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Reactivity of Tris(1-pyrazolyl)methane Towards Ru^0 Complexes

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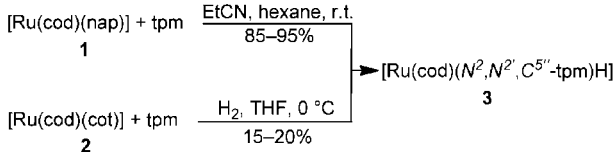
By treating tris(1-pyrazolyl)methane (tpm) with suitably activated [Ru(cod)(cot)] and [Ru(cod)(nap)] (cod = η^4-cycloocta-1,5-diene, cot = η^6-cycloocta-1,3,5-triene, nap = η^6-naphthalene) the (hydrido)Ru^{II} species [Ru(N^2,$N^{2'}$,$C^{5''}$-tpm)(cod)H] with cyclometalated tpm was obtained. This complex reacted with chloroform at room temperature to give [Ru(N^2,$N^{2'}$,$C^{5''}$-tpm)(cod)Cl] and dichloromethane. The coordination and symmetry of the novel complexes were elucidated by ^{1}H and ^{13}C NMR spectroscopy.

Introduction

Ru^{II} complexes containing tris(1-pyrazolyl)methane (tpm), which may act either as a bidentate or a *fac*-tridentate ligand, have been known for more than three decades and are well represented in the literature.[1] Recently, we contributed to this field of research by reporting on the synthesis and electrochemical, photochemical, and spectroelectrochemical behavior of the dinuclear symmetric species $[\{Ru(tpm)(L\text{-}L)\}_2(\mu\text{-}BL)]^{4+}$ (L-L = 2,2′-bipyridine, 1,10-phenanthroline, 2,2′-biquinoline; BL = pyrazine, 4,4′-bipyridine)[2] obtained from suitable mononuclear synthons by exploiting the "complexes-as-metals/complexes-as-ligands" synthetic strategy.[3] Within this framework, and aiming at novel Ru synthons, we decided to test the reactivity of tpm towards Ru^0 species, a topic not reported in the literature. Owing to their availability in our laboratories, we chose [Ru(cod)(nap)] (**1**) and [Ru(cod)(cot)] (**2**) (cod = η^4-cycloocta-1,5-diene, nap = η^6-naphthalene, cot = η^6-cycloocta-1,3,5-triene) as probe reactants. These pentacoordinate 18-electron complexes of a d^8 metal are rather stable at room temperature in dry solutions of noncoordinating solvents and can be activated towards the metathesis of cot by using nitriles[4] or dihydrogen.[5] In particular, we wondered whether tpm would behave as a tripodal N-donor ligand with retention of the formal oxidation state of the metal atom, as found with the d^8 metal complexes [M(tpm)(cod)]-ClO_4 [M = Rh^I or Ir^I],[6] or give rise to an oxidative addition with the consequent formation of a cyclometalated hexacoordinate Ru^{II} hydride, as in the d^6 species [Ir(N,N,C^5-tpm)(C_2H_4)(PPh_3)H]BF_4,[7] the sole example of cyclometalated tpm reported so far in the literature.

Results and Discussion

In the reactions of **1** and **2** with tpm (Scheme 1) we found that tpm, unlike its usual N_3 coordination, leads to cyclometalation at the 5-position of one of the pyrazolyl arms with the formation of the Ru^{II} hydride species **3**.



Scheme 1. Reaction of tpm with Ru^0 complexes **1** and **2**.

This behavior of tpm demonstrates that this ligand, at least at ordinary temperatures, is unable to stabilize a possible Ru^0 pentacoordinate species, because it is essentially a σ-donor system, unsuited to reducing the electron density on the metal atom by π-acceptance, instead giving rise to an oxidative addition that results in cyclometalation. This argument is strengthened by the fact that attempts to carry out the same reactions as reported in Scheme 1 by using tris(3,5-dimethyl-1-pyrazolyl)methane in place of tpm did not bear any results: The precursors decomposed, and the ligand was recovered unchanged.

