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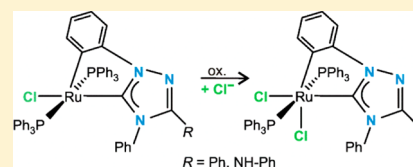
# Reactions of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with Nitron and with the “Enders Carbene”: Access to Ruthenium(III) NHC Complexes

Sandra Hitzel, Christian Färber,<sup>†</sup> Clemens Bruhn, and Ulrich Siemeling\*

Institute of Chemistry, University of Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

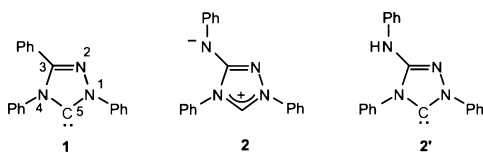
## Supporting Information

**ABSTRACT:** The reactions of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  with the “Enders carbene” 1,3,4-triphenyl-1,2,4-triazol-5-ylidene (**1**) and the “instant carbene” Nitron (**2**) respectively afforded the  $\text{Ru}^{\text{II}}$  chelates  $[\text{RuCl}(\text{3})(\text{PPh}_3)_2]$  (**3** = 3,4-diphenyl-1-*o*-phenylene-1,2,4-triazol-5-ylidene) and  $[\text{RuCl}(\text{4})(\text{PPh}_3)_2]$  (**4** = 4-phenyl-3-phenylamino-1-*o*-phenylene-1,2,4-triazol-5-ylidene) in a process involving the ortho metalation of the 1-Ph group of the respective carbene ligand. It proved possible to synthesize  $[\text{RuCl}(\text{3})(\text{PPh}_3)_2]$  more conveniently in higher yield by using the stable carbene precursor 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazole (MeO-1-H) instead of the free carbene **1** in the presence of triethylamine to trap the HCl generated by the ortho metalation. Aerobic oxidation of the  $\text{Ru}^{\text{II}}$  chelates in the presence of chloride ions furnished  $[\text{RuCl}_2(\text{3})(\text{PPh}_3)_2]$  and  $[\text{RuCl}_2(\text{4})(\text{PPh}_3)_2]$ , which are rare examples of  $\text{Ru}^{\text{III}}$  NHC complexes. The crystal structures of all four complexes were determined by single-crystal X-ray diffraction studies. In addition, the crystal structure of the hydrochloride of Nitron was also determined. In the  $\text{Ru}^{\text{II}}$  chelates, the pentacoordinate metal center is in a distorted-square-pyramidal environment with the carbon atom of the ortho-metallated 1-Ph group occupying the apical position. The coordination sphere of the  $\text{Ru}^{\text{III}}$  chelates is complemented by a second chlorido ligand, which is positioned *trans* to this carbon atom.



The report of the first N-heterocyclic carbene (NHC) by Arduengo and co-workers in 1991<sup>1</sup> triggered the development of such persistent singlet carbenes from laboratory curiosities to key compounds for manifold applications, particularly in catalysis.<sup>2</sup> The first applications of NHCs in transition-metal catalysis go back to work by Herrmann and co-workers, who realized the great potential of NHCs as ancillary ligands in palladium-mediated cross-coupling reactions<sup>3</sup> and in ruthenium-mediated olefin metathesis.<sup>4</sup> The 1,2,4-triazol-5-ylidene derivative **1** (Figure 1) introduced by Enders and co-

workers in 1995<sup>5</sup> soon proved to be extremely useful in organocatalysis and therefore was the first NHC to become commercially available.<sup>2c,o,t</sup> We recently demonstrated that Nitron (**2**), which was introduced as an analytical reagent for gravimetric anion analysis in 1905 and has been commercially available since then at a comfortably low price,<sup>6</sup> exhibits a reactivity in solution which is typical of an NHC.<sup>7</sup> This can be ascribed to the presence of the carbenic tautomer **2'** (Figure 1), which is akin to the “Enders carbene” **1** both structurally and electronically, as is reflected by their essentially identical Tolman



**Figure 1.** The 1,2,4-triazol-5-ylidene **1** (with numbering scheme for the heterocyclic ring), the conventional structure of Nitron (**2**), and the structure of its NHC-type tautomer **2'**.

