

# Improved Syntheses of Versatile Ruthenium Hydridocarbonyl Catalysts Containing Electron-Rich Ancillary Ligands

Nicholas J. Beach,<sup>a</sup> Ureshini L. Dharmasena,<sup>a</sup> Samantha D. Drouin,<sup>a</sup> and Deryn E. Fogg<sup>a,\*</sup>

<sup>a</sup> Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, ON, Canada K1N 6N5  
Fax: (+1)-613-562-5170; e-mail: dfogg@uottawa.ca

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**Abstract:** Clean, high-yield routes are established to the important catalyst chlorobis(tricyclohexylphosphine)ruthenium hydridocarbonyl [RuHCl(CO)(PCy<sub>3</sub>)<sub>2</sub>] **2** and its N-heterocyclic carbene (NHC) derivatives RuHCl(CO)(NHC)(PCy<sub>3</sub>) (**3a**: NHC = IMes; **3b**, NHC = H<sub>2</sub>IMes; IMes = 1,3-dimesitylimidazol-2-ylidene). These complexes are obtained by treating chlorotris(tricyclohexylphosphine)ruthenium hydridocarbonyl [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] **1** with tricyclohexylphosphine [PCy<sub>3</sub>], or with the appropriate NHC ligand, then PCy<sub>3</sub>. Advantages over prior routes to these complexes lie in the high yields from a conveniently accessible precursor, the absence of by-products that otherwise prove difficult to remove, and the short reaction times under experimentally convenient conditions.

**Keywords:** carbonyl ligands; hydride ligands; N-heterocyclic carbenes; phosphane ligands; ruthenium; synthetic methods

## Introduction

Efficient routes to five-coordinate group 8 hydridocarbonyl complexes containing electron-rich donor ligands are of considerable interest, given the exceptional versatility of such complexes in catalysis.<sup>[1–3]</sup> One of the most important examples, RuHCl(CO)(PCy<sub>3</sub>)<sub>2</sub> (**2**), has been extensively used for the challenging problem of polymer hydrogenation, a key technology in the synthesis of specialty materials, including engineering elastomers and thermoplastics.<sup>[4,5]</sup> Complex **2**, used either directly or generated *in situ*, is among the most efficient catalysts in current use for the reduction of C=C bonds in nitrile-butadiene polymers<sup>[5–8]</sup> and unsaturated polymers derived from ring-opening metathesis polymerization (ROMP).<sup>[9,10]</sup> Its recent applications to molecular transformations span

a wide range of applications. Reactions of alkenes range from hydrogenation<sup>[11,12]</sup> and isomerization,<sup>[11,13]</sup> to diverse addition and coupling reactions.<sup>[14]</sup> In particular, Yi's group has explored hydrovinylation<sup>[15,16]</sup> and dehydrogenative coupling of cyclic amines and alkenes,<sup>[17]</sup> and extensive studies by Marciniak and co-workers showcase the synthetic utility of **2** in silylative<sup>[14,18]</sup> and borylative<sup>[19]</sup> coupling, and related borylation<sup>[20]</sup> reactions. Triple bonds can also be activated: Beatty has reported that **2** functions as a precatalyst for the reductive hydrolysis of nitriles,<sup>[21]</sup> while Marciniak's group recently developed new catalytic routes to functionalized alkynylsilanes and alkynylgermanes by using **2** to activate *sp*-hybridized carbon-hydrogen bonds.<sup>[22,23]</sup>

Analogous catalysts containing an N-heterocyclic carbene ligand (**3**, Figure 1), though less explored, are now beginning to see use in olefin hydrogenation and isomerization.<sup>[10,24–26]</sup> In particular, **3a** is implicated in the synthesis of saturated neoglycopolymers relevant to tissue engineering *via* tandem ROMP-hydrogenation,<sup>[10]</sup> while Arisawa, Nishida and co-workers have exploited the isomerization activity of **3b** to develop new routes to indoles and related heterocycles *via* cycloisomerization of 1,6-dienes.<sup>[24]</sup>

