as well as with bidentate phosphines. Reaction of **2** with PCy_3 in dichloromethane promptly affords the five-coordinate complex **4**, which presents two trans phosphine ligands (J(PP) = 290 Hz) (Scheme 2). The ν_{CO} stretching band is at 1917 cm^{-1}, in agreement with the higher basicity of PCy_3 compared to L*. Complex **5** has been obtained in CH_2Cl_2 at room temperature by treatment of **2** with 2 equiv of PPh_2Me (Scheme 2), and its molecular structure has been confirmed by an X-ray diffraction study.[14] The ^{31}P NMR spectrum shows a typical meridional arrangement for the RuP_3 core with a large J(PP) (298 Hz) and two small J(PP) coupling constants (16.6 and 17.1 Hz). In the IR spectrum the ν_{CO} stretching band is at 1917 cm^{-1}, a lower value than **2** and consistent with the more basic metal center. These results clearly show that the steric properties of the phosphines play a fundamental role in the stabilization of five- (L* and PCy_3) vs six-coordinate complexes ($PMePh_2$). Reaction of **2** with the bidentate phosphine $Ph_2P(CH_2)_3PPh_2$ affords the 18-electron derivative **6**, by displacement of L*. The ^{31}P NMR spectrum of **6** shows a large J(PP) value (282 Hz) and two small J(PP) coupling constants (29 and 20 Hz), consistent with a T-shaped RuP_3 core similar to that in **5**.

Compound **2** also reacts with bidentate nitrogen ligands, affording six-coordinate complexes. Thus, treatment of **2** in dichloromethane with 1 equiv of 2-(aminomethyl)pyridine gives **7**, which was isolated in high yield (Scheme 3).

Since no suitable crystals of **7** were obtained for X-ray measurements, the structure in solution was investigated through ^{1}H−^{1}H correlation 2D NMR experiments. The assignments listed in Table 3 were inferred from the scalar connectivity pattern of TOCSY and DQF-COSY spectra.

To prevent possible sensitivity limitations from weakness of dipolar correlations in the laboratory frame, ROESY experiments were performed for drawing structural conclusions. Examination of ROESY maps shows dipolar correlations between the protons of the $RuCH_2$ moiety and those of the pyridine ligand (Figure 3). In particular, the ortho proton of the pyridine ring at δ 8.95 shows NOEs with both hydrogens of the $RuCH_2$ moiety, with a stronger connectivity with the resonance at δ 2.88 and a weaker one with that at δ 2.09, corresponding to approximate internuclear separations (see Materials and Methods) of ∼3.6 and ∼5.2 Å, respectively. The $RuCH_2$ hydrogen nucleus responsible for the upfield resonance (δ 2.09) exhibits, in turn, a much stronger NOE with one hydrogen of the $RuNH_2$ group, namely the proton at δ 1.71 (∼2.3−2.7 Å) and a weaker one with the other proton at δ 2.98 (∼3.0−3.2 Å). Furthermore, the same nucleus (i.e. at δ 2.09) shows clear NOEs with the methylene protons next to NH_2, which appear at δ 3.91 and 4.28. The last two connectivities are consistent with distances of ∼2.6−3.0 and ∼3.1−3.6 Å, respectively. In addition, the downfield metal-coordinated NH_2 proton (δ 2.98), but not those of the pyridine ring, shows NOE with the phenyl hydrogens of the phosphine. Likewise, the *o*-methyl group exhibits NOEs to phenyl hydrogens of the phosphine but no connectivity with the pyridine ligand, as confirmed by high-sensitivity laboratory-frame selective 1D NOE experiments.

A fast H/D exchange of the NH_2 protons has been observed by addition of a D_2O solution of NaOH to **7** in $CDCl_3$, which results in the disappearance of the signals at δ 2.98 and 1.71. In the ^{13}C NMR spectrum of **7** the doublet at δ 48.8 (^3J(CP) = 2.9 Hz) is for the CH_2NH_2 group, only slightly shifted downfield compared to that of the pure ligand (δ 47.8), whereas the carbon atoms of the pyridine ligand appear as singlets. The carbonyl stretching absorption band for **7** is at 1912 cm^{-1}, and this low value agrees with the presence of a strong trans σ-donor ligand. It is noteworthy that the length of the nitrogen ligand backbone affects the stability of the corresponding complex. Thus, treatment of **2** with 2-(aminoethyl)pyridine instead of 2-(aminomethyl)pyridine in $CDCl_3$ leads to substitution of L* and formation of a mixture of two cyclometalated isomers in about 1:1 molar ratio, as shown by ^{31}P NMR spectroscopy (δ 73.4 and 68.8), and this ratio does not significantly change after several hours at 70 °C. Similarly to **7**, reaction of **2** with ethylenediamine results in the substitution of

Scheme 3

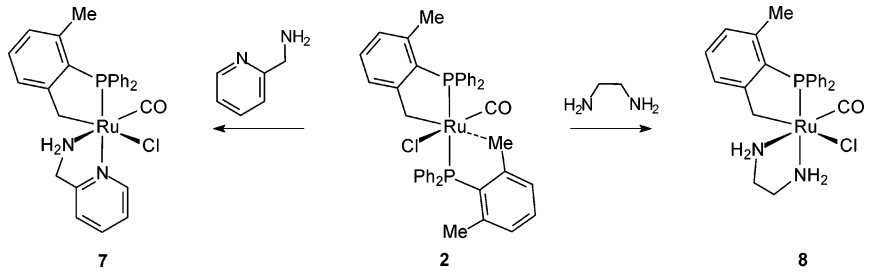


Table 3. ^{1}H NMR (500.2 MHz) Assignment List of 7 in $CDCl_3$ at 25 °C

group	δ (ppm)[a]	group	δ (ppm)[a]
$RuNH_2$	1.71; 2.98	Py H-5	7.18
$RuNCH_2$	3.91; 4.28	Py H-4	7.58
$RuCH_2$	2.09; 2.88	Py H-3	7.09
$PC_6H_4CH_3$	1.69	PC_6H_5	*o,* 7.78; *m,* 7.39
Py H-6	8.95	PC_6H_5	*o,* 7.60; *m,* 7.25

[a] Chemical shifts were measured with respect to internal TMS.

