Journal of Organometallic Chemistry 781 (2015) 11–22

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis, spectroscopy, structure, and reactivity of *bis*-azapentadienyl–ruthenium–phosphine complexes [1]

John R. Bleeke [a, *], Meghan Stouffer [a], Nigam P. Rath [b]

[a] Department of Chemistry, Washington University, One Brookings Drive, St. Louis, Missouri 63130, USA
[b] Department of Chemistry and Biochemistry, University of Missouri – St. Louis, One University Boulevard, St. Louis, Missouri 63121, USA

ARTICLE INFO

Article history:
Received 28 November 2014
Received in revised form
8 January 2015
Accepted 9 January 2015
Available online 19 January 2015

Keywords:
Heteropentadienyl ligands
Azapentadienyl–metal complexes
Ruthenium

ABSTRACT

We report the synthesis, spectroscopy, structure, and reactivity of the first examples of *bis*-azapentadienyl–ruthenium complexes. The parent compound, [(1,2,3-η^3)-(5-*tert*-butylazapentadienyl)]$_2$Ru(PPh$_3$)$_2$ (**1**), is produced by reacting Cl$_2$Ru(PPh$_3$)$_3$ with two equivalents of potassium *tert*-butylazapentadienide. Treatment of **1** with CNCMe$_3$, P(OMe)$_3$, PMe$_3$, or PEt$_3$ (L) in THF at room temperature yields single-ligand substitution products [(1,2,3-η^3)-(5-*tert*-butylazapentadienyl)]$_2$Ru(PPh$_3$)(L) (**2**, L = CNCMe$_3$; **3**, L = P(OMe)$_3$; **4**, L = PMe$_3$; **5**, L = PEt$_3$), and the double-ligand substitution product, [(1,2,3-η^3)-(5-*tert*-butylazapentadienyl)]$_2$Ru(PEt$_3$)$_2$ (**6**). Other double-ligand substitution products, [(1,2,3-η^3)-(5-*tert*-butylazapentadienyl)]$_2$Ru(L)$_2$ (**7**, L = PMe$_3$; **8**, L = P(OMe)$_3$), are obtained when **1** is treated with PMe$_3$ or P(OMe)$_3$ in THF at reflux. Compounds **7** and **8** exist in solution as equilibrium mixtures of two structural isomers. Electron-rich compounds **6** and **7** react with triflic acid to generate dicationic products,{[(1,2,3-η^3)-(CH$_2$CHCHCH=N(H)(CMe$_3$)]$_2$Ru(L)$_2$}$^{2+}$($^-$O$_3$SCF$_3$)$_2$ (**9**, L = PEt$_3$; **10**, L = PMe$_3$), in which *both* azapentadienyl nitrogen atoms have been protonated. All of the compounds reported herein have been characterized by NMR spectroscopy, and the structures of **2**, **3**, **4**, **6**, and **9** have been confirmed by single-crystal X-ray diffraction.

Introduction

Heteropentadienyl ligands (i.e., pentadienyl analogues in which one carbon has been replaced by a heteroatom such as O, S or NR) have attracted increasing attention because of their ability to access a wide variety of bonding modes in transition metal complexes [2,3]. Interconversions between these modes can enhance stoichiometric reactivity and perhaps even be used to open and close coordination sites in catalytic cycles. Recently, we have focused our efforts on azapentadienyl-transition metal complexes and have reported our findings in the Co [4], Rh [1], and Ir [1] systems. As expected, we have found that ligand shifts are integral to the reactivity of these complexes. Equally important, however, is the presence of the basic nitrogen atom, which represents a potential site of reactivity toward electrophiles, particularly when the nitrogen is not coordinated to the transition metal.

In this paper, we report the synthesis, spectroscopy, structure and reactivity of a new family of *bis*-azapentadienyl–ruthenium complexes. The parent compound, [(1,2,3-η^3)-(5-*tert*-butylazapentadienyl)]$_2$Ru(PPh$_3$)$_2$ (**1**), is generated in good yield from the reaction of Cl$_2$Ru(PPh$_3$)$_3$ [5] with two equivalents of potassium *tert*-butylazapentadienide (K$^+$ $^-$CH$_2$CH=CH–CH=NCMe$_3$) [6,7]. Interestingly, Paz-Sandoval et al. [8] have recently shown that the related reaction of Cl$_2$Ru(PPh$_3$)$_3$ with the trimethyltin derivative of *tert*-butylazapentadiene, Me$_3$SnCH$_2$–CH=CH–CH=NCMe$_3$ [9], leads *only* to the production of a *mono*-azapentadienyl-ruthenium compound, [(1,2,3,5-η^4)-(5-*tert*-butylazapentadienyl)]Ru(PPh$_3$)$_2$(Cl) [10]. Apparently, the more strongly nucleophilic character of our potassium salt enables the double displacement reaction, producing the *bis*-azapentadienyl–ruthenium product, **1**. Treatment of the parent compound with a range of ligands leads to ligand substitution and the production of a family of related compounds, some of which have been treated with the simplest of electrophiles, H$^+$. While members of this family have many structural similarities, they also exhibit some surprising differences, which are highlighted in this report.