The formation of **3** is much more convenient from **1** than from **2**, because **3** reacts further with dihydrogen despite the low reaction temperature. In fact, **3** was obtained almost pure by starting from **1**, whereas it must be purified by column chromatography when formed from **2**. Unlike the aforementioned Ir^{III} hydride, which is thermally unstable even at –10 °C, complex **3** is not only thermally stable at

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room temperature but also unreactive in air in which it can be safely manipulated. This stability is proven by the fact that the ν_{Ru-H} band at 2018 cm^{-1} persists for weeks in the IR spectrum (Figure 1) of a KBr pellet of **3** prepared and kept in air with no precautions.

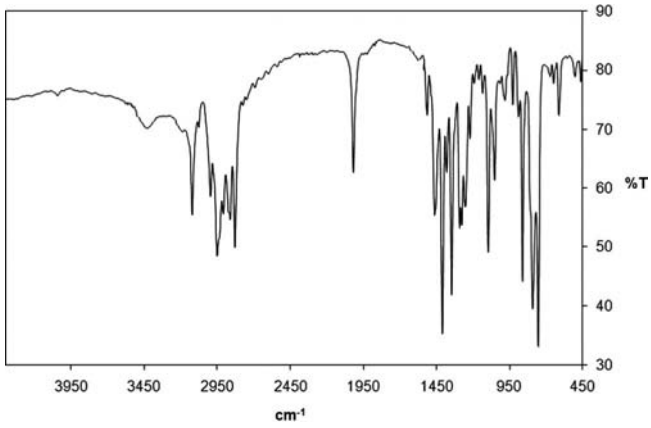
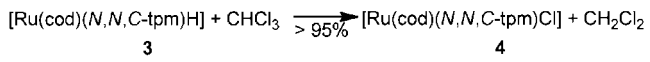


Figure 1. IR spectrum of complex **3** (KBr pellet).

The position of the ν_{Ru-H} band accounts for the reduced Ru–H bond strength with respect to analogous species in which tpm adopts the N_3 coordination mode, for example, $[Ru(tpm)(PPh_3)_2H]^+$, the ν_{Ru-H} band of which occurs at 2054 cm^{-1}.[8] Most likely this effect is caused by an increase in the negative charge on the Ru atom as a consequence, in addition to other minor differences, to the coordination of a formally anionic carbon atom instead of a neutral nitrogen atom.

Complex **3** promptly reacted with chloroform at room temperature to give dichloromethane and [Ru(cod)-(N^2,$N^{2'}$,$C^{5''}$-tpm)Cl] (**4**; Scheme 2). Reactions identical to that reported in Scheme 2 are known for similarly capped Ru^{II} hydrides, such as $[RuCp(PR_3)H]$[9] (PR_3 = PMe_nPh_{3-n}; n = 0–3) and $[RhTp(PPh_3)(CO)H]$.[10]

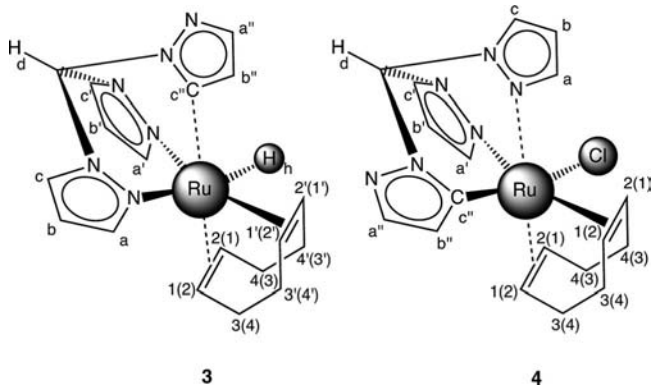


Scheme 2.

The structures of the novel complexes (Scheme 3) were elucidated by ^1H and ^{13}C NMR spectroscopy: The spectra are shown in Figures 2 and 3, and spectral data are reported in Table 1.