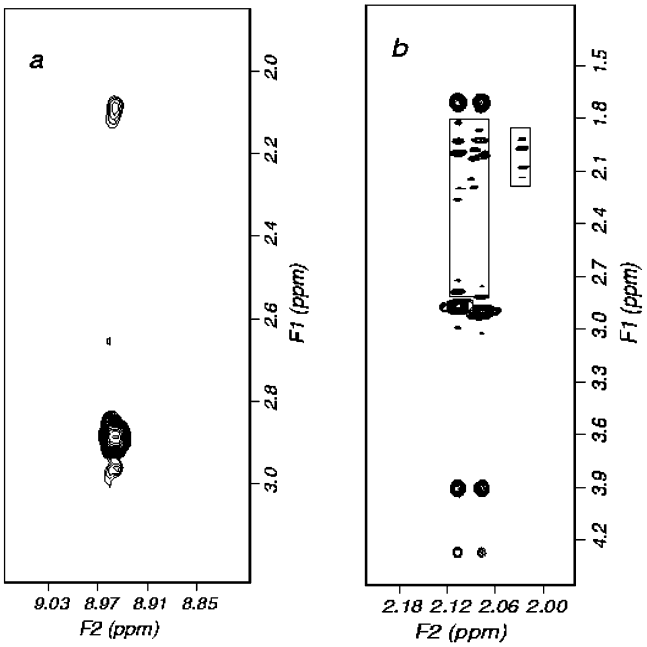


Figure 3. Expansions of the ROESY spectrum of **7** in $CDCl_3$: (a) connectivities of the ortho hydrogen (H-6) of the pyridine derivative ligand to the $RuCH_2$ protons; (b) connectivities of the upfield resonance of $RuCH_2$ pair to $RuNH_2CH_2$ protons at 1.71, 2.98, 3.91, and 4.28 ppm, respectively (see Table 3). Only negative contours are drawn, and therefore, diagonal autopeak contours are missing. The boxed regions enclose t_1-noise artifacts.

the phosphine and formation of **8** (Scheme 3). The ^{1}H spectrum shows broad signals for the amino protons, whereas in the ^{13}C NMR spectrum the ethylenediamine ligand shows two signals at δ 43.5 and 42.2, slightly shifted upfield compared to that of the free ligand (δ 44.3). The ν_{CO} of **8** is at 1910 cm^{-1}, close to **7** and in agreement with the presence of a trans amino group.

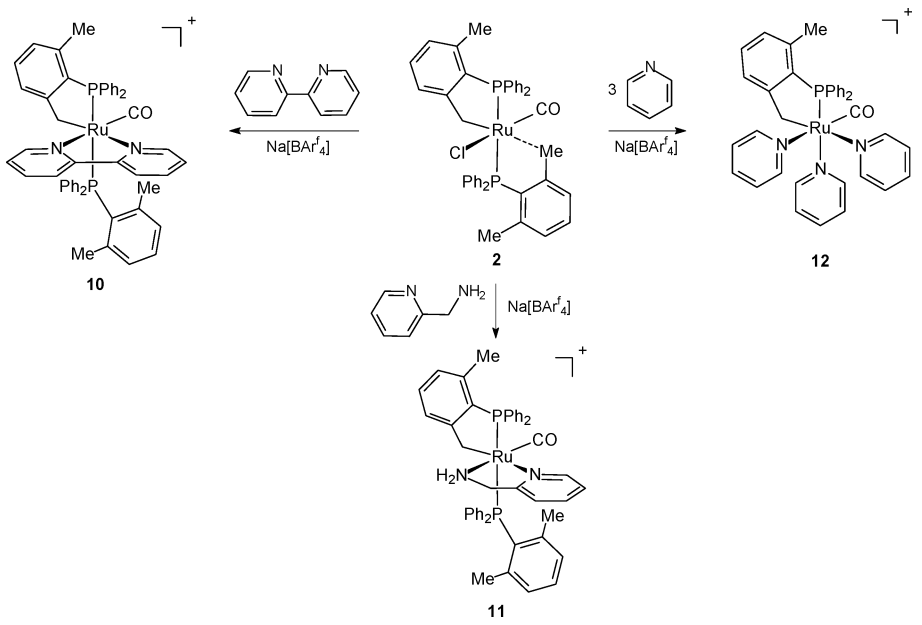
It is noteworthy that the reaction of **2** with bidentate pyridine ligands leads in only few cases to the formation of a single compound. Thus, treatment of **2** with an equimolar amount of 2,2′-bipyridine in $CDCl_3$ at room temperature gives a mixture of two isomers in about 1:1 molar ratio, as established by ^{31}P NMR measurements (δ 65.2 and 52.7). Reaction of **2** with 1 equiv of 2-acetylpyridine affords two isomers in a 1.3:1 molar ratio (^{31}P NMR δ 69.8 and 66.8, respectively), whereas with 2-benzoylpyridine formation of two products in a 1:1.7 molar ratio has been observed (^{31}P NMR δ 70.5 and 68.5). With 2 equiv of pyridine **2** leads a mixture of two compounds of general formula $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)(Py)_2$ in about a 1:1.2 molar ratio (^{31}P NMR δ 69.5 and 65.0), which, as for the previous cases, can be attributable to two isomers displaying a chloride trans to CO and a chloride trans to the CH_2 moiety, as for **7**. In the ^{1}H NMR spectrum the pyridine ortho protons are at δ 8.70−8.55 and 8.22, while the $RuCH_2$ moieties appear as doublets at δ 3.41 and 2.88 (J(HH) = 14.5 Hz) and δ 3.31 and 2.50 (J(HH) = 15.1 Hz). Attempts to obtain a single compound failed, because the isolated product still remains a mixture of two isomers. In contrast, no reaction of **2** with 2-bromopyridine, 2,6-dimethylpyridine, and 8-methylquinoline has been observed via NMR measurements.