* Corresponding author. Washington University, Campus Box 1134, One Brookings Drive, St. Louis, Missouri 63130-4899, USA. Tel.: +1 314 935 6809; fax: +1 314 935 4481.
E-mail address: bleeke@wustl.edu (J.R. Bleeke).

http://dx.doi.org/10.1016/j.jorganchem.2015.01.006
0022-328X/

Results and discussion

*Synthesis and spectroscopy of [(1,2,3-η³)-(5-tert-butylazapentadienyl)]₂Ru(PPh₃)₂ (**1**)*

Treatment of $Cl_2Ru(PPh_3)_3$ [5] with two equivalents of potassium *tert*-butylazapentadienide [6] leads to the production of [(1,2,3-η³)-(5-*tert*-butylazapentadienyl)]$_2$Ru(PPh$_3$)$_2$ (**1**) as a yellow-brown microcrystalline powder (see Scheme 1). The same product (albeit in reduced yield) is observed even when less than two equivalents of potassium *tert*-butylazapentadienide are used; there is no evidence of a *mono*-azapentadienyl-ruthenium product. The two azapentadienyl ligands in **1** are equivalent by NMR, consistent with the presence of a two-fold rotational symmetry axis. Hence, only one set of signals is observed by ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H NMR, the signal for the H4 protons appears downfield at δ 7.86 and is a doublet due to coupling to H3 ($J_{H4-H3} = 7.8$ Hz). The remaining protons on the coordinated allyl moieties appear at δ 4.53 (H2's), 3.03 (H1's), 1.80 (H3's), and 1.15 (H1's). In the $^{13}C\{^1H\}$ NMR, the uncoordinated C4 carbons resonate far downfield at δ 164.7 while the coordinated carbons appear at δ 86.2 (C2's), 55.6 (C3's), and 47.2 (C1's). The C3 signal shows strong coupling to phosphorus (J = 18.3 Hz), indicating that the azapentadienyl C3 carbons lie approximately *trans* to the phosphine ligands in the pseudo-octahedral coordination environment of **1** (*vide infra*).

The PPh$_3$ ligands are equivalent due to the presence of the two-fold rotational symmetry axis and hence give rise to a single peak, at δ 57.6, in the $^{31}P\{^1H\}$ NMR spectrum. In the infrared spectrum, the C═N stretch is observed at 1615.8 cm^{-1}. Attempts to obtain single crystals of **1** were unsuccessful, but the high resolution ESI mass spectrum showed the predicted isotopic envelope for $[M + H]^+$ and for the fragment ions resulting from loss of *tert*-butylazapentadiene, loss of triphenylphosphine, and loss of *both* *tert*-butylazapentadiene *and* triphenylphosphine from $[M + H]^+$.

Possible structural variants for [(1,2,3-η³)-(5-tert-butylazapentadienyl)]₂RuLL′ complexes

As shown in Fig. 1, there are actually ten possible structural variants for compounds of the type [(1,2,3-η^3)-(5-*tert*-butylazapentadienyl)]$_2$RuLL′. In structure **A** both ligands, L and L′, sit in the open mouths of the azapentadienyl allyl moieties ("mouth/mouth") and both azapentadienyl C3's lie *trans* to L or L′ ("C3/C3"). Overall, the structure is labelled "mC3/mC3". In structure **B**, one of the azapentadienyls has shifted to a backbone orientation (i.e., L′ sits under the backbone of one azapentadienyl allyl moiety), but the C3's still lie *trans* to L and L′ ("mC3/bC3"). In **C**, both azapentadienyls have adopted backbone orientations while retaining the *trans* relationships between the C3's and L/L′ ("bC3/bC3"). For the structures in the second row, one C1 and one C3 lie *trans* to L/L′, while in the third row, both C1's lie *trans* to L/L′. All of the various mouth/backbone combinations are included. Note that for structures in which the azapentadienyl groups do not possess 2-fold rotational symmetry, switching the positions of L and L′ will lead to additional isomers if L and L′ are different.