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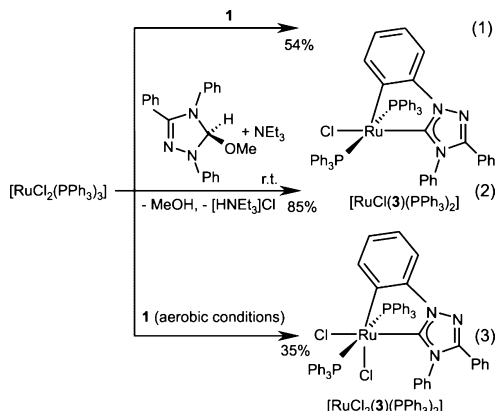
## RESULTS AND DISCUSSION

We have not been able to reproduce the published synthesis of  $[\text{RuCl}_2(\text{PPh}_3)_2(\text{1})]$ . In our hands, the reaction of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  with **1** (1 equiv) in dichloromethane at room temperature afforded the dark red cyclometalated  $\text{Ru}^{\text{II}}$  complex  $[\text{RuCl}(\text{3})(\text{PPh}_3)_2]$  in 54% yield, together with the poorly soluble triazolium chloride  $[\text{1-H}]\text{Cl}$  (Scheme 1, eq 1).

Strictly anaerobic conditions were necessary to obtain this  $\text{Ru}^{\text{II}}$  complex in pure form. Adventitious oxygen resulted in the formation of the  $\text{Ru}^{\text{III}}$  complex  $[\text{RuCl}_2(\text{3})(\text{PPh}_3)_2]$ , which was notoriously difficult to remove and hampered the NMR spectroscopic analysis of the crude product due to its paramagnetic nature. However, this unwanted oxidative process can be utilized for a rational synthesis of  $[\text{RuCl}_2(\text{3})(\text{PPh}_3)_2]$ . Performing the reaction of **1** with  $[\text{RuCl}_2(\text{PPh}_3)_3]$  in the

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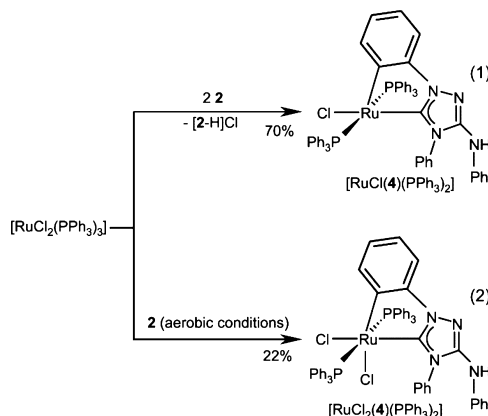
Scheme 1. Synthesis of  $[\text{RuCl}_n(3)(\text{PPh}_3)_2]$  ( $n = 1, 2$ )

presence of dry air afforded this  $\text{Ru}^{\text{III}}$  compound in 35% yield (Scheme 1, eq 3).