The compounds **7** and **8**, containing bidentate nitrogen ligands, have been found to be efficient catalytic precursors for the reduction of acetophenone to 1-phenylethanol via transfer hydrogenation, using 2-propanol as a hydrogen donor under reflux conditions. When **8** (0.1 mol %) is used with NaOH as cocatalyst (2 mol %), quantitative conversion of acetophenone (0.1 M solution) is achieved after 30 min (TOF = 2800 h^{-1}, at 50% conversion),[14] whereas at 0.5 mol % of catalyst the reaction is complete after 5 min (TOF = 11 000 h^{-1}). With compound **7** (0.05 mol %) acetophenone is reduced more quickly, leading to 98% conversion within 5 min and TOF = 60 000 h^{-1}, one of the highest values reported in the literature.[14] Following this procedure, different ketones such as propiophenone, 2-hexanone, 3-hexanone, and benzophenone have been quantitatively reduced to alcohols in less than 15 min with high TOF values (47 000, 63 000, 19 000, and 36 000 h^{-1}, respectively). It is noteworthy that even at low catalyst loading (ketone/Ru/NaOH = 10 000/1/200) acetophenone is quantitatively reduced (98% conversion, 1 h). It is likely that during catalysis a Cl/H exchange occurs and the high catalytic performances can be ascribed to the bifunctional Ru−H/N−H motif,[24] associated with the stable σ Ru−C bond, which confers additional stability.

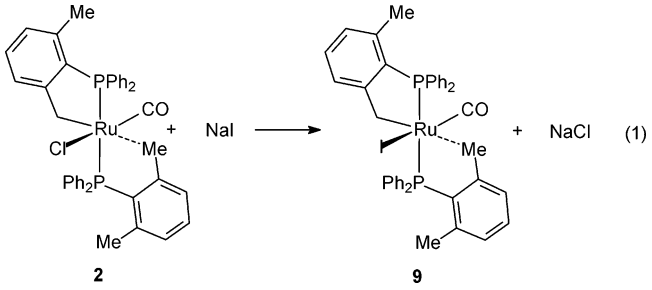
It is well-known that ruthenium chloride complexes can be quantitatively converted into the corresponding bromide and iodide derivatives by reaction with alkali-

(24) (a) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466. (b) Abdur-Rashid, K.; Claphman, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 15104.

Scheme 4



metal salts.[25] Thus, the iodide derivative **9** can be promptly obtained by treatment of **2** in acetone with NaI in excess, according to eq 1.



(1)

At room temperature the ^{31}P NMR spectrum of **9** reveals two broad doublets at δ 52.2 and 44.9 with a ^{2}J(PP) value of about 260 Hz, a value slightly smaller than that of **2**, but consistent with a trans arrangement, while upon cooling to −40 °C the peaks become sharper. In the ^{1}H NMR spectrum at 20 °C the signal of the two ortho methyl groups of L* is at δ 1.36, which at −40 °C splits into two resonances of equal intensity at δ 1.71 and 0.78, indicating that the rotation of the xylyl group is frozen out, a result which differs from **2**. Finally, in the IR spectrum **9** displays a ν_{CO} stretching band at 1922 cm^{-1} which is very close to that of **2**.

Cationic Complexes. With the aim of extending the chemistry of cyclometalated ruthenium complexes to cationic species bearing nitrogen ligands, which can be of interest for catalytic applications, we have investigated the reaction of **2** with mono- and bidentate pyridine ligands in the presence of Na[BAr$^{f}_{4}$] (Ar^{f} = 3,5-(CF$_3$)$_2$C$_6$H$_3$).[26] As a matter of fact, with the low coordinating anion [BAr$^{f}_{4}$]$^-$ numerous cationic 18-electron complexes and even highly coordinatively unsaturated species, such as [Ru(Ph)(CO)(P^{t}Bu$_2$Me)$_2$]$^+$,[27] [Ir(H)$_2$(P^{t}Bu$_2$Ph)$_2$]$^+$,[28] and [Pt(P−C){(2,6-Me$_2$C$_6$H$_3$)PR$_2$}]$^+$ (P−C = (2-CH$_2$-6-MeC$_6$H$_3$)PR$_2$; R = Ph, Cy),[13c] have been isolated. Treatment of **2** with equimolar amounts of 2,2′-bipyridine and Na[BAr$^{f}_{4}$] in dichloromethane at room temperature gives the six-coordinate species **10**, which was isolated in high yield by elimination of NaCl (Scheme 4).

The complex **10** shows two trans phosphorus atoms, as established by the ^{31}P NMR measurement (^{2}J(PP) = 256 Hz). The ^{1}H NMR spectrum exhibits two doublets at δ 8.90 (J(HH) = 5.3 Hz) and 7.90 (J(HH) = 5.6 Hz) for the two ortho protons of the coordinated 2,2′-bipyridine, whereas the resonances at δ 3.49 and 2.72 are for the nonequivalent cyclometalated CH$_2$ protons. The peak at δ 1.15 is for two methyl groups, and this is consistent with a free rotation of the xylyl group. Furthermore, for **10** the stretching frequency of the carbonyl ligand is at 1948 cm^{-1}, a value comparable to those of the related cationic complexes [Ru(CO)(C≡CR)-(Py)$_2$(PPh$_3$)$_2$][PF$_6$], showing one pyridine trans to CO (ν_{CO} in the range 1945−1950 cm^{-1}).[29] Similarly to **10**, complex **11** has been prepared by reacting **2** with Na[BAr$^{f}_{4}$] and 2-(aminomethyl)pyridine in CH$_2$Cl$_2$ and isolated in 88% yield. As for **10** the ^{2}J(PP) value of 269 Hz indicates a trans arrangement of the two phosphorus atoms, whereas in the ^{1}H NMR spectrum the two *o*-methyl groups of the xylyl appear as one resonance at δ 1.39. The carbonyl stretching frequency at 1937 cm^{-1} differs from that of **10** and suggests a structure with the CO trans to the amino group, according to the greater σ-donor character of the latter compared to the pyridine nitrogen. In complexes **10** and **11** the removal of the chloride and the availability of the "agostic" site allow the coordination of the bidentate nitrogen ligand without displacement of the phosphine. In contrast,

(25) (a) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233. (b) Wilczewski, T.; Bochénska, M.; Biernat, J. F. *J. Organomet. Chem.* **1981**, *215*, 87.