Although a crystal structure of **1** has not been obtained, its NMR spectra show two-fold symmetry, ruling out all of the possible structures except for **A**, **C**, **H**, and **J**. Furthermore, the strong coupling observed between C3 and phosphorus in the ^{13}C NMR points toward a C3/C3 structure, i.e., either **A** or **C**. While the "backbone/backbone" structure (**C**) is possible, it seems unlikely given the steric bulk of the PPh$_3$ ligands. Hence we conclude that the "mouth/mouth" orientation (**A**) is most likely for **1**, and this is how it is represented in Scheme 1 [11].

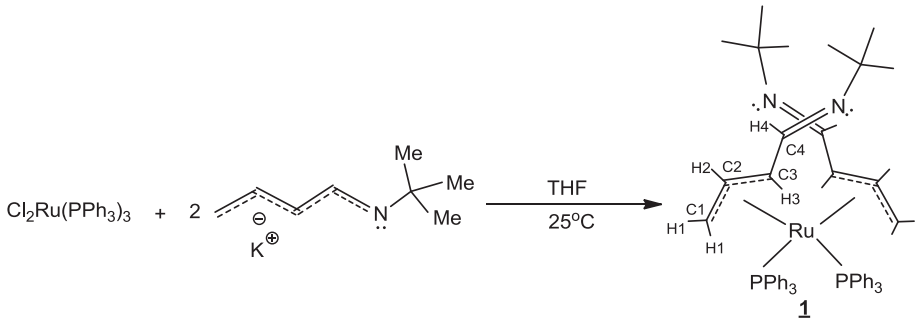
*Reactions of compound **1** with various ligands (L) at room temperature. Synthesis, spectroscopy and structure of [(1,2,3-η³)-(5-tert-butylazapentadienyl)]₂Ru(PPh₃)(L) (2, L = CNCMe₃; 3, L = P(OMe)₃; 4, L = PMe₃; 5, L = PEt₃) and [(1,2,3-η³)-(5-tert-butylazapentadienyl)]₂Ru(PEt₃)₂ (**6**)*

As shown in Scheme 2, treatment of compound **1** with a variety of potential ligands, including *tert*-butyl isocyanide, trimethyl phosphite, trimethylphosphine and triethylphosphine, at *room temperature* leads to ligand-substitution products **2**–**6**. Only in the case of PEt$_3$ is a *double* ligand substitution observed at room temperature.

*Synthesis and characterization of compound **2***

Treatment of **1** with excess *tert*-butyl isocyanide, the smallest and least electron-donating ligand of this group, produces [(1,2,3-η^3)-(5-*tert*-butylazapentadienyl)]$_2$Ru(PPh$_3$)(CNCMe$_3$) (**2**) as a yellow crystalline solid in 89% yield. As expected, the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **2** show two sets of signals for the inequivalent azapentadienyl ligands. In the $^{13}C\{^1H\}$ spectrum, the two C4's appear downfield at δ 160.8 and 160.4, while the coordinated carbons resonate at δ 99.5/88.3 (C2's), 62.4/62.3 (C3's) and 46.3/40.5 (C1's). Only one of the C3 carbons shows phosphorus coupling (J_{C-P} = 20.6 Hz), because only one lies *trans* to a PPh$_3$ ligand. In the $^{31}P\{^1H\}$ NMR spectrum, the PPh$_3$ ligand resonates at δ 53.7.

The X-ray crystal structure of **2** is presented in Fig. 2; selected bond distances are reported in the figure caption. The molecule exhibits a pseudo-octahedral coordination geometry in which the C1's (C1 and C9 in Fig. 2) and the C3's (C3 and C11) of the azapentadienyl ligands, the phosphine ligand and the isocyanide ligand occupy the six coordination sites. Overall, the structure is of the "mC3/bC3" type (type **B** in Fig. 1). The C3's of the azapentadienyl ligands (C3 and C11) lie *trans* to the PPh$_3$ and CNCMe$_3$ ligands, respectively, while the C1's (C1 and C9) lie *trans* to each other. In addition, the PPh$_3$ ligand is situated in the open mouth of allyl



Scheme 1.