Prior routes to **2** and **3** require forcing conditions and/or prolonged reaction, and result in contamination by small amounts of side-products. This is particularly problematic for use of the products in catalysis, as the batch-to-batch reproducibility of catalyst performance (and data) is undermined by the presence of contaminants in variable proportions. However, pu-

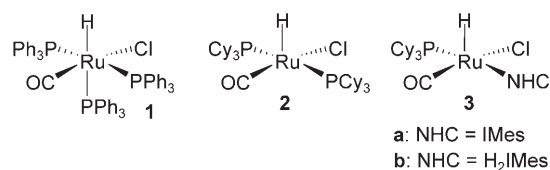
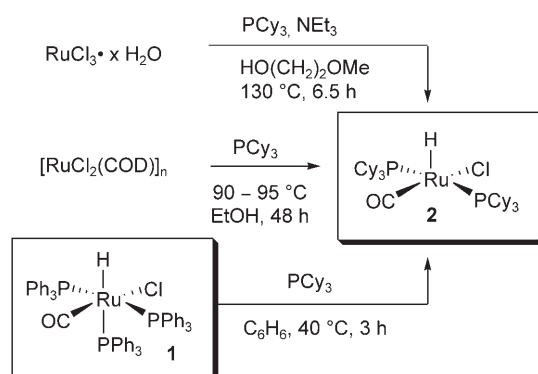


Figure 1.

rification is tedious, time-consuming, and costly in terms of ultimate yields of pure material. This Update describes improved routes to **2** and **3** from the readily available precursor  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  (**1**). In the interests of both efficiency and inhibition of side-reactions, reaction times and temperatures are kept to the minimum consistent with high yields.

## Results and Discussion

$\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$  (**2**) was originally synthesized by Moers and Langhout three decades ago, by prolonged thermolysis of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  with  $\text{PCy}_3$  in 2-methoxyethanol (bp  $130^\circ\text{C}$ ; Scheme 1).<sup>[27]</sup> Rempel and co-workers later reduced the reaction time to *ca.* 6 h by using triethylamine to take up the HCl produced, this modification affording **2** in 80% yield.<sup>[17]</sup> The dominant method in current use, reported by Yi and co-workers in 1999,<sup>[28]</sup> involves sealed-tube thermolysis of  $[\text{RuCl}_2(\text{COD})]_n$  and  $\text{PCy}_3$  in ethanol at  $90\text{--}95^\circ\text{C}$  for 48 h. The forcing conditions are necessitated by the oligomeric nature and consequently very low solubility of  $[\text{RuCl}_2(\text{COD})]_n$ . Heating above the normal boiling point of the solvent has the advantage of minimizing formation of the double carbonylation product



**Scheme 1.** Established and (bottom) new synthetic routes to **2**. For details of purity, see text.

$\text{RuCl}_2(\text{CO})_2(\text{PCy}_3)_2$  **5**, which we found is formed in larger amounts on carrying out the reaction in a Schlenk vessel equipped with a reflux condenser.

In our hands, synthesis of **2** from  $[\text{RuCl}_2(\text{COD})]_n$  at  $95^\circ\text{C}$  in a pressure vessel afforded the product in excellent crude yields ( $>90\%$ ), but small amounts of the dichlorocarbonyl complexes  $\text{RuCl}_2(\text{CO})(\text{PCy}_3)_2$  (**4**) and  $\text{RuCl}_2(\text{CO})_2(\text{PCy}_3)_2$  (**5**) were also present, which proved difficult to remove. These species are observed as  $^{31}\text{P}\{^1\text{H}\}$  NMR singlets at 35.2 and 27.2 ppm,<sup>[29]</sup> respectively, accompanying the singlet for **2** at 46.9 ppm (Table 1). Group 8 metal complexes have long been known to undergo carbonylation<sup>[30]</sup> in alcohol solvents at elevated temperatures, although the extent varies, in part owing to competing thermal decarbonylation of polycarbonyl products.<sup>[31–34]</sup> Formation of the monocarbonyl species **4** was also noted in the original synthesis of **2** from  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ;<sup>[27]</sup> this species was isolated as a principal product after 72 h reaction time.<sup>[35]</sup> Attempts to purify crude **2** by reprecipitation proved unsuccessful. Exhaustive extraction with ethanol and diethyl ether removed most of the by-products, but yields were then limited to *ca.* 65%.