(26) (a) Nishida, H.; Takada, N.; Yoshimura, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (b) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

(27) Huang, D.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2004.

(28) Cooper, A. C.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 9069.

(29) Echavarren, A. M.; López, J.; Santos, A.; Romero, A.; Hermoso, J. A.; Vegas, A. *Organometallics* **1991**, *10*, 2371.

treatment of **2** with $Na[BAr^f_4]$ and 3 equiv of pyridine in CH_2Cl_2 leads to the monophosphine derivative **12**, through elimination of L*. In this case the formation of a complex containing three pyridine ligands, compared to the species bearing 2,2′-bipyridine and 2-(aminomethyl)pyridine, is due to the lesser steric hindrance of pyridine. The ^1H NMR spectrum shows three resonances at δ 8.19, 8.10, and 7.87 for the ortho hydrogens of the nonequivalent pyridines, whereas in the ^{13}C NMR spectrum the related ortho carbon atoms are at δ 153.0, 152.0, and 151.6. Finally, the ν_{CO} value of **12** is at 1948 cm^{-1}, which is a value identical with that found for **10**, in agreement with the presence of a trans pyridine.

Concluding Remarks

In summary, we have found that the phosphine (2,6-$Me_2C_6H_3$)PPh_2 (L*), in addition to effectively protecting vacant sites at the metal center through δ-agostic interactions of the *o*-methyl group, allows the synthesis of a large number of cyclometalated ruthenium complexes. With $RuCl_2(L^*)_2$ (**1**) as the starting material, the five-coordinate derivative $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)(L^*)$ (**2**) can be easily obtained and subsequent reactions with phosphorus and nitrogen ligands allow the isolation of compounds of general formula $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)(L)_n$ ($n = 1, 2$). Some of these derivatives have been characterized by single-crystal X-ray diffraction and through 2D NMR experiments. The cationic cyclometalated complexes $[Ru\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(CO)(L^*)_m(L)_n]^+$ ($m = 0, 1$; $n = 1, 3$) are also prepared by reaction of **2** with $Na[BAr^f_4]$ in the presence of nitrogen ligands. It is noteworthy that the neutral derivatives containing ethylenediamine and 2-(aminomethyl)pyridine are highly active catalysts for the reduction of numerous ketones via transfer hydrogenation. The presence of a cyclometalated phosphine, which presents a robust metal−carbon bond preventing easy dissociation from the metal, is an important prerequisite for obtaining long-living catalytic species. Studies are currently in progress in our laboratories to expand the use of the PC cyclometalated ruthenium complexes in homogeneous catalysis.

Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were carefully dried by standard methods and distilled under argon before use. The ruthenium complex $RuCl_2(L^*)_2$ (**1**) was prepared according to literature procedures,[12a] whereas all other chemicals were purchased from Aldrich and used without further purification. NMR measurements were recorded on a Bruker AC 200 spectrometer. Chemical shifts, in ppm, are relative to TMS for ^1H and ^{13}C, whereas H_3PO_4 was used for ^{31}P. Infrared measurements were obtained using a Nicolet Magna 550 series FT-IR spectrometer. Elemental analyses (C, H, N) were carried out with a Carlo Erba 1106 elemental analyzer.

Synthesis of 2. Method 1. Triethylamine (1.90 mL, 13.6 mmol) and formaldehyde (1.00 mL, 37% solution in water, 13.4 mmol) were added to a suspension of **1** (2.00 g, 2.66 mmol) in 40 mL of ethanol under argon. The mixture was refluxed for 2 h and concentrated to half volume, and after filtration the product was dried under reduced pressure. Yield: 1.60 g (81%). Anal. Calcd for $C_{41}H_{37}ClOP_2Ru$: C, 66.17; H, 5.01. Found: C, 65.93; H, 5.04. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 7.8−6.9 (m, 26H; aromatic protons), 3.48 (d, J(HH) = 13.4 Hz, 1H; $RuCH_2$), 3.29 (dd, J(HH) = 13.4 Hz, J(HP) = 5.4 Hz, 1H; CH_2), 1.76 (s, 3H; CH_3), 1.64 (s, 6H; CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ 198.8 (dd, J(CP) = 14.0 Hz, J(CP) = 12.3 Hz; CO), 163.1 (dd, J(CP) = 36.7 Hz, J(CP) = 6.2 Hz; *C*CH_2), 144.6 (dd, J(CP) = 11.4 Hz, J(CP) = 2.2 Hz; agostic *C*CH_3), 142.1 (s; *C*CH_3), 135.0−126.5 (m, aromatic carbons), 22.9 (pseudo t, J(CP) = 3.2 Hz; $RuCH_2$), 22.3 (d, J(CP) = 3.7 Hz; CH_3), 18.4 (s broad; agostic CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 53.7 (d, J(PP) = 301 Hz), 32.8 (d, J(PP) = 301 Hz). IR (Nujol): ν(CO) 1923 cm^{-1}.

