

Available online at www.sciencedirect.com





Polyhedron 27 (2008) 734-738

# Synthesis and structural characterization of a coordinatively unsaturated ruthenium complex, $Cp^*Ru(Ph_2nacnac)$ , and its CO adduct

Hui Huang <sup>a</sup>, Russell P. Hughes <sup>a,\*</sup>, Arnold L. Rheingold <sup>b</sup>

<sup>a</sup> Departments of Chemistry, 6128 Burke Laboratories, Dartmouth College, Hanover, NH 03755, United States <sup>b</sup> Department of Chemistry and Biochemistry, University of California at San Diego, San Diego, CA 92093, United States

> Received 25 June 2007; accepted 1 November 2007 Available online 11 December 2007

## Abstract

Two new half sandwich ruthenium complexes with 2-*N*-phenylamino-4-*N*-phenylimino-2-pentene (Ph<sub>2</sub>nacnac) ligands have been synthesized and characterized. Single crystal X-ray diffraction analysis reveals the monomeric, highly air sensitive complex Cp\*Ru(Ph<sub>2</sub>nacnac) (4) has a coordinatively unsaturated structure and the coordination environment around Ru(II) is effectively a triangle made up of Ct(Cp\*)–N(1)–N(2). An air stable complex Cp\*Ru(Ph<sub>2</sub>nacnac)(CO) (5) is prepared by reaction of 4 with CO, and has a *pseudo*-tetrahedral geometry around the Ru(II) center, made up of Ct(Cp\*)–N(1)–N(2)–C(28). © 2007 Elsevier Ltd. All rights reserved.

Keywords: Ruthenium; CO; Nacnac; Synthesis; Crystallography; Structure reactivity

## 1. Introduction

Half sandwich ruthenium complexes are of considerable interest to coordination chemists since they have been widely used in organometallic synthesis and enantioselective catalysis [1-3]. Clearly it is important to understand any correlations between structure and reactivity of these compounds in order to better understand their behavior as structural templates and catalysts. Coordinatively unsaturated ruthenium complexes of general formula  $RuCp^{*}(X)(PR_{3})$  have been obtained previously using bulky phosphine ligands ( $\mathbf{R} = \text{cyclohexyl}$ , *iso*-propyl) [4,5], and analogues of general formula  $\operatorname{RuCp}(L)^+$  (L = bulky chelating diimine) have also been reported [6-8]. To the best of our knowledge, there are few precedents for neutral, coordinatively unsaturated half sandwich ruthenium complexes stabilized by chelating ligands. One example, 1 reported by Kölle, contains a chiral ligand methyl(bis-5-methyl-

\* Corresponding author. *E-mail address:* rph@dartmouth.edu (R.P. Hughes). tetrahydrooxazol) ligand, but was only characterized by NMR spectroscopy [9]. Yamaguchi et al. reported Cp\*Ru-(amidinate) (2) as the first example in which amidinate ligands play an important role in effectively stabilizing a coordinatively unsaturated metal center [10]. An example with a less bulky chelate Cp\*Ru(acac) (3), initially reported as a neutral unsaturated monomer [11], was subsequently shown to be a dimer [12].



In recent years, transition metal complexes with  $\beta$ -diketiminate (nacnac) ligands have been the subject of considerable interest [13–18]. Here, we report on a brief

<sup>0277-5387/\$ -</sup> see front matter @ 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2007.11.002

investigation on the synthesis, characterization, and the crystal structure analysis of two half sandwich ruthenium complexes with the " $Ph_2nacnac$ " ligand.

## 2. Experimental

## 2.1. General

Air-sensitive reactions were performed in oven-dried glassware, using standard SCHLENK techniques, under an atmosphere of nitrogen, which was deoxygenated over BASF catalyst and dried over Aquasorb, or in a Braun drybox. Methylene chloride and hexane were dried over an alumina column under nitrogen [19]. Methanol was distilled from Linde type 4 Å molecular sieves. NMR spectra were recorded on a Varian Unity Plus 300 or 500 FT spectrometer. <sup>1</sup>H NMR spectra were referenced to the protio impurity in the solvent: C<sub>6</sub>D<sub>6</sub>  $\delta$  (7.16 ppm), CD<sub>2</sub>Cl<sub>2</sub>  $\delta$  (5.32 ppm). Coupling constants are reported as absolute values in units of Hertz. IR spectra were recorded on a Per-kin–Elmer FTIR 1600 Series spectrophotometer. Elemental analyses were performed by Schwartzkopf (Woodside, NY).

