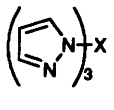
# Preparation and Crystal Structures of Cationic Dienehydrido and Dienyl Ruthenium Complexes containing *N,N',N''*-Trimethyl-1,4,7-triazacyclononane†

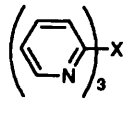
**San-Ming Yang, Wing-Chi Cheng, Kung-Kai Cheung, Chi-Ming Che* and Shie-Ming Peng**
*Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*

The reaction between [{Ru(cod)Cl$_2$}$_n$] (cod = cycloocta-1,5-diene) and *N,N',N''*-trimethyl-1,4,7-triazacyclononane (tacn) in ethanol–water gave [Ru(tacn)(1,2,5,6-η-cod)H]ClO$_4$ **1**. When *tert*-butyl alcohol was used as the solvent, [Ru(tacn)(1,2,3,4,5-η-C$_8$H$_{11}$)]ClO$_4$ **2** was obtained. The Ru-H moiety in **1** is characterized by a $^1$H NMR signal at δ −6.11 and a ν(Ru–H) stretch at 2040 cm$^{-1}$. Crystal structure analysis shows that the co-ordinated cod of **1** is in the tub form, whereas complex **2** has an η$^5$-cyclooctadienyl ligand.

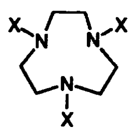
The co-ordination chemistry of facially co-ordinating ligands such as L$^1$–L$^4$, 1,4,7-triazacyclononane (L$^5$) and *N,N',N''*-trimethyl-1,4,7-triazacyclononane (tacn), which are isostructural to cyclopentadienyl and pentamethylcyclopentadienyl, has been an area of considerable interest in recent years.[1–3] In this context, tacn is of particular interest to the study of high-valent organometallic complexes.[3,4] This ligand resembles pentamethylcyclopentadienyl in that it is also a sterically bulky and facially co-ordinating ligand. As with other macrocyclic tertiary amines, it is a good ligand for the generation of high-valent metal complexes. In fact, a highly reactive *cis*-dioxoruthenium(VI) complex of tacn has recently been prepared and characterized.[3d] We herein describe the preparation, crystal structure and spectroscopic properties of two cationic organoruthenium(II) complexes, which are formed from the reaction of tacn with [{Ru(cod)Cl$_2$}$_n$] (cod = cycloocta-1,5-diene).



L$^1$ X = B
L$^2$ X = CH



L$^3$ X = COH
L$^4$ X = CH



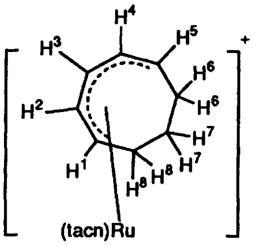
L$^5$ X = H
tacn X = Me

## Experimental

All reactions were performed using standard Schlenk-line techniques under a nitrogen atmosphere. Solvents were degassed by purging with nitrogen for 20 min. The compound [{Ru(cod)Cl$_2$}$_n$][5] and tacn[6] were prepared according to the literature methods. Trifluoroacetic acid was distilled before use. Other reagents were used as received. Infrared spectra were obtained using a Shimadzu IR-408 spectrophotometer, UV/VIS spectra on a Perkin-Elmer Lambda 19 UV/NIR spectrophotometer. Proton NMR spectra were obtained from a JEOL 270 Fourier-transform-NMR spectrometer with SiMe$_4$ as internal reference. Microanalyses were conducted by Butterworth Laboratories Ltd.