The ^1H NMR spectrum of complex **3** (Figure 2a) shows a singlet at δ = –7.32 ppm due to the hydrido ligand (H_h in Scheme 3). Moreover, three distinct sets of ^1H signals ascribable to the protons of the pyrazole rings can be distinguished. In particular, two different AMX systems are observed with chemical shifts and J coupling constants similar to those of the pyrazole rings in [tris(pyrazolyl)methane]- and [tris(pyrazolyl)borato]ruthenium complexes;[11–14] these can be assigned to the protons on the tpm rings *N*-bonded to the ruthenium atom. The assignment of these signals to a specific pyrazole ring has been tentatively made on the basis of the ^1H and ^{13}C NMR chemical shifts reported in the literature for *N*-coordinated pyrazole ligands in the *trans* position relative to η^2-coordinated cod or hydrido ligands in [TpRu(cod)H],[13] [Tp^{Ms}Ru(cod)H],[15] and [TpOs-(cod)H][16] complexes [Tp = tris(pyrazolyl)borate, Tp^{Ms} = hydridotris(3-mesitylpyrazolyl)borate]. The protons H_a, $H_{a'}$, H_c, and $H_{c'}$ have been assigned on the basis of that for pyrazoles $^3J_{bc} > {}^3J_{ab}$ (and $^3J_{b'c'} > {}^3J_{a'b'}$).[17,18]

The number and frequency of the corresponding ^{13}C NMR resonances (Table 1, Figure 2b) confirm this interpretation. The ^1H NMR signals of the third set of pyrazole protons correspond to an AX system, whereas three resonances are observed in the ^{13}C NMR spectrum. These findings indicate that the remaining pyrazole ring is bonded



Scheme 3. Structures of complexes **3** and **4** with the atomic labelling for the NMR assignments.

Table 1. ^1H and ^{13}C NMR spectroscopic data of complexes **3** and **4** with assignments as shown in Scheme 3.

Complex **3** ([D_6]DMSO, 25 °C)			Complex **4** ($CDCl_3$, 25 °C)		
Position[a]	δ_H [ppm]	δ_C [ppm]	Position[a]	δ_H [ppm]	δ_C [ppm]
h	–7.32	–	d	9.72	79.8
d	9.20	78.8	a,a′	7.62	144.1
a	8.36	143.6	b,b′	6.21	108.1
b	6.57	106.8	c,c′	7.94	131.5
c	8.38	132.0	a′′	7.71	139.5
a′	7.68	140.9	b′′	6.95	117.6
b′	6.37	107.3	c′′	–	[b]
c′	8.28	131.2	1(2)	4.41	86.4
a′′	7.10	138.6	2(1)	3.52	82.8
b′′	5.83	112.3	3a(4a)	2.18	31.0
c′′	–	165.9	3e(4e)	2.80	31.0
1(2)	4.10	78.3	4a(3a)	2.12	29.5
2(1)	2.90	75.5	4e(3e)	3.15	29.5
1′(2′)	3.55	66.6			
2′(1′)	2.35	63.2			
3a(4a)	1.90	34.3			
3e(4e)	2.32	34.3			
4a(3a)	1.95	31.5			
4e(3e)	2.55	31.5			
3′a(4′a)	2.50	30.5			
3′e(4′e)	2.05	30.5			
4′a(3′a)	2.02	27.6			
4′e(3′e)	1.90	27.6			

[a] "a" and "e" indicate the axial and equatorial CH_2 protons of cod, respectively. [b] Given the low solubility of **4** in $CDCl_3$, the ^{13}C δ values were obtained from a ^1H-^{13}C HMQC experiment in which the signal of $C_{c''}$ was not detected.

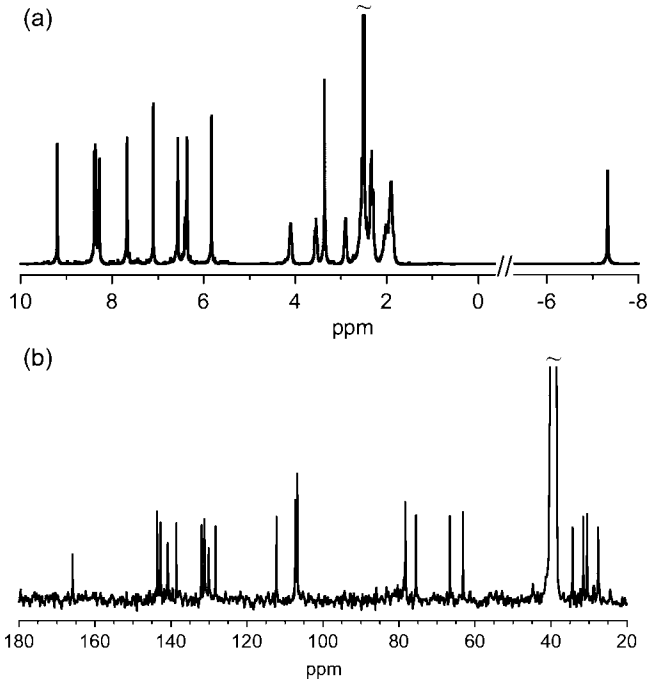


Figure 2. (a) ^1H and (b) ^{13}C NMR spectra of complex **3** in [D_6]-DMSO.