Method 2. $RuCl_3 \cdot xH_2O$ (2.07 g, $x = 2.5$; 8.20 mmol) and L* (5.58 g, 19.2 mmol) were refluxed for 2 h in 40 mL of ethanol, giving a purple precipitate of **1**. Triethylamine (5.4 mL, 38.7 mmol) and formaldehyde (3.00 mL, 37% solution in water, 40.2 mmol) were added at room temperature, and the suspension was refluxed for 2 h. The product was filtered, washed with ethanol, and dried under reduced pressure. Yield: 4.09 g (67%).

Synthesis of 3. A solution of **2** (200 mg, 0.269 mmol) in 4 mL of CH_2Cl_2 was stirred for 1 h under a CO atmosphere and concentrated. The product was precipitated with methanol, filtered, and dried under reduced pressure. Yield: 154 mg (74%). Anal. Calcd for $C_{42}H_{37}ClO_2P_2Ru$: C, 65.33; H, 4.83. Found: C, 65.62; H, 4.90. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): 8.3−6.9 (m, 26H; aromatic protons), 3.10 (dd, J(HH) = 14.8 Hz, J(HP) = 5.4 Hz, 1H; $RuCH_2$), 2.90 (dd, J(HH) = 14.8 Hz, J(HP) = 6.3 Hz, 1H; $RuCH_2$), 2.02 (s, 6H; CH_3), 1.74 (s, 3H; CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 54.8 (d, J(PP) = 292 Hz), 25.6 (d, J(PP) = 292 Hz). IR (Nujol): ν(CO) 2020, 1957 cm^{-1}.

Synthesis of 4. Tricyclohexylphosphine (170 mg, 0.606 mmol) was added to a solution of **2** (300 mg, 0.403 mmol) in 4 mL of CH_2Cl_2 under argon. The solution was stirred for 2 h and concentrated. The product was precipitated with methanol, filtered, washed with methanol, and dried under reduced pressure. Yield: 151 mg (51%). Anal. Calcd for $C_{39}H_{51}ClOP_2Ru$: C, 63.79; H, 7.00. Found: C, 64.10; H, 6.85. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 7.7−6.9 (m, 13H; aromatic protons), 3.81 (d, J(HH) = 12.3 Hz, 1H; $RuCH_2$), 3.37 (ddd, J(HH) = 12.3 Hz, J(HP) = 5.7 Hz, J(HP) = 3.4 Hz, 1H; CH_2Ru), 2.45 (m, 3H; CH of Cy), 2.3−1.0 (m, 30H, CH_2 of Cy), 1.82 (s, 3H; CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 203.9 (s; CO), 163.5 (dd, J(CP) = 38.3 Hz; J(CP) = 4.7 Hz; *C*CH_2), 141.7 (d, J(CP) = 1.5 Hz; *C*CH_3), 134.1−127.8 (m; aromatic carbons), 35.4 (d, J(CP) = 16.6 Hz; *C*H of Cy), 29.8 (d, J(CP) = 17.7 Hz; CH_2 of Cy), 27.8 (dd, J(CP) = 23.6 Hz, J(CP) = 9.6 Hz; CH_2 of Cy), 26.2 (s; CH_2 of Cy), 22.3 (d, J(CP) = 3.2 Hz; CH_3), 18.3 (s; $RuCH_2$). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 54.4 (d, J(PP) = 290 Hz), 30.3 (d, J(PP) = 290 Hz). IR (Nujol): ν(CO) 1917 cm^{-1}.

Synthesis of 5. PPh_2Me (213 mg, 1.06 mmol) was added to a solution of **2** (314 mg, 0.422 mmol) in 4 mL of CH_2Cl_2 under argon. The solution was stirred for 4 h and concentrated. The product was precipitated with diethyl ether, filtered, washed with diethyl ether, and dried under reduced pressure. Yield: 220 mg (61%). Anal. Calcd for $C_{47}H_{44}ClOP_3Ru$: C, 66.08; H, 5.19. Found: C, 66.30; H, 5.14. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 7.7−6.7 (m, 33H; aromatic protons), 3.01 (dt, J(HH) = 15.6 Hz, J(HP) = 4.7 Hz, 1H; $RuCH_2$), 2.70 (ddd, J(HH) = 15.6 Hz, J(HP) = 7.6 Hz, J(HP) = 4.9 Hz, 1H; CH_2Ru), 1.80 (dd, J(HP) = 8.5 Hz, J(HP) = 1.5 Hz, 3H; PCH_3), 1.53 (d, J(HP) = 6.4 Hz, 3H; PCH_3), 1.40 (s, 3H; CCH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 203.9 (s; CO), 162.9 (dd, J(CP) = 45.4 Hz, J(CP) = 6.9 Hz; *C*CH_2), 141.4 (s; *C*CH_3), 139.5−127.8 (m; aromatic carbons), 33.4 (d, J(CP) = 63.7 Hz; $RuCH_2$), 21.8 (d, J(CP) = 3.3 Hz; CH_3), 14.9 (d, J(CP) = 22.7 Hz; PCH_3), 10.5 (d, J(CP) = 27.2 Hz; PCH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ 50.2 (dd, J(PP) = 298 Hz, J(PP) = 16.6 Hz), 15.6 (dd, J(PP) = 298 Hz, J(PP) = 17.1 Hz), −1.2

(pseudo t, J(PP) = 16.6 Hz, J(PP) = 17.1 Hz). IR (Nujol): ν(CO) 1917 cm^{-1}.