 $RuCl_3 \cdot 3H_2O$  (Johnson Matthey Ltd.) and pentamethylcyclopentadiene (Cp\*H) (Acros) were used without further purification. [Cp\*RuCl\_2]<sub>2</sub> [20] and Ph<sub>2</sub>nacnac [21] were prepared according to published methods.

## 2.1.1. Synthesis of $Cp^*Ru(Ph_2nacnac)$ (4)

 $[Cp^*RuCl_2]_2$  (50 mg, 0.17 mmol) and dry  $K_2CO_3$ (150 mg, 1.15 mmol) were suspended in dry N<sub>2</sub> saturated MeOH (10 mL) and allowed to stir for 6 h to give an intensely red solution with some solid. Ph<sub>2</sub>nacnac (41 mg, 0.17 mmol) was added to the solution, which was allowed to react for a half hour to give a red solution. The solvent was removed in vacuo to give a dark red solid, which was extracted with hexane (50 mL) and filtered. The solvent was removed from the filtrate to give the product as a dark red solid; 50 mg, 81%. Recrystallization by slow evaporation from hexane gave dark red crystals suitable for Xray diffraction. Anal. Calc. for C<sub>27</sub>H<sub>32</sub>N<sub>2</sub>Ru: C, 66.77; H, 6.64; N, 5.77. Found: C, 66.39; H, 6.94; N, 5.78%. <sup>1</sup>H NMR ( $C_6D_6$ , 300 MHz, 25 °C)  $\delta$  1.08 (15H, s,  $C_5(CH_3)_5$ ); 1.90 (6H, s, CH<sub>3</sub>); 5.39 (1H, s, HC); 7.00-7.26 (10H, m, H-Ph).

## 2.1.2. Synthesis of $Cp^*Ru(Ph_2nacnac)(CO)$ (5)

Cp\*Ru(Ph<sub>2</sub>nacnac) (23 mg, 0.047 mmol) was dissolved in hexane (10 mL) to give a red solution. CO (1.0 mL, 0.047 mmol) was added by syringe. The color lightened. CO (3 mL/time × 17 times) was added by syringe and the solution was allowed to react overnight to give a brown yellow solution. The solvent was removed *in vacuo* to give the adduct as yellow solid, with a little brown red tint; 24 mg, 99%. Recrystallization by slow evaporation from hexane gave yellow crystals suitable for X-ray diffraction. *Anal.* Calc. For C<sub>28</sub>H<sub>32</sub>N<sub>2</sub>ORu: C, 65.47; H, 6.28; N, 5.46. Found: C, 65.82; H, 6.81; N, 5.46%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 25 °C)  $\delta$  1.23 (1;H, s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 1.72 (6H, s, CH<sub>3</sub>); 4.50 (1H, s, HC); 6.97 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, *p*-H-Ph); 7.05 (4H, d, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, *o*-H-Ph); 7.26 (4H, t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, *m*-H-Ph). IR (hexane, cm<sup>-1</sup>):  $v_{CO}$  1910 (vs).

## 2.1.3. X-ray crystallography

Crystal data and other parameters for complexes 4 and 5 are given in Table 1. Intensity data were collected at 213(2) K, on Bruker Smart CCD diffractometers using graphite-monochromated Mo K $\alpha$  radiation (k =0.71073 Å). Of the 17,362 and 7558 reflections that were collected, 5488 ( $R_{int} = 0.0413$ ) and 4186 ( $R_{int} = 0.0249$ ) were unique for complexes 4 and 5, respectively. Empirical absorption corrections were employed. The structures were solved by direct methods. The final refinement was done by full-matrix least squares based on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms, and the hydrogen atoms were generated geometrically.

## 3. Results and discussion

Complex 4 was obtained via two steps in a one pot reaction with an overall yield of 81%. [Cp\*RuCl<sub>2</sub>]<sub>2</sub> was stirred with K<sub>2</sub>CO<sub>3</sub> in MeOH to give [Cp\*Ru(OMe)]<sub>2</sub>, which reacted with the Ph<sub>2</sub>nacnac ligand to give 4 as a red air-sensitive solid. Reaction of 4 with CO in hexane afforded 5 as a yellow solid in high yield as shown in Scheme 1. This yellow complex is moderately stable in air, unlike its acac analogue [11]. The CO stretching frequency in the IR of 5 is at 1910 cm<sup>-1</sup> in hexane, while that for the acac analogue Cp\*Ru(acac)(CO) is 1915 cm<sup>-1</sup> (KBr) [11]. There