*Preparations*.—[Ru(tacn)(1,2,5,6-η-cod)H]ClO$_4$ **1**. The compound tacn (0.5 g, 2.9 mmol) was added to degassed ethanol–water (30 cm$^3$, 1 : 5 v/v) and the mixture purged with nitrogen for 20 min. Then [{Ru(cod)Cl$_2$}$_n$] (0.8 g, 2.9 mmol) and zinc dust (*ca.* 2 g) were added and the suspension refluxed for 12 h. The resulting solution was filtered and solid NaClO$_4$ was added to afford compound **1** as a pale yellow solid. This was collected on frit, washed with diethyl ether and air-dried. Yield 0.2 g (14%) (Found: C, 42.10; H, 7.10; N, 8.65. Calc. for C$_{17}$H$_{34}$ClN$_3$O$_4$Ru: C, 42.45; H, 7.10; N, 8.75%). $^1$H NMR (CD$_3$CN): δ −6.11 (1 H, s, Ru–H), 1.50–1.64 (4 H, m, CH$_2$ of cod), 2.20–2.30 (2 H, m), 2.42–2.68 (14 H, m, CH$_2$ of tacn and two N–Me), 2.70–2.82 (2 H, m), 2.86–3.00 (2 H, m, CH$_2$ of tacn), 3.04–3.20 (4 H, m), 3.32–3.42 (2 H, br m, olefinic H of cod), 3.51 (3 H, s, N–Me). IR (cm$^{-1}$): 2040 [ν(Ru–H)], 1623 [ν(C=C)].

[Ru(tacn)(1,2,3,4,5-η-C$_8$H$_{11}$)]ClO$_4$ **2**. The procedure was the same as that for **1** except *tert*-butyl alcohol was used instead of ethanol. Compound **2** was obtained as a yellow solid. Yield 0.2 g (14%) (Found: C, 43.25; H, 7.15; N, 8.95. Calc. for C$_{17}$H$_{32}$ClN$_3$O$_4$Ru·H$_2$O: C, 41.10; H, 6.90; N, 8.45%). $^1$H NMR (CD$_3$CN): δ 0.90–1.05 (1 H, m, H$^7$), 1.15–1.25 (1 H, m, H$^7$), 1.35–1.50 (4 H, m, two H$^6$ and two H$^8$), 2.40–2.50 (2 H, m, CH$_2$ of tacn), 2.50–2.75 (14 H, CH$_2$ of tacn and two N–Me), 2.85–3.00 (2 H, m, CH$_2$ of tacn), 3.10–3.25 (2 H, m, H$^1$ and H$^5$), 3.70–3.85 (5 H, m, H$^2$ and H$^4$, and N–Me), 5.90 (1 H, t, *J* 6.11 Hz, H$^3$).



*Crystal Structural Determinations*.—*Crystal data*. C$_{17}$H$_{34}$ClN$_3$O$_4$Ru·H$_2$O **1**, *M* = 498.01, triclinic, space group $P\bar{1}$, *a* = 9.223(1), *b* = 9.640(1), *c* = 12.382(1) Å, α = 81.87(1), β = 79.31(1), γ = 75.06(1)°, *U* = 1040.1(1.0) Å$^3$, *Z* = 2, $D_c$ = 1.590 g cm$^{-3}$, μ(Mo-Kα) = 8.99 cm$^{-1}$, *F*(000) = 518.

A crystal of dimensions 0.1 × 0.1 × 0.2 mm was used for data collection at 22 °C on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized Mo-Kα radiation (λ = 0.710 73 Å) using the ω–2θ scan mode. Intensity data (2θ$_{max}$ = 56, *h* 0 to 12, *k* −12 to 12, *l* −16 to 16) were corrected for Lorentz and polarization effects and empirical absorption based on the ψ-scans of six strong reflections.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

4700 Independent reflections were obtained, 4142 reflections with $F_o \geqslant 6\sigma(F_o)$ were considered observed and used in the structural analysis. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares using the Enraf-Nonius SDP-1985 programs.[7] The Ru, Cl, O, N and C atoms were refined anisotropically and H atoms at calculated positions and isotropic thermal parameters equal to 1.3 times that of the attached C atom were not refined. The H atoms of the water molecule were not found. Convergence for 244 variables by least-squares refinement on $F$ with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.04F_o^2)^2]$ for reflections with $I \geqslant 3\sigma(I)$, was reached at $R = 0.038$ and $R' = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ 0.053 and $S = 1.951$ for 4142 reflections; $(\Delta/\sigma)_{max} = 0.01$. A final Fourier difference map was featureless, with maximum positive and negative peaks of 0.89 and 0.52 e Å$^{-3}$ respectively. The oxygen atom [O(5)] of the water molecule is 2.95 Å from O(3) and 2.84 Å from O(4) of the perchlorate ion.