Synthesis of 6. 1,3-Bis(diphenylphosphino)propane (208 mg, 0.504 mmol) was added to a solution of **2** (300 mg, 0.403 mmol) in 10 mL of CH_2Cl_2 under argon. The solution was stirred for 2 h and concentrated. The product was precipitated with methanol, filtered, and dried under reduced pressure. Yield: 190 mg (54%). Anal. Calcd for $C_{48}H_{44}ClOP_3Ru$: C, 66.55; H, 5.12. Found: C, 66.71; H, 5.06. ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): 7.6−6.6 (m, 33H; aromatic protons), 3.92 (pseudo t, J(HH) = J(HP) = 14.4 Hz, 1H; $RuCH_2$), 3.06 (pseudo t, J(HH) = J(HP) = 14.4 Hz, 1H; $RuCH_2$), 2.58 (m, 2H; CH_2), 2.34−1.69 (m, 4H, CH_2), 1.42 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 204.2 (s; CO), 163.1 (dd, J(CP) = 38.4, J(CP) = 6.5 Hz; $CCCH_2$), 141.2 (s; $CCCH_3$), 134.9−127.8 (aromatic carbons), 35.2 (dt, J(CP) = 53.6, J(CP) = 4.3 Hz; $RuCH_2$), 27.1 (d, J(CP) = 8.6 Hz; CH_2), 26.6 (d, J(CP) = 13.4 Hz; CH_2), 21.4 (d, J(CP) = 2.7 Hz; CH_3), 19.2 (s, CH_2). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 47.5 (dd, J(PP) = 282 Hz, J(PP) = 20 Hz), 28.4 (dd, J(PP) = 282 Hz, J(PP) = 29 Hz), 2.8 (dd, J(PP) = 20 Hz, J(PP) = 29 Hz). IR (Nujol): ν(CO) 1919 cm^{-1}.

Synthesis of 7. 2-(Aminomethyl)pyridine (90 μL, 0.87 mmol) and $CaCO_3$ (39 mg, 0.39 mmol) were added to a solution of **2** (535 mg, 0.72 mmol) in 10 mL of CH_2Cl_2 under argon. The suspension was refluxed overnight, filtered, and concentrated. The product was precipitated with diethyl ether, filtered, and dried under reduced pressure. Yield: 308 mg (76%). Anal. Calcd for $C_{27}H_{26}ClN_2OPRu$: C, 57.70; H, 4.66; N, 4.98. Found: C, 57.34; H, 4.61; N, 5.04. ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 9.01 (d, J(HH) = 5.6 Hz, 1H; o-C_5H_4N), 7.9−6.9 (m, 16H; aromatic protons), 4.35 (d pseudo t, J(HH) = 16.1 Hz, J(HH) = 4.4 Hz, 1H; CH_2N), 4.01 (d pseudo t, J(HH) = 16.2 Hz, J(HH) = 6.4 Hz, 1H; CH_2N), 3.05 (m, 1H; NH_2), 2.95 (d, J(HH) = 14.9 Hz, 1H; $RuCH_2$), 2.15 (d, J(HH) = 14.8 Hz, 1H; $RuCH_2$), 1.85 (m, 1H; NH_2), 1.76 (s, 3H; CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 205.4 (d, J(CP) = 19.1 Hz; CO), 164.1 (d, J(CP) = 31.8 Hz; CCH_2Ru), 159.7 (s; $NCCH_2$), 152.3 (s; ortho CH of C_5H_4N), 141.3 (s, $CCCH_3$), 136.4 (s; para C_5H_4N), 135.1−120.9 (aromatic carbons), 48.8 (d, J(CP) = 2.9 Hz; CH_2NH_2), 23.1 (d, J(CP) = 3.6 Hz; $RuCH_2$), 22.3 (d, J(CP) = 3.8 Hz; CH_3). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 67.9 (s). IR (Nujol): ν(CO) 1912 cm^{-1}.

Synthesis of 8. Ethylenediamine (240 μL, 3.59 mmol) and $CaCO_3$ (116 mg, 1.16 mmol) were added to a solution of **2** (1.76 g, 2.36 mmol) in 10 mL of CH_3OH under argon. The solution was refluxed for 2 h and concentrated. The product was precipitated with diethyl ether, filtered, and dried under reduced pressure. Yield: 900 mg (74%). Anal. Calcd for $C_{23}H_{26}ClN_2OPRu$: C, 53.75; H, 5.10; N, 5.45. Found: C, 53.90; H, 5.20; N, 5.20. ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 7.9−6.9 (m, 13H; aromatic protons), 3.55−3.10 (m, 2H), 2.97 (d, J(HH) = 14.6 Hz, 1H; $RuCH_2$), 2.90−2.05 (m, 4H), 1.98 (d, J(HH) = 14.6 Hz, 1H; $RuCH_2$), 1.78 (s, 3H; CH_3), 1.7−1.3 (m, 2H). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 204.6 (d, J(CP) = 18.1 Hz; CO), 163.8 (d, J(CP) = 31.7 Hz; CCH_2Ru), 141.3 (s; $CCCH_3$), 134.3−126.9 (m; aromatic carbons), 43.5 (s; CH_2NH_2), 42.2 (s; CH_2NH_2), 23.8 (d, J(CP) = 3.9 Hz; $RuCH_2$), 22.3 (d, J(CP) = 3.5 Hz; CH_3). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 68.9 (s). IR (Nujol): ν(CO) 1910 cm^{-1}.

Synthesis of 9. Sodium iodide (270 mg, 1.80 mmol) was added to a solution of **2** (240 mg, 0.32 mmol) in 5 mL of acetone under argon. The solution was stirred for 2 h at room temperature, and the solvent was evaporated under reduced pressure. The solid was dissolved in CH_2Cl_2, and after filtration the product was precipitated with heptane, filtered, and dried under reduced pressure. Yield: 215 mg (80%). Anal. Calcd for $C_{41}H_{37}IOP_2Ru$: C, 58.93; H, 4.46. Found: C, 59.02; H, 4.61. ^{1}H NMR (200.1 MHz, CD_2Cl_2, −40 °C): δ 8.0−6.9 (m, 26H; aromatic protons), 2.57 (d, J(HH) = 16.0, 1H; $RuCH_2$), 2.29 (dd, J(HH) = 16.0, J(HP) = 4.5, 1H; $RuCH_2$), 1.71 (s, 3H; CH_3), 1.60 (s, 3H; CH_3), 0.78 (s, 3H; CH_3). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, −40 °C): δ 50.2 (d, J(PP) = 256 MHz), 44.2 (d, J(PP) = 256 MHz). IR (Nujol): ν(CO) 1922 cm^{-1}.