Table 1 Crystal data for complexes **4** and **5** 

	4	5
Formula	$C_{27}H_{32}N_2Ru$	C <sub>28</sub> H <sub>32</sub> N <sub>2</sub> ORu
Formula weight	485.62	513.63
Space group	P2(1)/n	$P\overline{1}$
a (Å)	9.363(6)	7.2099(19)
b (Å)	23.983(15)	11.924(3)
<i>c</i> (Å)	11.137(7)	14.596(4)
α (°)		79.706(4)
β (°)	110.285(10)	75.865
γ (°)		81.585
$V(Å^3)$	2346(3)	1190.4(5)
Ζ	4	2
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.375	1.433
$\mu$ [Mo K $\alpha$ ] (mm <sup>-1</sup> )	0.684	0.681
Temp. (K)	213(2)	213(2)
Diffractometer	bruker smart apex CCD	bruker smart apex CCD
Radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
Crystal size (mm)	$0.30 \times 0.20 \times 0.10$	$0.40 \times 0.15 \times 0.08$
<i>F</i> (000)	1008	532
Measured reflections	17362	7558
Independent reflections	5488	4186
R (F), %	0.0446	0.0292
$R(wF^2), \%$	0.0991	0.0769

Table 2



was no reaction when complex  $\mathbf{4}$  was treated with  $H_2$  or ethylene.

The principal structural features of complex 4 are given in Fig. 1, while crystallographic data are summarized in Table 1 and selected bond lengths and angles appear in Table 2. In this complex, the plane of the nacnac ligand (N(2)-Ru(1)-N(1)) is perpendicular to the Cp<sup>\*</sup> plane, which differs from the dimeric acac analogue 3, in which the ligand plane is tilted with respect to the Ru-Cp\* by 37.5° [11]. The angle involving the metal center and the bis(ketenimine) ligand deviates significantly from 90°,  $N(1)-Ru(1)-N(2) = 87.70(9)^{\circ}$  and the bond distances Ru(1)-N(1) and Ru(1)-N(2) are 2.053(2) and 2.046(2) Å, respectively. The distance between Ru(1) and the center of the Cp\* ring is 1.800 Å. The five atoms in the bis(ketenimine) ligand and Ru(1) are coplanar. For example, the biggest deviation of C(11) to the least square plane (Ru(1)-N(2)-C(13)-C(12)-C(11)-N(1)) is 0.009 Å. The two C-C distances of 1.388(4) and 1.397(4) Å and the two C-N distances of 1.341(3) and 1.349(4) Å suggest significant delocalization within the  $\pi$ -system of the nacnac ligand. There are no intermolecular interactions in the solid state, consistent with the observation that the red color of 4 observed in the solid state is maintained in hexane solution.

During preparation of this manuscript, two similar complexes were reported. In nickel analogue **6**, reported by Bai et al. [22] the Ni–N distances were found to be 1.937(3) and 1.948(3) Å with a N–Ni–N angle of 94.19(11)°. The angle between the plane of the cyclopentadienyl ligand and NiN<sub>2</sub> plane was 90.8°. When **6** was treated with