$C_{17}H_{32}ClN_3O_4Ru$ **2**, $M = 478.98$, orthorhombic, space group $P2_12_12_1$, $a = 8.783(2)$, $b = 14.815(4)$, $c = 15.047(3)$ Å, $U = 1957.8(8)$ Å$^3$, $Z = 4$, $D_c = 1.625$ g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 10.816 cm$^{-1}$, $F(000) = 992$.

A crystal of dimensions 0.50 × 0.60 × 0.70 mm was used for data collection at 298 K on a Nonius diffractometer with graphite monochromatized Mo-K$\alpha$ radiation ($\lambda = 0.7107$ Å) using the $\theta$–$2\theta$ scan mode ($2\theta_{max} = 50.0°$). Data reduction and structure refinement were performed using the NRCVAX program.[8] 1983 Unique reflections were measured, 1927 of which with $I \geqslant 2\sigma(I)$ were used in the structural analysis. The number of variables was 236 and the same weighting scheme as for **1** was used in the least-squares refinement. The final $R$, $R'$ and $S$ values were 0.041, 0.044 and 1.86 respectively. A final Fourier difference map was featureless with maximum positive and negative peaks of 178 and $-0.81$ e Å$^{-3}$ respectively.

Tables 1 and 2 list the atomic coordinates of compounds **1** and **2** respectively. Selected bond distances and angles are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results and Discussion

Dienylruthenium(II) amine complexes were reported previously by Singleton and co-workers.[9a] They found that $[\{Ru(cod)Cl_2\}_n]$ reacted with $NH_2NMe_2$ to give $[Ru(NH_2NMe_2)_3(cod)H]PF_6$,[9] which has the hydride and cod *cis* to each other. Our interest in dienylruthenium(II) complexes of macrocyclic amines stemmed from the recent findings that Ru$^{II}$–cod complexes may play an important role in the cycloaddition reactions of olefins and/or alkynes.[10]

Ruthenium complexes of tacn were first studied by Wieghardt and co-workers,[3a] but those reported are mostly dimeric. It was only recently that both Wieghardt and co-workers[3b,c] and Che and co-workers[3d,e] reported the preparation of some monomeric ruthenium complexes of tacn.

In this work $[\{Ru(cod)Cl_2\}_n]$ was found to react with tacn in refluxing aqueous ethanol and aqueous *tert*-butyl alcohol to give compounds **1** and **2** respectively. They are stable diamagnetic solids. Assignments of the $^1$H NMR spectra of complexes **1** and **2** are hampered by the overlapping of the methylene protons between tacn and the $\pi$-bonded moiety. For **1**, the $^1$H NMR signal at $\delta$ $-6.11$ and IR absorption band at 2040 cm$^{-1}$ are characteristic of the Ru–H moiety.[11] In addition, the broad olefinic protons at $\delta$ 3.32–3.42 are at higher field relative to those in other Ru$^{II}$–cod complexes.[12,13] This is likely a consequence of the enhanced $\pi$ basicity of Ru$^{II}$ by tacn, which is a good $\sigma$ donor. Similar reasoning can also be employed to explain why the 1,2,3,4,5-$\eta$-$C_8H_{11}$ protons in **2** appear at relatively higher field than in $[Ru(C_6H_6)(1,2,3,4,5\text{-}\eta\text{-}C_8H_{11})]^+$.[13] The NMR data manifest a $C_s$ symmetry for both **1** and **2**.

For complex **1**, no deuterium exchange was observed in $CD_3CN$–$D_2O$. The Ru–H moiety is quite inert and it does not react with either $(CD_3)_2CO$ or neat $CF_3CO_2H$ in $CD_3CN$.