$[\text{RuCl}(3)(\text{PPh}_3)_2]$  and  $[\text{RuCl}_2(3)(\text{PPh}_3)_2]$  both contain the chelating NHC ligand **3** formed from **1** by ortho metalation of the 1-phenyl substituent. Cycloruthenation reactions<sup>11</sup> involving **1** are not unprecedented and have been found to occur selectively with the 1-Ph substituent.<sup>12</sup> Baratta et al. have obtained the hexacoordinate  $\text{Ru}^{\text{II}}$  complex  $[\text{RuCl}(3)(\text{PPh}_3)(\text{ampy})]$  (ampy = 2-(aminomethyl)pyridine) from the reaction of the hydrido complex  $[\text{RuHCl}(\text{PPh}_3)_2(\text{ampy})]$  with **1**,<sup>13</sup> and Simal et al. have prepared the  $\text{Ru}^{\text{II}}$  complex  $[\text{RuCl}(3)(p\text{-cymene})]$  from  $[\{\text{RuCl}(\mu\text{-Cl})(p\text{-cymene})\}_2]$  and **1** in the presence of Hünig's base.<sup>14</sup> The ortho-metalation process is accompanied by elimination of  $\text{H}_2$  and  $\text{HCl}$ , respectively, in these two cases.  $\text{HCl}$  elimination occurs in our case as well. This might explain why  $[\text{RuCl}(3)(\text{PPh}_3)_2]$  was obtained in a yield of only ca. 50%, since obviously **1** also acts as a base in this reaction, "mopping up" the  $\text{HCl}$  produced in the cyclometalation. Gratifyingly, it was possible to improve the yield of  $[\text{RuCl}(3)(\text{PPh}_3)_2]$  by using  $\text{NEt}_3$  for this purpose. It turned out that it is not even necessary to use the free carbene **1** in this reaction. Its stable precursor  $\text{MeO-1-H}$  can be applied instead without compromising the yield. The established synthesis of **1** requires heating of  $\text{MeO-1-H}$  to 80 °C in vacuo for 24 h to ensure quantitative elimination of  $\text{MeOH}$ .<sup>15</sup> We found that this compound can be used conveniently even at room temperature as a source of **1**. The reaction of  $\text{MeO-1-H}$  with  $[\text{RuCl}_2(\text{PPh}_3)_3]$  furnished  $[\text{RuCl}(3)(\text{PPh}_3)_2]$  in 85% isolated yield, together with the poorly soluble triethylammonium chloride (Scheme 1, eq 2). In contrast, temperatures of at least 80 °C were applied in the few previous cases, where metal complexes of **1** were synthesized directly from  $\text{MeO-1-H}$ .<sup>16</sup> The only exception appears to be  $[\text{RuCl}_2(\text{=CHPh})(\text{PPh}_3)(\textbf{1})]$ , which was described to be formed already at 40 °C from  $[\text{RuCl}_2(\text{=CHPh})(\text{PPh}_3)_2]$  and  $\text{MeO-1-H}$  in  $\text{C}_6\text{D}_6$  solution.<sup>16c</sup> The reaction of  $\text{MeO-1-H}$  with  $[\text{RuCl}_2(\text{PPh}_3)_3]$  in the presence of dry air afforded  $[\text{RuCl}_2(3)(\text{PPh}_3)_2]$  in less reproducible yields usually inferior to that obtained by the method shown in Scheme 1.

With these results obtained with the "Enders carbene" **1** in hand, we performed analogous experiments using the inexpensive "instant carbene" Nitron (**2**) and indeed found very similar behavior. Instead of using  $\text{NEt}_3$  as a base to trap any  $\text{HCl}$  produced by cyclometalation, we performed the reaction of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  with **2** using 2 equiv of the latter, since **2** readily forms insoluble salts of the type  $[\text{2-H}]\text{X}$ . This procedure afforded the dark red cyclometalated  $\text{Ru}^{\text{II}}$  complex  $[\text{RuCl}(\textbf{4})(\text{PPh}_3)_2]$  in

70% yield, together with  $[\text{2-H}]\text{Cl}$ , which precipitated in essentially quantitative yield (Scheme 2, eq 1). Again, great

Scheme 2. Synthesis of  $[\text{RuCl}_n(\textbf{4})(\text{PPh}_3)_2]$  ( $n = 1, 2$ )

care was necessary to prevent oxidative contamination with  $[\text{RuCl}_2(\textbf{4})(\text{PPh}_3)_2]$ . When the reaction was performed in the presence of dry air, this  $\text{Ru}^{\text{III}}$  complex was isolated in 22% yield (Scheme 2, eq 2). The high sensitivity of the 16-valence-electron (VE) complexes  $[\text{RuCl}(3)(\text{PPh}_3)_2]$  and  $[\text{RuCl}(\textbf{4})(\text{PPh}_3)_2]$  toward aerobic oxidation is in contrast to the behavior of the 18-VE complex  $[\text{RuCl}(3)(p\text{-cymene})]$ <sup>14</sup> and closely related species,<sup>12</sup> which are perfectly air stable.