A common element in these synthetic routes is the reliance on an alcohol solvent as the source of the hydride and carbonyl ligands. This is problematic because it is difficult to achieve complete selectivity over the extent of carbonylation (and, to a lesser extent, hydride installation). In exploring alternative, more convenient routes to **2**, we began by seeking a precursor containing one pre-installed hydride and CO ligand, accessible in high yields and purity from the ultimate starting material  $\text{RuCl}_3$ , and bearing neutral ancillary donors sufficiently labile to undergo ligand exchange under mild conditions. These criteria led us to the classic hydride complex  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  **1**, itself commercially available, and accessible in one step and quantitative yields from  $\text{RuCl}_3$ .<sup>[36]</sup>

Addition of excess  $\text{PCy}_3$  to a stirred suspension of **1** in benzene or toluene effects quantitative conversion to **2** within 3 h at  $40^\circ\text{C}$ . An aliquot removed at this

**Table 1.** Key NMR data for precursor and target complexes.<sup>[a]</sup>

| Complex  | $\delta_{\text{P}}$ (ppm)                           | $\delta_{\text{H}}$ (ppm)               |
|--|---|---|
| $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ , <b>1</b> <sup>[b]</sup>          | 39.1 (d, 2P), 12.9 (t, 1P); $^2J_{\text{PP}}$ 13 Hz | −7.2 (dt, $^2J_{\text{PH}}$ 105, 23 Hz) |
| $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ , <b>2</b>                         | 46.9 (s)  | −24.2 (t, $^2J_{\text{PH}}$ 18 Hz)      |
| $\text{RuCl}_2(\text{CO})(\text{PCy}_3)_2$ , <b>4</b>                        | 35.2 (s)  | –                                       |
| $\text{RuCl}_2(\text{CO})_2(\text{PCy}_3)_2$ , <b>5</b>                      | 27.2 (s)  | –                                       |
| $\text{RuHCl}(\text{CO})(\text{IMes})(\text{PPh}_3)_3$ , <b>8a</b>           | 42.1 (s)  | −23.9 (d, $^2J_{\text{PH}}$ 24 Hz)      |
| $\text{RuHCl}(\text{CO})(\text{H}_2\text{IMes})(\text{PPh}_3)_3$ , <b>8b</b> | 41.0 (s)  | −24.0 (d, $^2J_{\text{PH}}$ 24 Hz)      |
| $\text{RuHCl}(\text{CO})(\text{IMes})(\text{PCy}_3)_3$ , <b>3a</b>           | 47.8 (s)  | −24.8 (d, $^2J_{\text{PH}}$ 21 Hz)      |
| $\text{RuHCl}(\text{CO})(\text{H}_2\text{IMes})(\text{PCy}_3)_3$ , <b>3b</b> | 46.8 (s)  | −24.9 (d, $^2J_{\text{PH}}$ 21 Hz)      |

<sup>[a]</sup> Spectra measured at 298 K in  $\text{C}_6\text{D}_6$  unless otherwise noted.

<sup>[b]</sup> Very low solubility in  $\text{C}_6\text{D}_6$ ; spectra measured in  $\text{CDCl}_3$ .

time showed solely NMR signals for **2** and free  $\text{PPh}_3$ . The product was isolated by stripping off the solvent, extracting the free phosphane with diethyl ether, and filtering the slurry cold ( $-35^\circ\text{C}$ ) to minimize the solubility of **2**. Two cycles of washing with cold diethyl ether and ethanol afforded clean **2** in nearly 90% yield. NMR analysis showed only the hydride triplet and  $^{31}\text{P}\{^1\text{H}\}$  NMR singlet due to **2**. Advantages of this route are the high yield and purity of the product, as well as the experimental convenience associated with the short reaction time. Several routes to **2** from first-generation Grubbs' metathesis catalysts of the type  $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHR})$  (**6**) have also been reported.<sup>[37]</sup> These are of considerable interest from the perspective of tandem catalysis<sup>[38]</sup> (whether designed, or unintended), but their synthetic utility is otherwise limited by the cost of the Ru-alkylidene precursor.