**Table 1** Positional parameters of the non-hydrogen atoms of complex **1**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ru | −0.246 52(3) | 0.159 93(2) | 0.236 78(2) |
| Cl | 0.164 1(1) | −0.384 4(1) | 0.277 74(9) |
| O(1) | 0.174 2(7) | −0.417 6(6) | 0.175 3(4) |
| O(2) | 0.270 5(6) | −0.312 1(6) | 0.287 7(5) |
| O(3) | 0.033 1(9) | −0.297(1) | 0.307 4(9) |
| O(4) | 0.160(1) | −0.497 6(7) | 0.348 3(6) |
| O(5) | 0.234 4(6) | 0.275 7(7) | 0.517 1(5) |
| N(1) | −0.267 1(4) | 0.404 7(3) | 0.196 1(3) |
| N(2) | −0.011 1(3) | 0.174 6(3) | 0.235 1(3) |
| N(3) | −0.268 4(4) | 0.230 7(4) | 0.403 4(2) |
| C(1) | −0.366 9(6) | 0.486 5(4) | 0.115 6(4) |
| C(2) | 0.111 0(5) | 0.062 4(5) | 0.180 2(4) |
| C(3) | −0.359 6(6) | 0.157 8(6) | 0.495 6(3) |
| C(4) | −0.112 6(6) | 0.416 8(6) | 0.150 6(7) |
| C(5) | 0.009 1(6) | 0.317 1(5) | 0.181 7(6) |
| C(6) | 0.008 8(6) | 0.161 4(9) | 0.351 2(4) |
| C(7) | −0.113 9(6) | 0.203 9(9) | 0.429 0(4) |
| C(8) | −0.340 2(9) | 0.385 6(6) | 0.398 5(5) |
| C(9) | −0.316(1) | 0.470 6(5) | 0.299 3(5) |
| C(10) | −0.227 3(4) | 0.135 2(4) | 0.063 0(3) |
| C(11) | −0.373 1(5) | 0.184 5(5) | 0.016 3(3) |
| C(12) | −0.512 5(5) | 0.205 0(6) | 0.102 8(4) |
| C(13) | −0.484 4(4) | 0.191 6(4) | 0.220 3(3) |
| C(14) | −0.438 8(4) | 0.059 9(4) | 0.280 3(3) |
| C(15) | −0.409 3(5) | −0.083 8(4) | 0.234 4(4) |
| C(16) | −0.282 0(6) | −0.109 4(4) | 0.141 3(4) |
| C(17) | −0.183 8(4) | −0.000 7(4) | 0.120 4(3) |

**Table 2** Positional parameters of the non-hydrogen atoms of complex **2**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ru | 0.524 83(7) | 0.987 43(3) | 0.857 47(4) |
| N(1) | 0.360 6(7) | 1.098 3(4) | 0.872 8(5) |
| N(2) | 0.679 7(7) | 1.105 4(4) | 0.861 3(5) |
| N(3) | 0.506 1(9) | 1.035 5(4) | 0.715 7(4) |
| C(1) | 0.438 2(11) | 1.184 4(6) | 0.892 2(7) |
| C(2) | 0.601 9(12) | 1.173 9(6) | 0.915 4(7) |
| C(3) | 0.707 2(10) | 1.139 2(8) | 0.769 0(7) |
| C(4) | 0.656 8(13) | 1.077 9(8) | 0.700 0(6) |
| C(5) | 0.382 9(12) | 1.103 4(7) | 0.709 3(6) |
| C(6) | 0.283 7(11) | 1.106 1(9) | 0.785 3(8) |
| C(7) | 0.249 2(13) | 1.080 2(7) | 0.942 9(8) |
| C(8) | 0.835 2(12) | 1.095 8(8) | 0.901 5(7) |
| C(9) | 0.484 5(14) | 0.967 1(6) | 0.644 7(6) |
| C(10) | 0.570 7(12) | 0.949 2(6) | 0.995 2(6) |
| C(11) | 0.680 3(12) | 0.909 0(7) | 0.935 9(8) |
| C(12) | 0.647 4(12) | 0.860 4(6) | 0.857 9(7) |
| C(13) | 0.499 7(17) | 0.852 3(5) | 0.817 9(6) |
| C(14) | 0.359 8(11) | 0.876 0(5) | 0.856 3(7) |
| C(15) | 0.288 9(14) | 0.836 0(7) | 0.937 0(8) |
| C(16) | 0.393 9(15) | 0.812 5(7) | 1.011 5(8) |
| C(17) | 0.464 8(15) | 0.896 3(7) | 1.051 7(6) |
| Cl | 1.009 0(2) | 0.350 0(1) | 0.805 8(1) |
| O(1) | 1.008 5(10) | 0.284 6(5) | 0.737 5(5) |
| O(2) | 1.003 8(13) | 0.436 3(5) | 0.769 9(7) |
| O(3) | 0.881 6(9) | 0.337 8(7) | 0.859 5(6) |
| O(4) | 1.146 1(9) | 0.343 8(7) | 0.854 8(6) |