Synthesis of 10. Complex **2** (200 mg, 0.268 mmol), 2,2′-bipyridine (44 mg, 0.281 mmol), and Na[BAr^f_4] (240 mg, 0.271 mmol) were dissolved in 5 mL of dichloromethane under argon. The mixture was stirred for 1 h at room temperature and filtered to eliminate NaCl. The solution was concentrated to half volume, and the compound was precipitated with pentane (10 mL), filtered, and dried under reduced pressure. Yield: 388 mg (84%). Anal. Calcd for $C_{83}H_{57}N_2P_2F_{24}OBRu$: C, 57.69; H, 3.32; N, 1.60. Found: C, 57.41; H, 3.22; N, 1.64. ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.90 (d, J(HH) = 5.3 Hz, 1H; o-H bipy), 7.90 (d, J(HH) = 5.6 Hz, 1H; o-H bipy), 7.7−6.1 (m, 46H; aromatic protons), 3.49 (dd, J(HH) = 14.4 Hz, J(HP) = 5.0 Hz, 1H; CH_2−Ru), 2.72 (dd, J(HH) = 14.4 Hz, J(HP) = 5.0 Hz, 1H; CH_2−Ru), 1.55 (s, 3H; CH_3), 1.15 (s, 6H; CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 206.0 (CO), 163.8−116.4 (m, aromatic carbons), 26.3 (d, J(CP) = 4.7 Hz; $RuCH_2$), 22.0 (d, J(CP) = 3.5 Hz; CH_3), 21.8 (broad; 2 CH_3). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 71.9 (d, J(PP) = 256 Hz), 53.2 (d, J(PP) = 256 Hz). IR (Nujol): ν(CO) 1948 cm^{-1}.

Synthesis of 11. Complex **2** (200 mg, 0.270 mmol) was dissolved in 5 mL of dichloromethane, and Na[BAr^f_4] (238 mg, 0.274 mmol) was added. After 30 min 2-(aminomethyl)pyridine (28 μL, 0.272 mmol) was added, and the mixture was stirred for 90 min at room temperature and filtered. The solution was concentrated to half volume, and the compound was precipitated with pentane (10 mL), filtered, and dried under reduced pressure. Yield: 397 mg (88%). Anal. Calcd for $C_{79}H_{57}N_2P_2F_{24}OBRu$: C, 56.48; H, 3.42; N, 1.67. Found: C, 56.15; H, 3.22; N, 1.66. ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.36 (d, J(HH) = 5.7 Hz, 1H; o-H Py), 7.8−6.7 (m, 41 H; aromatic protons), 3.11 (dd, J(HH) = 17.2 Hz, J(HH) = 7.0 Hz, 1H; CH_2N), 2.92−2.65 (m, 2H; RuC*H*H and C*H*HN), 2.36 (d, J(HH) = 13.4 Hz, 1H; $RuCH_2$), 2.04 (broad, 2H; NH_2), 1.71 (s, 3H; CH_3), 1.39 (s, 6H; CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 204.3 (t, J(CP) =14.5 Hz; CO), 163.8−160.1 (m; aromatic carbons), 153.3 (NCH Py), 142.2−117.5 (m; aromatic carbons), 48.7 (CH_2N), 24.8 (d, J(CP) = 5.0 Hz; 2 CH_3), 21.9 (d, J(CP) = 3.6 Hz; CH_3), 21.5 (broad; $RuCH_2$). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 71.5 (d, J(PP) = 269 Hz), 54.3 (d, J(PP) = 269 Hz). IR (Nujol): ν(CO) 1937 cm^{-1}.

Synthesis of 12. Complex **2** (200 mg, 0.268 mmol) and Na[BAr^f_4] (238 mg, 0.268 mmol) were dissolved in 5 mL of dichloromethane, and the mixture was stirred at room temperature for 1 h under argon. Pyridine (68.5 μL, 0.85 mmol) was added, and the suspension was stirred at room temperature for 6 h and filtered to eliminate NaCl. The solution was concentrated to half volume, and the compound was precipitated with pentane (10 mL), filtered, and dried under reduced pressure. Yield: 326 mg (80%). Anal. Calcd for $C_{68}H_{45}N_3P_1F_{24}OBRu$: C, 53.71; H, 2.99; N, 2.77. Found: C, 53.65; H, 2.88; N, 2.71. ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.19 (d, J(HH) = 5.2 Hz, 2H; o-H Py), 8.10 (m, 2H; o-H Py), 7.87 (m, 2H; o-H Py), 7.7−6.9 (m, 34H; aromatic protons), 3.22 (d, J(HH) = 15.5 Hz, 1H; CH_2−Ru), 2.59 (d, J(HH) = 15.3 Hz, 1H; CH_2−Ru), 1.74 (s, 3H; CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 204.9 (d, J(CP) = 17.7 Hz; CO), 163.7−160.1 (m; aromatic carbons), 153.0, 152.0, 151.6 (ortho C Py), 141.8−116.4 (m; aromatic carbons), 28.2 (d, J(CP) = 3.5 Hz; $RuCH_2$), 22.3 (s, CH_3).^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 64.0 (s). IR (Nujol): ν(CO) 1948 cm^{-1}.

Typical Procedure for the Catalytic Transfer Hydrogenation. The ruthenium complexes (5.0 μmol of **7**, 10.0 μmol of **8**) were dissolved in 5 mL of a 0.04 M solution of NaOH in 2-propanol. The ketone (2 mmol) was dissolved in 19 mL of 2-propanol, and the solution was heated to reflux under argon. By addition of 1 mL of the solution containing the ruthenium complex, the reduction of the ketone starts immediately (**7**, 0.05 mol %; **8**, 0.1 mol %; NaOH, 2 mol %) and the yield was

determined by GC analysis using a Supelcowax 10 column (30 m long, 0.25 mm i.d.).