to the ruthenium atom through a carbon atom at the 5-position (c′′ in Scheme 3), in analogy to what has been observed in cyclometalated pyrazole complexes of iridium[7] and platinum,[19] thus providing evidence for cyclometalation of the tpm. The apical tpm hydrogen atom (H_d in Scheme 3) appears only slightly deshielded with respect to the free ligand (δ = 9.20 vs. 8.93 ppm in [D_6]DMSO solution) in spite of the high hydrogen-bonding ability of DMSO, which in coordinated tpm can result in a deshielding effect of more than 1.5 ppm.[2] Most likely the formal negative charge on the ligand (also revealed by the low chemical shift values of $H_{a''}$ and $H_{b''}$) strongly reduces the hydrogen-bonding ability of the tpm methine group. Note that in complex **4** the H_d proton resonates at δ = 9.72 ppm in $CDCl_3$ solution (Table 1), an increase of 1.29 ppm compared with free tpm in the same solvent, which accounts for the very different inductive effect exerted by a chlorido ligand with respect to a hydrido ligand and also confirms that such effects on the benzyl-like position are particularly efficient, because they are mediated by three aromatic rings.[2]

The cod signals in the ^1H and ^{13}C NMR spectra of **3** (Table 1, Figure 2) indicate a totally asymmetric environment for this ligand. In fact, four multiplets and four different resonances are observed in the ^1H and ^{13}C NMR spectra, respectively, which can be ascribed to four inequivalent olefinic protons and carbon atoms in cod. Moreover, the CH_2 groups give eight multiplets in the ^1H NMR spectrum and, correspondingly, four peaks in the ^{13}C NMR spectrum. Although the NMR spectroscopic data do not allow an unambiguous assignment of the cod signals, they can in part (primed and unprimed positions) be tentatively attributed as reported in Table 1 on the basis of literature data for similar systems.[13] Overall, the ^1H and ^{13}C NMR spectroscopic data indicate that complex **3** is octahedral with C_1 symmetry, as shown in Scheme 3.

The structure of complex **4** was elucidated by ^1H NMR (Figure 3) and ^1H-^{13}C HMQC NMR experiments. The obtained data (Table 1) show that the N^2,$N^{2'}$,$C^{5''}$ coordination of tpm is maintained from **3** to **4**, but complex **4** has a higher symmetry with respect to complex **3**. In fact, for complex **4** the pyrazole rings *N*-bonded to the ruthenium atom are equivalent, and the CH and CH_2 groups of cod are equivalent in pairs, as also observed in other systems,[20] which clearly indicates that a symmetry plane containing the *C*-bonded pyrazole ring and the chlorido ligand and passing through the bonds joining the sp^3 carbon atoms of cod, is present in the molecule. These findings indicate that complex **4** is octahedral with C_s symmetry, as shown in Scheme 3. Note that a quasi-isomer of **4** is reported in the literature, namely the cationic species $[Ru(tpm)(cod)Cl]^+$, prepared from Ru^{II} precursors, in which the tripodal ligand adopts the more usual N_3 coordination.[21,22]

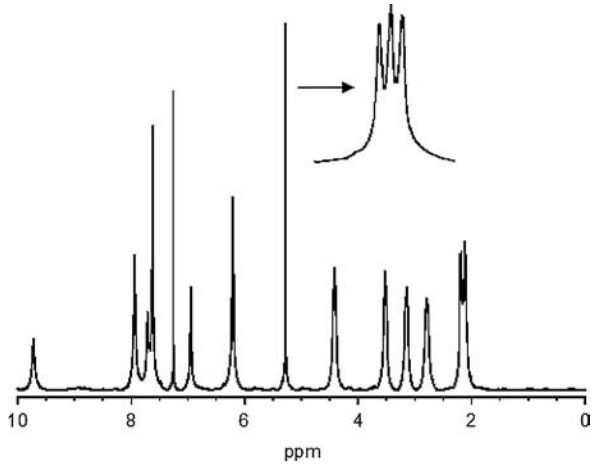


Figure 3. ^1H NMR spectrum of the solution resulting from a suspension of **3** in $CDCl_3$. The inset shows the structure of the signal due to the deuterium-coupled hydrogen atom of $CHDCl_2$.