Using a $D_2O$–$CD_3CD_2OD$ (5:1 v/v) solvent system for the synthesis no deuterium incorporation was found in the product. This would exclude the possibility that the Ru–H moiety of **1** was formed by $\alpha$-hydride migration of ethanol, a reaction pathway previously reported by Vaska and Diluzio.[14] Hence the hydride ligand in **1** is suggested to come from cod, but further investigation is needed.

**Table 3** Selected bond distances (Å) and angles (°) for complexes **1** and **2**

| | | | | | |
|---|---|---|---|---|---|
| [Ru(tacn)(1,2,4,5-η-cod)H]ClO$_4$ **1** | | | | | |
| Ru–N(1) | 2.308(4) | Ru–C(10) | 2.168(3) | C(10)–C(17) | 1.398(5) |
| Ru–N(2) | 2.208(3) | Ru–C(13) | 2.180(4) | C(13)–C(14) | 1.384(6) |
| Ru–N(3) | 2.222(3) | Ru–C(14) | 2.178(5) | Ru–C(17) | 2.162(4) |
| N(1)–Ru–C(10) | 90.4(1) | N(2)–Ru–C(10) | 97.7(1) | N(2)–Ru–C(13) | 167.8(1) |
| N(1)–Ru–C(13) | 89.8(1) | N(1)–Ru–C(14) | 124.5(1) | N(1)–Ru–C(17) | 126.8(1) |
| N(2)–Ru–C(14) | 155.2(1) | N(2)–Ru–C(17) | 94.6(1) | N(3)–Ru–C(10) | 168.8(1) |
| N(3)–Ru–C(13) | 101.1(1) | N(3)–Ru–C(14) | 94.5(1) | N(3)–Ru–C(17) | 153.1(1) |
| C(10)–Ru–C(13) | 78.9(1) | C(10)–Ru–C(14) | 78.9(1) | C(10)–Ru–C(17) | 37.7(1) |
| C(13)–Ru–C(14) | 37.0(1) | C(13)–Ru–C(17) | 89.8(2) | C(14)–Ru–C(17) | 79.4(1) |
| Ru–C(13)–C(12) | 114.2(2) | Ru–C(14)–C(13) | 71.6(2) | | |
| [Ru(tacn)(1,2,3,4,5-η$^5$-C$_8$H$_{11}$)]ClO$_4$ **2** | | | | | |
| Ru–N(1) | 2.198(6) | Ru–N(2) | 2.215(6) | Ru–N(3) | 2.255(6) |
| Ru–C(10) | 2.186(9) | Ru–C(11) | 2.146(10) | Ru–C(12) | 2.168(9) |
| Ru–C(13) | 2.100(7) | Ru–C(14) | 2.197(8) | C(10)–C(11) | 1.44(2) |
| C(10)–C(17) | 1.48(1) | C(11)–C(12) | 1.41(2) | C(12)–C(13) | 1.44(2) |
| C(13)–C(14) | 1.40(2) | C(14)–C(15) | 1.49(2) | C(15)–C(16) | 1.49(2) |
| C(16)–C(17) | 1.52(2) | | | | |
| N(1)–Ru–N(2) | 79.1(2) | N(1)–Ru–N(3) | 79.4(3) | N(1)–Ru–C(10) | 102.4(3) |
| N(1)–Ru–C(11) | 139.8(4) | N(1)–Ru–C(12) | 166.9(3) | N(1)–Ru–C(13) | 132.3(4) |
| N(1)–Ru–C(14) | 97.4(3) | N(2)–Ru–N(3) | 79.6(3) | N(2)–Ru–C(10) | 93.9(3) |
| N(2)–Ru–C(11) | 91.2(3) | N(2)–Ru–C(12) | 112.3(3) | N(2)–Ru–C(13) | 145.5(4) |
| N(2)–Ru–C(14) | 176.5(3) | N(3)–Ru–C(10) | 172.8(3) | N(3)–Ru–C(11) | 137.5(4) |
| N(3)–Ru–C(12) | 108.3(3) | N(3)–Ru–C(13) | 91.5(3) | N(3)–Ru–C(14) | 100.5(3) |
| C(10)–Ru–C(11) | 38.9(4) | C(10)–Ru–C(12) | 71.4(4) | C(10)–Ru–C(13) | 92.3(3) |
| C(10)–Ru–C(14) | 86.3(4) | C(11)–Ru–C(12) | 38.1(5) | C(11)–Ru–C(13) | 72.9(5) |
| C(11)–Ru–C(14) | 91.0(4) | C(12)–Ru–C(13) | 39.3(5) | C(12)–Ru–C(14) | 71.1(4) |
| C(13)–Ru–C(14) | 38.0(5) | C(11)–C(10)–C(17) | 123.8(8) | C(10)–C(11)–C(12) | 126.2(10) |
| C(11)–C(12)–C(13) | 125.3(9) | Ru–C(13)–C(12) | 72.9(5) | Ru–C(13)–C(14) | 74.7(5) |
| C(12)–C(13)–C(14) | 126.8(8) | C(14)–C(15)–C(16) | 116.6(9) | C(15)–C(16)–C(17) | 111.3(9) |
| C(10)–C(17)–C(16) | 117.5(9) | C(13)–C(14)–C(15) | 127.0(9) | | |