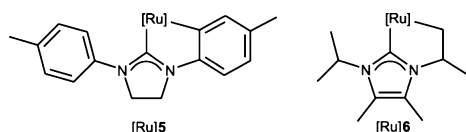
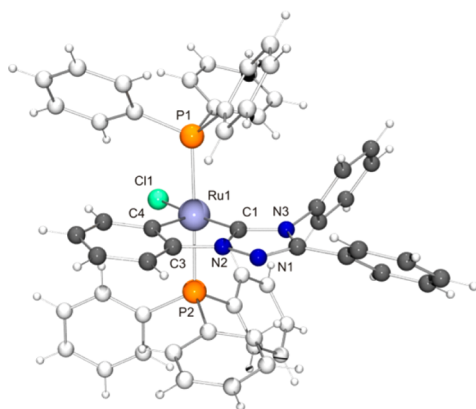
We have determined the structures of all four ruthenium complexes by single-crystal X-ray diffraction studies. In addition, we have also determined the crystal structure of the hydrochloride of Nitron, which crystallized as the solvate  $[\text{2-H}]\text{Cl} \cdot \text{CH}_3\text{OH}$  from a methanol solution (see the Supporting Information). Pertinent bond parameters of the ruthenium complexes are collected in Table 1, together with those of the hexacoordinate  $\text{Ru}^{\text{II}}$  complexes  $[\text{RuCl}(3)(\text{PPh}_3)(\text{ampy})]$  and  $[\text{RuCl}(3)(p\text{-cymene})]$  and the related five-coordinate complexes  $[\text{RuCl}(5)(\text{PEt}_3)_2]$ <sup>17</sup> and  $[\text{RuCl}(6)(\text{PPh}_3)_2]$ ,<sup>18</sup> which contain cycloruthenated NHC ligands derived from 1,4-di-*p*-tolylimidazol-5-ylidene (**5**) and 1,4-diisopropyl-2,3-dimethylimidazol-5-ylidene (**6**) (Figure 2). The molecular structures of the  $\text{Ru}^{\text{II}}$  chelate  $[\text{RuCl}(3)(\text{PPh}_3)_2]$  and of the  $\text{Ru}^{\text{III}}$  chelate  $[\text{RuCl}_2(\textbf{4})(\text{PPh}_3)_2]$  are shown in Figures 3 and 4, respectively (see the Supporting Information for the molecular structures of  $[\text{RuCl}(\textbf{4})(\text{PPh}_3)_2]$  and  $[\text{RuCl}_2(3)(\text{PPh}_3)_2]$ ).

The  $\text{Ru}^{\text{II}}$  atom of  $[\text{RuCl}(3)(\text{PPh}_3)_2]$  and  $[\text{RuCl}(\textbf{4})(\text{PPh}_3)_2]$ , respectively, is in a pentacoordinate environment, which is best described as distorted square pyramidal, with the  $\text{C}_{\text{aryl}}$  atom of the ortho-metalated 1-Ph group in the apical position. The  $\text{PPh}_3$  ligands are in a *trans* arrangement. The  $\text{Cl-Ru-C}_{\text{carbene}}$  coordination angles of 166.22(7)° (**3**) and 170.07(11)° (**4**), respectively, are much wider than the  $\text{Cl-Ru-C}_{\text{aryl}}$  angle, which has values of 116.76(7)° (**3**) and 112.53(10)° (**4**), respectively. This trend is also observed for the other five-coordinate complexes: viz.,  $[\text{RuCl}(5)(\text{PEt}_3)_2]$  and  $[\text{RuCl}(6)(\text{PPh}_3)_2]$ . The  $\text{Ru-C}_{\text{carbene}}$  (ca. 1.98 Å) and  $\text{Ru-C}_{\text{aryl}}$  bond lengths (ca. 2.04 Å) of  $[\text{RuCl}(3)(\text{PPh}_3)_2]$  and  $[\text{RuCl}(\textbf{4})(\text{PPh}_3)_2]$  as well as the bite angle of their respective bidentate ligands (ca. 77°) are indistinguishable within experimental error and compare well with those of the other complexes given in Table 1. All  $\text{Ru}^{\text{II}}$  complexes of Table 1 have the chlorido ligand *trans* to the carbene ligand, the  $\text{Ru-Cl}$  bond lengths being essentially identical for the five-coordinate cases ( $\sim 2.46$  Å). We now turn