A comparison of the topological features of complexes **3** and **4** is particularly interesting: Although in both species the monoatomic ligand (hydrido or chlorido, respectively) is in a *cis* position with respect to the two double bonds of cod, its relationship with the cyclometalated pyrazole ring is *cis* in complex **3**[23] but *trans* in complex **4**. Note that the stereochemistry of the latter does not seem to respect the electronic requirements of the chloride ion, which is a π-donor ligand, although fairly weak.

Conclusions

We have proven that in reactions with Ru^0 species tpm can act as a tripodal ligand through two nitrogen atoms at the 2-position of two pyrazole rings and the carbon atom

(bearing a formal negative charge) at the 5-position of the third pyrazole ring, giving rise to a cyclometalated product. Such behavior of tpm is unprecedented for Ru^{II} complexes, and to the best of our knowledge it has only been reported in one case.[7] Out of the possible mechanisms,[24] the cyclometalation reported herein involves an aromatic C–H oxidative addition that most likely is facilitated by the combined effect of the two N atoms in the ring, which reduces the charge density at the 5-position.

Experimental Section

Materials and Instrumentation: All chemicals (Aldrich) were used as received. Solvents were of HPLC grade and were purified according to standard methods. Complexes **1**[4] and **2**[25] were prepared as reported in the literature. All reactions were carried out under argon. IR spectra (KBr pellets) were recorded with a Perkin–Elmer Spectrum RX1 FT spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker AMX300WB instrument working at 300.13 MHz for ^1H and 75.47 MHz for ^{13}C. Chemical shifts (δ) are given in ppm relative to TMS as internal standard. All signals in the ^1H NMR spectra were assigned on the basis of ^1H-^1H COSY experiments. ^{13}C NMR resonances were assigned with the support of ^1H-^{13}C HMQC experiments performed by using an inverse probe. All spectra were recorded at 298 K. Electrospray ionization mass spectra (ESI-MS) were recorded by using a solution of the complex in methanol. The spectra were acquired with an Applied Biosystems Sciex API 4000 triple quadrupole mass spectrometer (MDS Sciex Concord, ON, Canada) by the flow injection analysis technique. Data were acquired and elaborated by using the Data System Software Analyst 1.4.2.