Selected bond lengths (Å) and angles (°)	for 4 and 5
Complex 4	
Ru(1) - N(2) 2.046(2)	N(2)-Ru(1)-N(1) 87.70(9)
Ru(1)–N(1) 2.053(2)	N(2)-Ru(1)-C(3) 125.37(10)
Ru(1)-C(3) 2.141(3)	N(1)-Ru(1)-C(3) 128.84(10)
Ru(1)-C(5) 2.159(3)	N(2)-Ru(1)-C(5) 112.13(10)
Ru(1)–C(1) 2.168(3)	N(1)-Ru(1)-C(5) 143.35(9)
Ru(1)-C(2) 2.190(3)	N(2)-Ru(1)-C(1) 146.73(9)
Ru(1)-C(4) 2.199(3)	N(1)-Ru(1)-C(1) 110.40(9)
N(1)-C(11) 1.341(3)	N(2)-Ru(1)-C(2) 164.06(9)
N(2)-C(13) 1.349(4)	N(1)-Ru(1)-C(2) 104.07(10)
C(11)-C(12) 1.388(4)	N(2)-Ru(1)-C(4) 103.14(10)
C(12)-C(13) 1.397(4)	N(1)-Ru(1)-C(4) 166.84(9)
	C(11)–N(1)–Ru(1) 128.78(18)
	C(16)–N(1)–Ru(1) 117.33(17)
	C(13)-N(2)-Ru(1) 129.28(19)
	C(22)-N(2)-Ru(1) 116.99(16)
Complex 5	
Ru(1)-C(28) 1.837(2)	C(28)-Ru(1)-N(2) 95.25(9)
Ru(1)–N(2) 2.1309(19)	C(28)-Ru(1)-N(1) 94.79(9)
Ru(1)-N(1) 2.1363(19)	N(2)-Ru(1)-N(1) 88.30(7)
Ru(1)-C(22) 2.181(2)	N(2)-Ru(1)-C(22) 134.06(8)
Ru(1)–C(24) 2.214(2)	N(1)-Ru(1)-C(22) 136.60(8)
Ru(1)–C(20) 2.221(2)	N(2)-Ru(1)-C(24) 98.68(8)
Ru(1)-C(26) 2.290(2)	N(1)-Ru(1)-C(24) 153.56(8)
Ru(1)–C(18) 2.299(2)	N(2)-Ru(1)-C(20) 153.88(8)
O(1)–C(28) 1.157(3)	N(1)-Ru(1)-C(20) 100.60(8)
N(1)-C(10) 1.325(3)	N(2)-Ru(1)-C(26) 92.45(8)
N(1)-C(12) 1.429(3)	N(1)-Ru(1)-C(26) 117.42(8)
N(2)–C(7) 1.331(3)	N(2)-Ru(1)-C(18) 118.77(8)
N(2)–C(6) 1.437(3)	N(1)-Ru(1)-C(18) 92.80(8)
C(7)–C(9) 1.399(3)	C(10)-N(1)-Ru(1) 125.37(15)
C(9)–C(10) 1.403(3)	C(12)-N(1)-Ru(1) 116.17(14)
	C(7)-N(2)-Ru(1) 125.94(15)
	C(6)-N(2)-Ru(1) 115.86(14)
	O(1)–C(28)–Ru(1) 173.1(2)

[PhMe<sub>2</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] a cationic complex 7 was formed by protonation at the CH carbon of the nacnac ligand (Scheme 2). In that structure, the Ni–N distances were found to be 1.928(3) and 1.942(3) Å, a little longer than those reported for **6**, consistent with the poorer donor ability of the protonated nacnac ligand. However, the N–Ni–N bite angle in **7** is 95.50(12)°, similar to that in **6**. Similarly,



Fig. 1. ORTEP diagram of complex 4 showing atom numbering scheme. (A) Full view; (B) side view (2 Ph groups omitted for clarity).



the angle between the NiN<sub>2</sub> and Cp<sup>\*</sup> planes in 7 is 90.5° (see Scheme 3).

A similar 16-electron Ru cationic complex 8 was reported by Phillips et al. [23] The Ru-N bond distances are 1.997(5) and 1.994(5) Å, shorter than those in 4 (2.053(2) and 2.046(2) Å), and the arene centroid to Ru distance is 1.670 Å, also shorter than the Cp\*-Ru distance in 4 (1.800 Å). These differences can perhaps be attributed to the effect of the cationic Ru atom in 8. The bite angle N-Ru-N is 88.5(2)°, similar to that of 4. Though neutral complex 4 has no reaction with  $H_2$  and ethylene, 8 can react with H<sub>2</sub> and ethylene in THF to give 9 and 10, respectively by incorporation of the CH carbon of the nacnac ligand in the reaction chemistry.

In contrast to the lack of reactivity of 4 towards H<sub>2</sub> or ethylene, reaction with CO occurred cleanly to afford adduct 5, the principal structural features of which are given in Fig. 2. Crystallographic data are summarized in Table 1, and selected bond lengths and angles appear in Table 2. The coordination environment around Ru(1) is pseudo-tetrahedral. The angle involving the metal center and the bis(ketenimine) ligand deviates from  $90^{\circ}$  (N(1)–

Α

 $Ru(1)-N(2) = 88.30(7)^{\circ}$  with bond distances Ru(1)-N(1)and Ru(1)-N(2) of 2.1363(19) and 2.1309(19) Å, respectively. The distance between Ru(1) and the center of the Cp\* ring is 1.885 Å. In this complex, the least squares plane of the nacnac ligand and Ru(1) (Ru(1)-N(2)-C(7)-C(9)-C(10)-N(1)) is tilted toward the Cp<sup>\*</sup> plane with an interplanar angle of 45.6°. There is still significant delocalization within the  $\pi$ -system of the nacnac ligand, suggested by the two similar C-C distances of 1.399(2) and 1.403(3) Å and the two similar C-N distances of 1.331(3) and 1.325(3) Å. The Ru-nacnac ring itself is, however, less planar than that in 4, with the largest deviation from the least squares plane of (Ru(1)-N(2)-C(7)-C(9)-C(10)-N(1)) being the Ru atom, which is displaced from the plane by 0.100 Å. The Ru–carbonyl bond distance Ru(1)–C(28) (1.837(2) Å) is shorter than those in two cationic analogues, 11 (1.865(8) Å) [24], and 12, 1.880(3) Å [25]. The Ru-C(O) bond distance in the analogue Cp\*Ru(amidinate)(CO) is 1.828(7) Å [10] that is identical within experimental error to that of 5.