**Table 1.** Selected Bond Lengths (Å) and angles (deg) for the Ru Complexes of This Study and for Related Ru<sup>II</sup> Complexes with Cycloruthenated NHC Ligands

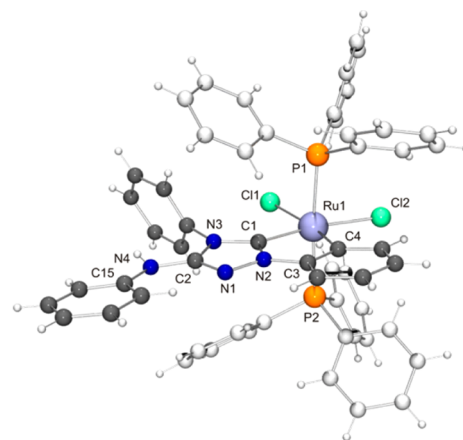
compd	Ru–C <sub>carbene</sub>	Ru–C <sub>aryl</sub>	Ru–Cl	Cl–Ru–C <sub>carbene</sub>	Cl–Ru–C <sub>aryl</sub>	C <sub>aryl</sub> –Ru–C <sub>carbene</sub>	ref
[RuCl(3)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>	1.972(2)	2.044(2)	2.4516(6)	166.22(7)	116.76(7)	76.72(10)	this work
[RuCl(4)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>	1.978(4)	2.037(3)	2.4679(9)	170.07(11)	112.53(10)	77.29(14)	this work
[RuCl(3)(PPh <sub>3</sub> )(ampy)] <sup>b</sup>	1.970(2)	2.070(2)	2.5040(6)	175.12(7)	98.96(6)	78.96(9)	13
[RuCl(3)( <i>p</i> -cymene)] <sup>c</sup>	2.004(3)	2.071(3)	2.4187(8)	84.06(8)	87.63(8)	76.77(11)	14
[RuCl(5)(PEt <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>	1.911(9)	2.006(8)	2.455(2)	171.5(3)	110.2(3)	78.3(4)	17
[RuCl(6)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>	1.970(2)	2.116(2) <sup>d</sup>	2.4535(4)	159.34(6)	125.05(6)	75.61(8)	18
[RuCl <sub>2</sub> (3)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>b</sup>	2.032(8)	1.988(14)	2.394(2) <sup>e</sup>	171.2(3) <sup>e</sup>	91.7(3) <sup>e</sup>	79.5(5)	this work
			2.418(3) <sup>f</sup>	89.9(3) <sup>f</sup>	169.0(3) <sup>f</sup>		
[RuCl <sub>2</sub> (4)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>b</sup>	2.052(7)	2.087(8)	2.394(2) <sup>e</sup>	170.1(2) <sup>e</sup>	93.6(2) <sup>e</sup>	77.1(3)	this work
			2.435(2) <sup>f</sup>	89.4(2) <sup>f</sup>	166.2(2) <sup>f</sup>		

<sup>a</sup>Coordination number (CN) 5. <sup>b</sup>CN 6. <sup>c</sup>CN 6 if the 6-VE donor  $\eta^6$ -*p*-cymene is counted as occupying three coordination sites. <sup>d</sup>Ru–CH<sub>2</sub>. <sup>e</sup>Cl *trans* to C<sub>carbene</sub>. <sup>f</sup>Cl *trans* to C<sub>aryl</sub>.

**Figure 2.** Schematic structures of ruthenium complexes containing the anionic bidentate NHC ligands 5 and 6.**Figure 3.** Molecular structure of [RuCl(3)(PPh<sub>3</sub>)<sub>2</sub>] in the crystal. Selected bond lengths (Å) and angles (deg) not discussed in the text: C1–N2 1.360(3), C1–N3 1.391(3), P1–Ru1 2.3626(7), P2–Ru1 2.3780(6); N2–C1–N3 102.1(2), P1–Ru1–P2 175.89(2).