[Ru(N^2,$N^{2'}$,$C^{5''}$-tpm)(cod)H] (3): Anhydrous propionitrile (1.2 mL) was added to a mixture of **1** (0.285 g, 0.84 mmol) and tpm (0.181 g, 0.84 mmol) in anhydrous and deaerated *n*-hexane under argon. The orange solution that formed was stirred at room temp. for 4 h. During this time the color progressively disappeared, and a grey solid formed. The suspension was filtered under argon, and the residue was repeatedly washed with anhydrous *n*-hexane and vacuum-dried (0.320 g, 90%). IR (KBr): $\tilde{\nu}_{max}$ = 3122 (m), 2995 (m), 2952 (m), 2861 (m), 2830 (m), 2018 (m), 1465 (s), 1409 (s), 1378 (m), 1345 (s), 1293 (m), 1275 (m), 1221 (w), 1135 (w), 1097 (m), 1049 (w), 977 (w), 927 (w), 886 (w), 860 (m), 792 (s), 751 (s), 647 (w), 612 (w), 604 (w), 500 (w) cm^{-1}. ^1H NMR ([D$_6$]DMSO, 298 K): δ = –7.32 (s, 1 H, h-H), 1.90 (br. m, 2 H, 3a-H, 4′e-H), 1.95 (br. m, 1 H, 4a-H), 2.02 (br. m, 1 H, 4′a-H), 2.05 (br. m, 3′e-H), 2.32 (m, 1 H, 3e-H), 2.35 (m, 1 H, 2′-H), 2.50 (br. m, 1 H, 3′a-H), 2.55 (br. m, 1 H, 4e-H), 2.90 (m, 1 H, 2-H), 3.55 (m, 1 H, 1′-H), 4.10 (m, 1 H, 1-H), 5.83 (d, $^3J_{a''b''}$ = 1.5 Hz, 1 H, b′′-H), 6.37 (dd, 1 H, b′-H), 6.57 (dd, 1 H, b-H), 7.10 (d, 1 H, a′′-H), 7.68 (d, $^3J_{a'b'}$ = 2.2 Hz, 1 H, a′-H), 8.28 (d, $^3J_{b'c'}$ = 2.7 Hz, 1 H, c′-H), 8.36 (d, $^3J_{ab}$ = 1.9 Hz, 1 H, a-H), 8.38 (d, $^3J_{bc}$ = 2.6 Hz, 1 H, c-H), 9.20 (s, 1 H, d-H) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 298 K): δ = 165.9 (C-c′′), 143.6 (C-a), 140.9 (C-a′), 138.6 (C-a′′), 132.0 (C-c), 131.2 (C-c′), 112.3 (C-b′′), 107.3 (C-b′), 106.8 (C-b), 78.8 (C-d), 78.3 (C-1), 75.5 (C-2), 66.6 (C-1′), 63.2 (C-2′), 34.3 (C-3), 31.5 (C-4), 30.5 (C-3′), 27.6 (C-4′) ppm. MS (ESI): isotope cluster centered at *m*/*z* = 423.1 (100%), superimposable on the isotope cluster calcd. for $[M - H]^+$. $C_{18}H_{22}N_6Ru$ (423.48): calcd. C 51.05, H 5.27, N 19.85; found C 50.93, H 5.36, N 19.63. The same product was obtained, although in much lower yield and with very poor purity, by treating **2** with tpm at 0 °C in anhydrous and deaerated THF solution saturated with dihydrogen for 20 h.

[Ru(N^2,$N^{2'}$,$C^{5''}$-tpm)(cod)Cl] (4): A suspension of **3** (0.025 g, 0.059 mmol) in anhydrous and deaerated chloroform (15 mL) kept under argon was warmed to 40 °C. The mixture became a bright-green homogeneous solution, which, after a few minutes, was rotary-evaporated. The green solid residue was washed with pentane and vacuum-dried (0.026 g, 96%). IR (KBr): $\tilde{\nu}_{max}$ = 3120 (m), 2958 (m), 2872 (m), 1447 (m), 1406 (s), 1370 (w), 1338 (m), 1288 (s), 1275 (s), 1252 (m), 1223 (w), 1097 (m), 1057 (m), 987 (w), 920 (w), 863 (m), 783 (s), 759 (s), 731 (m), 668 (w), 648 (w), 609 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 298 K): δ = 2.12 (d, J_{gem} = 8.1 Hz, 2 H, 4a-H), 2.18 (d, J_{gem} = 8.7 Hz, 2 H, 3a-H), 2.80 (m, 2 H, 3e-H), 3.15 (m, 2 H, 4e-H), 3.52 (br. m, 2 H, 2-H), 4.41 (br. m, 2 H, 1-H), 6.21 (br. s, 2 H, b-H, b′-H), 6.95 (br. s, 1 H, b′′-H), 7.62 (br. s, 2 H, a-H, a′-H), 7.71 (br. s, 1 H, a′′-H), 7.94 (br. s, 2 H, c-H, c′-H), 9.72 (s, 1 H, d-H) ppm. A high spectral resolution could not be achieved due to sample inhomogeneity and low solubility of the complex in $CDCl_3$. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ = 144.1 (C-a, C-a′), 139.5 (C-a′′), 131.5 (C-c, C-c′), 117.6 (C-b′′), 108.1 (C-b, C-b′), 86.4 (C-1), 82.8 (C-2), 79.8 (C-d), 31.0 (C-3), 29.5 (C-4) ppm. For this sample, given the low solubility, ^{13}C signals were obtained only from the ^1H-^{13}C HMQC experiment and therefore the C-c′ signal was not detected. $C_{18}H_{21}ClN_6Ru$ (457.93): calcd. C 47.21, H 4.62, N 18.35; found C 47.09, H 4.48, N 18.28.