The corresponding mono-NHC derivatives **3a/b** form, among other products, during decomposition of the second-generation Grubbs' catalysts  $\text{RuCl}_2(\text{NHC})(\text{PCy}_3)(=\text{CHPh})$  (**7a**: NHC = IMes; **7b**: NHC =  $\text{H}_2\text{IMes}$ ) by primary alcohols.<sup>[11,37]</sup> Clean, quantitative synthesis of **3b** has been reported *via* cross-metathesis of **7b** with vinyloxytrimethylsilane, followed by heating at  $50^\circ\text{C}$ .<sup>[24]</sup> Routes to **3** from non-alkylidene precursors have centered on use of **2** as a precursor.  $\text{RuHCl}(\text{CO})(\text{IMes})(\text{PCy}_3)$  **3a** was originally prepared by Yi, Nolan, and co-workers in *ca.* 70% yield, by reaction of **2** with IMes in toluene at  $80^\circ\text{C}$  for 2 h, followed by 18 h further reaction at room temperature (Scheme 2).<sup>[25]</sup> Dinger and Mol reported that the corresponding  $\text{H}_2\text{IMes}$  complex **3b** is likewise accessible by this approach. They were able to reduce the reaction time to a total of 3 h by increasing the thermolysis temperature to  $100^\circ\text{C}$ ,<sup>[11]</sup> but commented on the presence of by-products that could not be separated from the desired product.

We find that  $\text{RuHCl}(\text{CO})(\text{NHC})(\text{PPh}_3)$  **8a/b** give clean access to **3a/b** by selective exchange of the triphenylphosphane ligand with  $\text{PCy}_3$ . The precursor

complexes **8** are themselves accessible in high yield and excellent purity by reaction of **1** with equimolar amounts of IMes or  $\text{H}_2\text{IMes}$ .<sup>[26,39]</sup> The ligand exchange with  $\text{PCy}_3$  proceeds slowly at room temperature ( $<10\%$  over 12 h), but reaction is complete within 2 h at  $80^\circ\text{C}$ . No other ruthenium species were evident by *in situ* NMR analysis, and the products were isolated as yellow, microcrystalline powders in *ca.* 85% yield. Their identities were confirmed by comparison to the NMR values reported for **3a**<sup>[11,25]</sup> or **3b**,<sup>[24]</sup> respectively. In each case, the upfield location of the hydride doublet indicates a square pyramidal geometry with apical hydride and one basal phosphane ligand. The NHC signals show the expected multiplicities and integration values, confirming that the ligand remains intact.

## Conclusions

The foregoing describes clean, high-yield routes to coordinatively unsaturated ruthenium hydridocarbonyl complexes containing electron-rich  $\text{PCy}_3$  and NHC ligands.  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  **1** is a convenient precursor to the versatile catalyst  $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$  **2** and also, *via* the  $\text{RuHCl}(\text{CO})(\text{NHC})(\text{PPh}_3)$  complexes **8a/b**, to the NHC derivatives  $\text{RuHCl}(\text{CO})(\text{NHC})(\text{PCy}_3)$  **3a/b**.