X-ray Structure Determination of 2. Data collection for **2** was carried out at 150(2) K on a Nonius DIP-1030H system, with graphite-monochromated Mo Kα radiation. A total of 30 frames were collected, each with an exposure time of 20 min, over a half of reciprocal space with a rotation of 6° about φ, the detector being at 80 mm from the crystal. Cell refinement, indexing, and scaling of the data set were carried out using the programs Mosflm and Scala.[30] The structure was solved by Patterson and Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[31] The crystal structure of **2** was refined in the noncentrosymmetric space group $P2_1$ as a racemic twin with a Flack parameter of 0.30(8). All non-H atoms were refined with anisotropic temperature factors. The contribution of hydrogen atoms at calculated positions were included in final cycles of refinements. All the calculations were performed using the WinGX System, version 1.64.04.[32] Details of the X-ray experiment, data reduction, and final structure refinement calculation are summarized in Table 1.

NMR Measurements of 7. All 1D and 2D ^{1}H NMR spectra were obtained at 500.1 MHz with a Bruker Avance instrument, equipped with a triple-axis gradient unit, using a ~0.05 M solution of compound **7** in $CDCl_3$. During the measurements the sample temperature was kept at 298 K. Chemical shifts were referenced on the internal TMS peak. A spectral width of 5482.456 Hz was always selected, with 16 K points for 1D acquisitions and 2K × 512 or 2K × 256 ($t_2 \times t_1$) for 2D acquisition matrices. Typically 32−64 scans/FID were collected. Zero-filling to 32K for 1D spectra and 4K × 4K for 2D spectra was always applied prior to Fourier transformation. A sine-bell apodization function shifted by $\pi/2$ was employed for 2D processing in both time dimensions. Total correlation spectroscopy (TOCSY) experiments[33] were acquired using a DIPSI2 spin-lock train[34] of 50 ms, with $\gamma B_1 \approx 8.5$ kHz and echo−antiecho F_1 quadrature detection.[35] Double-quantum filtered correlation spectroscopy (DQF-COSY) experiments[36] were performed using a pulsed field gradient ratio to select the desired coherence order[37] and TPPI (time proportional phase incrementation) for F_1 quadrature detection.[38] Dipolar correlation spectra[39] were collected in the rotating frame by rotating frame Overhauser spectroscopy (ROESY),[40] with the application of a continuous spin lock field ($\gamma B_1 \approx 2.5$ kHz) of 150−250 ms and TPPI F_1 quadrature detection.[38] Some dipolar correlations were also monitored by 1D experiments using the high-sensitivity laboratory-frame selective NOE measurement type first described by Stonehouse and colleagues,[41] with mixing times ranging between 200 and 800 ms. These experiments were performed with selective inversion of the resonances at δ 8.95 and 1.69 (see Table 3 for assignments) to control the qualitative and quantitative results obtained from ROESY. In particular, ROESY quantitative assessments were performed by calculating the inverse sixth power of the cross-peak volume ratios, using the connectivities of an aromatic ortho pair (δ 8.95−7.18) or a geminal pair (δ 2.09−2.88) as calibrant and the corresponding internuclear separations of 2.49 and 1.69 Å, respectively.[42] The latter calibrant, expected to introduce systematic underestimation of the unknown parameter, was employed to establish distance lower limits whenever necessary. The experimental ROESY cross-peak volumes were corrected for offset effects before being used to evaluate distances,[43] but no correction was applied to account for simultaneous laboratory-frame NOE contributions.[44] The reliability of the ROESY estimates was controlled, however, by calculating the distance between the ortho pyridine hydrogen (δ 8.95) and one of the $RuCH_2$ pair (δ 2.09) from laboratory-frame NOE data. The value of 3.4 Å obtained from this check satisfactorily compared with the corresponding ROESY-based counterpart (3.6 Å).

Acknowledgment. This work was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST). We also thank Dr. P. Martinuzzi for assistance in NMR measurements and Mr. P. Polese for carrying out the elemental analyses.

Supporting Information Available: Tables of crystal and data collection parameters, atomic coordinates, bond lengths, bond angles and thermal displacement parameters for **2** and **5** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049408L

(30) Collaborative Computational Project, Number 4. *Acta Crystallogr.* **1994**, *D50*, 760.
(31) Sheldrick, G. M., SHELX97 Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen, Göttingen, Germany, 1998.
(32) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(33) Braunschweiler, L.; Ernst, R. R. *J. Magn. Reson.* **1983**, *53*, 521.
(34) Shaka, A. J.; Lee, C. J.; Pines, A. *J. Magn. Reson.* **1988**, *77*, 274.
(35) Cavanagh, J.; Rance, M. *J. Magn. Reson.* **1990**, *88*, 72.
(36) Piantini, U.; Sørensen, O. W.; Ernst, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6800.
(37) Keeler, J.; Clowes, R. T.; Davis, A. L.; Laue, E. D. *Methods Enzymol.* **1994**, *239*, 145.
(38) Marion, D.; Wüthrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 967.
(39) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 286.
(40) Bothner-By, A. A.; Stephens, R. L.; Lee, J.; Warren, C. D.; Jeanloz, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 811.
(41) (a) Stonehouse, J.; Adell, P.; Keeler, J.; Shaka, A. J. *J. Am. Chem. Soc.* **1994**, *116*, 6037. (b) Stott, K.; Stonehouse, J.; Keeler, J.; Hwang, T.-L.; Shaka, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 4199.
(42) Esposito, G.; Pastore, A. *J. Magn. Reson.* **1988**, *76*, 331.
(43) Farmer, B. T.; Brown, L. R. *J. Magn. Reson.* **1987**, *72*, 197.
(44) Griesinger, C.; Ernst, R. R. *Chem. Phys. Lett.* **1988**, *152*, 239.