Acknowledgments

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[1] For a recent review, see: H. R. Bigmore, S. C. Lawrence, P. Mountford, C. S. Tredget, *Dalton Trans.* **2005**, 635–651.
[2] M. Guelfi, F. Puntoriero, S. Serroni, G. Denti, *Eur. J. Inorg. Chem.* **2011**, 709–720.
[3] S. Serroni, G. Denti, *Inorg. Chem.* **1992**, *31*, 4251–4255, and references therein.
[4] P. Pertici, G. Vitulli, *Comments Inorg. Chem.* **1991**, *11*, 175–194.
[5] M. A. Bennett, H. Neumann, M. Thomas, X. Q. Wang, P. Pertici, G. Vitulli, P. Salvadori, *Organometallics* **1991**, *10*, 3237–3245.
[6] M. A. Esteruelas, L. A. Oro, M. C. Apreda, C. Foces-Foces, F. H. Cano, R. M. Claramunt, C. Lopez, J. Elguero, M. Begtrup, *J. Organomet. Chem.* **1988**, *344*, 93–108.
[7] D. M. Heinekey, W. J. Oldham, J. S. Wiley, *J. Am. Chem. Soc.* **1996**, *118*, 12842–12843.
[8] H. S. Chu, Z. Xu, S. M. Ng, C. P. Lau, Z. Lin, *Eur. J. Inorg. Chem.* **2000**, 993–1000.
[9] S. T. N. Freeman, F. R. Lemke, C. M. a-Har, S. P. Nolan, J. L. Petersen, *Organometallics* **2000**, *19*, 4828–4833.
[10] N.-Y. Sun, S. J. Simpson, *J. Organomet. Chem.* **1992**, *434*, 341–349.
[11] Y. Takahashi, M. Akita, S. Hikichi, Y. Moro-oka, *Organometallics* **1998**, *17*, 4884–4888.
[12] A. E. Corrochano, F. A. Jalon, A. Otero, M. M. Kubicki, P. Richard, *Organometallics* **1997**, *16*, 145–148.
[13] F. A. Jalón, A. Otero, A. Rodriguez, *J. Chem. Soc., Dalton Trans.* **1995**, 1629–1633.
[14] C. Gemel, G. Trimmel, C. Slugovc, S. Kremel, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1996**, *15*, 3998–4004.
[15] C. Pariya, C. D. Incarvito, A. L. Rheingold, K. H. Theopold, *Polyhedron* **2004**, *23*, 439–444.
[16] P. W. Dickinson, G. S. Girolami, *Inorg. Chem.* **2006**, *45*, 5215–5224.
[17] L. A. Oro, M. Esteban, R. M. Claramunt, J. Elguero, C. Foces-Foces, F. H. Cano, *J. Organomet. Chem.* **1984**, *276*, 79–97.

[18] G. Minghetti, M. A. Cinellu, A. L. Bandini, G. Banditelli, F. De Martin, M. Manassero, *J. Organomet. Chem.* **1986**, *315*, 387–399.
[19] A. J. Canty, N. J. Minchin, J. M. Patrick, A. H. White, *J. Chem. Soc., Dalton Trans.* **1983**, 1253–1259.
[20] J. Elguero, M. Esteban, M. F. Grenier-Loustalot, L. A. Oro, M. T. Pinillos, *J. Chim. Phys. Phys.-Chim. Biol.* **1984**, *81*, 25–254.
[21] D. C. Wilson, J. H. Nelson, *J. Organomet. Chem.* **2003**, *682*, 272–289.
[22] M. Fajardo, A. de la Hoz, E. Diéz-Barra, F. A. Jalón, A. Otero, A. Rodriguez, J. Tejeda, D. Belletti, M. Lanfranchi, M. A. Pellinghelli, *J. Chem. Soc., Dalton Trans.* **1993**, 1935–1939.
[23] This configuration is usual for *ortho*-metalated (hydrido)Ru^{II} complexes; for example, see: J. Matthes, S. Gründemann, A. Toner, Y. Guari, B. Donnadieu, J. Spandl, S. Sabo-Etienne, E. Clot, H.-H. Limbach, B. Chaudret, *Organometallics* **2004**, *23*, 1424–1433.
[24] M. Albrecht, *Chem. Rev.* **2010**, *110*, 576–623.
[25] K. Itoh, H. Nagashima, T. Ohshima, N. Oshima, H. Nishiyama, *J. Organomet. Chem.* **1994**, *272*, 179–188.

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