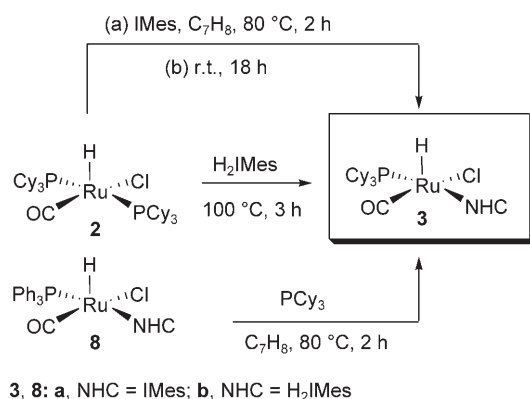
## Experimental Section

### General Procedures

Reactions were carried out under argon, using standard Schlenk or glove-box techniques. Dry, oxygen-free solvents were obtained using an Anhydrous Engineering solvent purification system, and stored over Linde 4 Å molecular sieves.  $\text{C}_6\text{D}_6$  was degassed by consecutive freeze/pump/thaw cycles and dried over activated sieves (Linde 4 Å).  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  **1**<sup>[36]</sup> and  $\text{RuHCl}(\text{CO})(\text{NHC})(\text{PPh}_3)$  **8**<sup>[26]</sup> were prepared according to literature methods. NMR spectra were recorded on a Bruker Avance 300 or AMX-500 spectrometer at 298 K, using the residual proton signals of the deuterated solvent as internal standard ( $^1\text{H}$  NMR). Peaks are reported in ppm, relative to TMS ( $^1\text{H}$ ) or 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) at 0 ppm. Microanalysis was carried out by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

### $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ (**2**); New Route from $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (**1**)

To a pale pink suspension of **1** (0.500 g, 0.525 mmol) in benzene (200 mL) was added solid  $\text{PCy}_3$  (0.450 g, 1.61 mmol), causing an immediate color change to pale yellow. A homogeneous solution was formed after stirring for 3 h at  $40^\circ\text{C}$ : an aliquot removed at this time showed solely  $^{31}\text{P}$  NMR signals for **2** and free  $\text{PPh}_3$ . The solvent was stripped off under vacuum, and  $\text{Et}_2\text{O}$  (15 mL) was added to extract the free



**Scheme 2.** Reported and (bottom) new synthetic routes to **3a** and **3b**. For details of purity, see text.

phosphane. After chilling the suspension to  $-35^{\circ}\text{C}$  to minimize the solubility of **2**, the yellow product was filtered off, washed with EtOH ( $2 \times 5\text{ mL}$ ) and Et<sub>2</sub>O ( $2 \times 5\text{ mL}$ ), then dried under vacuum; yield 0.330 g (86%). NMR data agree with the reported<sup>[28]</sup> values; no other products are observed. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 46.9$  (s); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 2.72\text{--}1.15$  (m, 66H, Cy),  $-24.21$  (t, 1H, RuH, <sup>2</sup>J<sub>HP</sub> = 18.0 Hz).

### Reported (Sealed Tube) Route to **2** from [RuCl<sub>2</sub>(COD)]<sub>n</sub><sup>[28]</sup>

A stirred suspension of [RuCl<sub>2</sub>(COD)]<sub>n</sub> (0.193 g, 0.560 mmol) and PCy<sub>3</sub> (0.386 g, 1.4 mmol) in EtOH (6 mL) was heated in a Parr autoclave at  $90^{\circ}\text{C}$  for 48 h, then cooled to room temperature. The crude product was filtered off, washed extensively with EtOH, then Et<sub>2</sub>O, to extract RuCl<sub>2</sub>(CO)(PCy<sub>3</sub>)<sub>2</sub><sup>[29]</sup> and RuCl<sub>2</sub>(CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub><sup>[35]</sup> and dried under vacuum; yield 0.163 g (65%); contains traces (2–4%) of RuCl<sub>2</sub>(CO)(PCy<sub>3</sub>)<sub>2</sub>.