our attention to [RuCl<sub>2</sub>(3)(PPh<sub>3</sub>)<sub>2</sub>] (Table 1, Supporting Information) and [RuCl<sub>2</sub>(4)(PPh<sub>3</sub>)<sub>2</sub>] (Table 1, Figure 4). The Ru<sup>III</sup> atom is in a distorted pseudo-octahedral coordination environment in each case. The PPh<sub>3</sub> ligands are in the *trans* orientation already observed for the respective Ru<sup>II</sup> analogue, leading to a *cis* orientation of the chlorido ligands. The Ru–Cl bond *trans* to the C<sub>aryl</sub> atom is slightly, but significantly, longer than that *trans* to the C<sub>carbene</sub> atom, in accord with the notion that hydrocarbyl ligands have an even higher *trans* influence than carbene ligands.<sup>19</sup> The hexacoordinate nature of both complexes causes a trend toward elongation of the metal bond lengths in comparison to the respective pentacoordinate Ru<sup>II</sup> analogue.

Note that Ru<sup>III</sup> NHC complexes are rare. A common feature of the few examples known to date is the presence of an anionic, and chelating, NHC ligand. This profile is also shown by 3 and 4. The first example was reported by Arnold and Scarisbrick in 2004, utilizing a tridentate alkoxy-functionalized bis(carbene) ligand.<sup>20</sup> Its synthesis involved a redox reaction of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] with the corresponding silver(I) NHC complex, affording elemental

**Figure 4.** Molecular structure of [RuCl<sub>2</sub>(4)(PPh<sub>3</sub>)<sub>2</sub>] in the crystal. Selected bond lengths (Å) and angles (deg) not discussed in the text: C1–N2 1.347(9), C1–N3 1.399(9), P1–Ru1 2.413(2), P2–Ru1 2.416(2); N2–C1–N3 102.1(6), Cl1–Ru1–Cl2 100.01(7), P1–Ru1–P2 175.41(8).

silver and the Ru<sup>III</sup> chelate. Very recently, Severin and co-workers reported a dinuclear mixed-valence Ru<sup>II</sup>/Ru<sup>III</sup> complex, which also contains an anionic, alkoxy-functionalized NHC chelate ligand.<sup>21</sup> The final example is a hexacoordinate scorpionate complex containing two anionic tris(carbene)borate ligands, which was recently reported by Chen et al. as the first structurally characterized Ru<sup>III</sup> NHC complex.<sup>22</sup> Similar to the case for [RuCl<sub>2</sub>(3)(PPh<sub>3</sub>)<sub>2</sub>] and [RuCl<sub>2</sub>(4)(PPh<sub>3</sub>)<sub>2</sub>], the synthesis of this complex utilized a Ru<sup>II</sup> starting material and involved aerobic oxidation during workup. The authors note that the Ru<sup>III</sup>–C<sub>carbene</sub> bond lengths (mean value 2.073 Å) are very similar to those reported for hexacoordinate Ru<sup>II</sup> NHC complexes.

## CONCLUSION

Our study has furnished the following main results. First, we cannot confirm the report by Melis and Verpoort which describes the synthesis of [RuCl<sub>2</sub>(1)(PPh<sub>3</sub>)<sub>2</sub>] from [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] and the “Enders carbene” 1.<sup>10</sup> Instead, we find the clean formation of the chelate [RuCl(3)(PPh<sub>3</sub>)<sub>2</sub>] as a result of a cycloruthenation process, which involves the 1-Ph group of 1. Second, instead of the free carbene 1 its precursor MeO-1-H can be conveniently used for the synthesis of this product. Third, the Ru<sup>II</sup> chelate [RuCl(3)(PPh<sub>3</sub>)<sub>2</sub>] is surprisingly air-sensitive, giving easy access to the corresponding Ru<sup>III</sup> chelate [RuCl<sub>2</sub>(3)-(PPh<sub>3</sub>)<sub>2</sub>]. Last, but not least, the behavior of the inexpensive



analytical reagent Nitron (2) in this study is strictly analogous to that of the "Enders carbene" **1**, which further supports the notion of the presence of the carbenic tautomer **2'** in solution (Figure 1).<sup>7</sup>