Fig. 2. ORTEP diagram of complex 5 showing atom numbering scheme. (A) Full view; (B) side view (2 Ph groups omitted for clarity).

 $PF_6$ 

## 4. Conclusions

It is evident that the Ru–nacnac complex **4** is disappointingly unreactive with small molecules, unlike some of its cationic analogues. This likely due to decreased Lewis acidity of the metal center in a neutral complex, coupled with the steric effects of the phenyl groups on the  $\alpha$ -N-atoms.

#### Acknowledgement

R.P.H. is grateful to the National Science Foundation for generous financial support.

## Appendix A. Supplementary material

CCDC 651859 and 651860 contain the contains the supplementary crystallographic data for **4** and **5**. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit @ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2007.11.002.

## References

- [1] G. Consiglio, F. Morandini, Chem. Rev. 87 (1987) 761.
- [2] M. Jiménez-Tenorio, M.C. Puerta, P. Valerga, Eur. J. Inorg. Chem. (2004) 17.
- [3] V. Cadierno, M.P. Gamasa, J. Gimeno, Coord. Chem. Rev. 248 (2004) 1627.

- [4] B.K. Campion, R.H. Heyn, T.D. Tilley, Organometallics, J. Chem. Soc. Chem. Commun. (1988) 278.
- [5] T. Arliguie, C. Border, B. Chaudret, J. Devillers, R. Poilblanc, Organometallics 8 (1989) 1308.
- [6] M. Jiménez-Tenorio, M.C. Puerta, P. Valerga, J. Am. Chem. Soc. 115 (1993) 9794.
- [7] C. Gemel, K. Mereiter, R. Schmid, K. Kirchner, Organometallics 16 (1997) 5601.
- [8] C. Gemel, V.N. Sapunov, K. Mereiter, M. Ferencic, R. Schmid, K. Kirchner, Inorg. Chim. Acta 286 (1999) 114.
- [9] U. Koelle, Chem. Rev. 98 (1998) 1313.
- [10] Y. Yamaguchi, H. Nagashima, Organometallics 19 (2000) 725.
- [11] U. Koelle, J. Kossakowski, G. Raabe, Angew. Chem., Int. Ed. Engl. 29 (1990) 773.
- [12] M.E. Smith, F.J. Hollander, R.A. Andersen, Angew. Chem., Int. Ed. Engl. 32 (1993) 1294.
- [13] B.C. Bailey, F. Basuli, J.C. Huffman, D.J. Mindiola, Organometallics 25 (2006) 3963.
- [14] H. Hamaki, N. Takeda, N. Tokitoh, Organometallics 25 (2006) 2457.
- [15] S. Harder, J. Brettar, Angew. Chem., Int. Ed. Engl. 45 (2006) 3474.
- [16] G. Bai, P. Wei, A.K. Das, D.W. Stephan, Dalton Trans. (2006) 1141.
- [17] G. Bai, P. Wei, D.W. Stephan, Organometallics 25 (2006) 2649.
- [18] U.J. Kilgore, F. Basuli, J.C. Huffman, D.J. Mindiola, Inorg. Chem. 45 (2006) 487.
- [19] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, Organometallics 15 (1996) 1518.
- [20] T.D. Tilley, R.H. Grubbs, J.E. Bercaw, Organometallics 3 (1984) 274.
- [21] J.E. Parks, R.H. Holm, Inorg. Chem. 7 (1968) 1408.
- [22] G. Bai, P. Wei, A. Das, D.W. Stephan, Organometallics 25 (2006) 5870.
- [23] A.d. Phillips, G. Laurenczy, R. Scopelliti, P.J. Dyson, Organometallics 26 (2007) 1120.
- [24] D. Duraczynska, J.H. Nelson, Dalton Trans. (2005) 92.
- [25] H. Brunner, J. Klankermayer, M. Zabel, Organometallics 21 (2002) 5746.