### Route to **2** from [RuCl<sub>2</sub>(COD)]<sub>n</sub> (Normal Boiling Point)

A suspension of [RuCl<sub>2</sub>(COD)]<sub>n</sub> (0.250 g, 0.446 mmol) and PCy<sub>3</sub> (0.500 g, 1.80 mmol) in EtOH (10 mL) was stirred at  $78^{\circ}\text{C}$  for 3 days under N<sub>2</sub>. The reaction mixture was allowed to cool, following which the orange product was filtered off, washed with EtOH ( $5 \times 3\text{ mL}$ ) then Et<sub>2</sub>O ( $5 \times 3\text{ mL}$ ), and dried under vacuum. The crude product was taken up in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and filtered through Celite to remove a dark, insoluble impurity. The filtrate was reduced to  $\sim 0.2\text{ mL}$ , then Et<sub>2</sub>O (20 mL) was added. The suspension was stirred for 2 days, with periodic changes of solvent, to extract **4**, **5**, and an unidentified impurity characterized by a <sup>31</sup>P{<sup>1</sup>H} NMR singlet at 24.4 ppm. The remaining bright yellow precipitate was filtered, washed with Et<sub>2</sub>O ( $10 \times 5\text{ mL}$ ) and dried under vacuum to yield spectroscopically clean **2**, yield: 0.120 g (37%).

### RuHCl(CO)(IMes)(PCy<sub>3</sub>) (**3a**)

To a stirred yellow-orange solution of RuHCl(CO)(IMes)(PPh<sub>3</sub>) (**8a**; 0.500 g, 0.683 mmol) in toluene (20 mL) was added solid PCy<sub>3</sub> (0.390 g, 1.39 mmol). Less than 10% **3a** was observed after 12 h at room temperature by <sup>31</sup>P NMR analysis, but conversion was complete within 2 h on heating to  $80^{\circ}\text{C}$ , although no color change occurred. The solution was concentrated under vacuum to ca. 0.5 mL, following which hexanes (30 mL) were added, and the mixture was chilled to  $-35^{\circ}\text{C}$ . The microcrystalline product was filtered off, washed with cold hexanes ( $3 \times 10\text{ mL}$ ), and dried under vacuum; yield: 0.430 g (84%). NMR data in C<sub>6</sub>D<sub>6</sub> are in good agreement with values reported in CD<sub>2</sub>Cl<sub>2</sub>,<sup>[25]</sup> with the minor exception of the multiplicity of the aromatic protons. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 47.8$  (s); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 6.83$  (s, 2H, Mes *m*-CH), 6.79 (s, 2H, Mes *m*-CH), 6.22 (s, 2H, NCH=CHN), 2.49 (s, 6H, CH<sub>3</sub>), 2.38 (s, 6H, CH<sub>3</sub>), 2.21–1.14 (m, 33H, Cy), 2.12 (s, 6H, CH<sub>3</sub>),  $-24.82$  (d, <sup>2</sup>J<sub>PH</sub> = 21.3 Hz, 1H, RuH).

### RuHCl(CO)(H<sub>2</sub>IMes)(PCy<sub>3</sub>) (**3b**)

Complex **3b** was prepared by reaction of RuHCl(CO)-(H<sub>2</sub>IMes)(PPh<sub>3</sub>) (0.485 g, 0.661 mmol) with PCy<sub>3</sub> (0.370 g, 1.32 mmol) in toluene at  $80^{\circ}\text{C}$ , as for **3a** above. In situ <sup>31</sup>P NMR analysis indicated quantitative conversion after 2 h, and **3b** was isolated; yield: 0.416 g (84%). NMR data in C<sub>6</sub>D<sub>6</sub> are in good agreement with the values reported<sup>[11,24]</sup> in CD<sub>2</sub>Cl<sub>2</sub>. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 46.8$  (s); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 6.85$  (s, 2H, Mes *m*-CH), 6.81 (s, 2H, Mes *m*-CH), 3.25 (s, 4H, NCH<sub>2</sub>), 2.67–2.55 (overlapping s, 12H, CH<sub>3</sub>), 2.22–2.20 and 1.89–1.09 (m, 33H, Cy), 2.13 (s, 6H, CH<sub>3</sub>),  $-24.90$  (d, <sup>2</sup>J<sub>PH</sub> = 21.3 Hz, 1H, RuH); anal. calcd. for C<sub>40</sub>H<sub>60</sub>ClN<sub>2</sub>OPRu: C 63.85, H, 8.04, N, 3.72%; found: C 64.32, H 8.30, N 3.85%.

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