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Text giving experimental details and characterization data for all new complexes, figures showing NMR spectra (<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P) of [RuCl(3)(PPh<sub>3</sub>)<sub>2</sub>] and [RuCl(4)(PPh<sub>3</sub>)<sub>2</sub>] and molecular structures of [RuCl(4)(PPh<sub>3</sub>)<sub>2</sub>], [RuCl<sub>2</sub>(3)(PPh<sub>3</sub>)<sub>2</sub>], and [2-H]Cl·CH<sub>3</sub>OH, and CIF files giving crystallographic information for [RuCl(3)(PPh<sub>3</sub>)<sub>2</sub>]·PhCH<sub>3</sub>, [RuCl(4)(PPh<sub>3</sub>)<sub>2</sub>], [RuCl<sub>2</sub>(3)(PPh<sub>3</sub>)<sub>2</sub>], [RuCl<sub>2</sub>(4)(PPh<sub>3</sub>)<sub>2</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, and [2-H]Cl·CH<sub>3</sub>OH. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail for U.S.: [siemeling@uni-kassel.de](mailto:siemeling@uni-kassel.de).

### Present Address

<sup>†</sup>Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany.

### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Arduengo, A. J., III; Harlow, R. L.; Kline, M. J. *Am. Chem. Soc.* **1991**, *113*, 361–363.
- (2) Selected reviews: (a) Hock, S. J.; Schaper, L.-A.; Hermann, W. A.; Kühn, F. E. *Chem. Soc. Rev.* **2013**, *42*, 5073–5089. (b) Budagumpi, S.; Endud, S. *Organometallics* **2013**, *32*, 1537–1562. (c) Fèvre, M.; Pinaud, J.; Gnanou, Y.; Vignolle, J.; Taton, D. *Chem. Soc. Rev.* **2013**, *42*, 2142–2172. (d) Oehninger, L.; Rubbiani, R.; Ott, I. *Dalton Trans.* **2013**, *42*, 3269–3284. (e) Siemeling, U. *Eur. J. Inorg. Chem.* **2012**, 3523–3536. (f) Liu, W.; Gust, R. *Chem. Soc. Rev.* **2013**, *42*, 755–773. (g) Díez-González, S., Ed. *N-Heterocyclic Carbenes*; Royal Society of Chemistry: Cambridge, U.K., 2011. (h) Gil, W.; Trzeciak, A. M. *Coord. Chem. Rev.* **2011**, *255*, 473–483. (i) Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940–6952. (j) de Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862–892. (k) Samojłowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev.* **2009**, *109*, 3708–3742. (l) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122–3172. (m) Glorius, F., Ed. *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Springer: Berlin, 2007; Topics in Organometallic Chemistry 21. (n) Dragutan, V.; Dragutan, I.; Delaude, L.; Demonceau, A. *Coord. Chem. Rev.* **2007**, *251*, 765–794. (o) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606–5655. (p) Kantchev, E. A. B.; O'Brien, C. J.; Orgen, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768–2813. (q) Colacino, E.; Martinez, J.; Lamaty, F. *Coord. Chem. Rev.* **2007**, *251*, 726–764. (r) Nolan, S. P., Ed. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH: Weinheim, Germany, 2006. (s) Alder, R. W.; Blake, M. E.; Chaker, L.; Harvey, J. N.; Paolini, F.; Schütz, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5896–5911. (t) Enders, D.; Balensiefer, T. *Acc. Chem. Res.* **2004**, *37*, 534–541. (u) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239–2246. (v) Cavell, K. J.; McGuinness, D. S. *Coord. Chem. Rev.* **2004**, *248*, 671–681. (w) César, V.; Bellemin-Lapontaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619–636. (x) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951–961. (y) Peris, E.; Crabtree, R. H. *C. R. Chim.* **2003**, *6*, 33–37. (z) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, 617–618, 70–80.
- (3) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371–2374.
- (4) (a) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490–2493. For closely related seminal work, see: (b) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678. (c) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247–2250. (d) Ackermann, L.; Fürstner, A.; Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787–4790.
- (5) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J.-P.; Ebel, K.; Brode, S. *Angew. Chem., Int. Ed.* **1995**, *34*, 1021–1023.
- (6) (a) Harris, D. C. *Lehrbuch der quantitativen Analyse*; Vieweg: Braunschweig, Germany, 1998; Chapter 25.2. (b) Hioki, A.; Watanabe, T.; Terajima, K.; Fudagawa, N.; Kubota, M.; Kawase, A. *Anal. Sci.* **1990**, *6*, 757–762. Seminal papers: (c) Heck, J. E.; Hunt, H.; Mellon, M. G. *Analyst* **1934**, *59*, 18–25. (d) Vürtheim, A. *Recl. Trav. Chim. Pays-Bas* **1927**, *46*, 97–101. (e) Gutbier, A. *Angew. Chem.* **1905**, *18*, 494–499. (f) Busch, M. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 861–866.
- (7) (a) Färber, C.; Leibold, M.; Bruhn, C.; Maurer, M.; Siemeling, U. *Chem. Commun.* **2012**, *48*, 227–229. For related work, see: (b) Pidlynyi, N.; Namyslo, J. C.; Drafz, M. H. H.; Nieger, M.; Schmidt, A. J. *Org. Chem.* **2013**, *78*, 1070–1079. (c) César, V.; Tourneux, J.-C.; Vujkovic, N.; Brousses, R.; Lugan, N.; Lavigne, G. *Chem. Commun.* **2012**, *42*, 2349–2351.
- (8) (a) Delaude, L.; Demonceau, A. In ref 2g, pp 196–227. (b) Despagne-Ayoub, E.; Ritter, T. In ref 2m, pp 193–218. (c) Burling, S.; Paine, B. M.; Whittlesey, M. K. In ref 2r, pp 27–53. (d) Belling, S.; Bleichert, S. In ref 2r, pp 1–25.
- (9) Melis, K.; Verpoort, F. *J. Mol. Catal. A: Chem.* **2003**, *194*, 39–47.
- (10) Melis, K.; Verpoort, F. *J. Mol. Catal. A: Chem.* **2003**, *201*, 33–41.
- (11) For a recent review, see: Djukic, J. P.; Sortais, J.-B.; Barloy, L.; Pfeffer, M. *Eur. J. Inorg. Chem.* **2009**, 817–853.
- (12) For work with other *N*-phenyl-1,2,4-triazol-5-ylidenes, see: Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber./Recl.* **1997**, *130*, 1253–1260.
- (13) Baratta, W.; Schütz, J.; Herdtweck, E.; Herrmann, W. A.; Rigo, P. *J. Organomet. Chem.* **2005**, *690*, 5570–5575.
- (14) Simal, F.; Jan, D.; Delaude, L.; Demonceau, A.; Spirlet, M.-R.; Noels, A. F. *Can. J. Chem.* **2001**, *79*, 529–535.
- (15) Enders, D.; Breuer, K.; Kallfass, U.; Balensiefer, T. *Synthesis* **2003**, 1292–1295.
- (16) (a) Oehlke, E.; Kong, S.; Arciszewski, P.; Wiebalck, S.; Abram, U. *J. Am. Chem. Soc.* **2012**, *134*, 9118–9121. (b) Braband, B.; Neubacher, S.; Grosskopf, S.; Abram, U. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1645–1650. (c) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, D. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546–2558. (d) Braband, H.; Abram, U. *Chem. Commun.* **2003**, 2436–2437.
- (17) (a) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Thomas, S. J. *Chem. Soc., Dalton Trans.* **1979**, 1929–1942. (b) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 196–198.
- (18) Burling, S.; Mas-Marzá, E.; Valpuesta, J. E. V.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2009**, *28*, 6676–6686.
- (19) For a review, see: (a) Coe, B. J.; Gelnwright, S. J. *Coord. Chem. Rev.* **2000**, *203*, 5–80. Seminal paper: (b) Cowie, M.; Ibers, J. A. *Inorg. Chem.* **1976**, *15*, 552–557.
- (20) Arnold, P.; Scarisbrick, A. C. *Organometallics* **2004**, *23*, 2519–2521.
- (21) Tskhovrebov, A. G.; Solari, E.; Scopelliti, R.; Severin, K. *Organometallics* **2012**, *31*, 7235–7340.
- (22) Chen, F.; Wang, G.-F.; Li, Y.-Z.; Chen, X.-T.; Xue, Z.-L. *Inorg. Chem. Commun.* **2012**, *21*, 88–91.