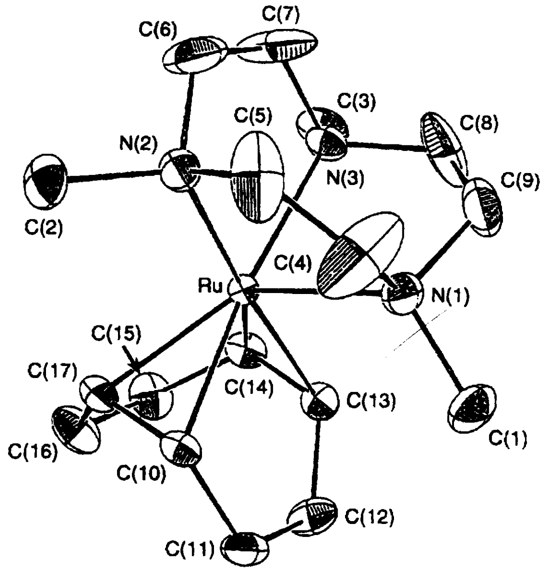

**Fig. 1** A perspective view of the complex cation of **1**. The hydride was not located

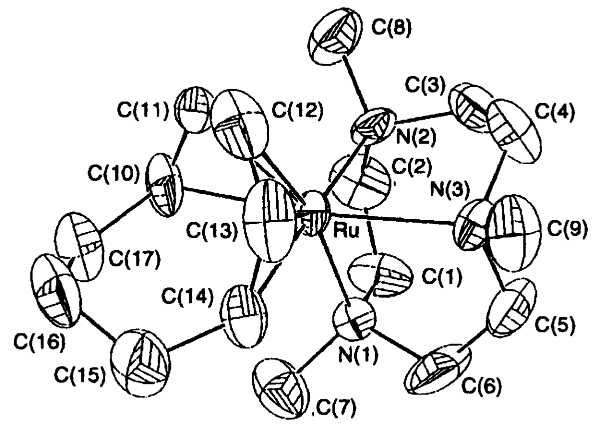

**Fig. 2** A perspective view of the complex cation of **2**

*Structures of Complexes* **1** *and* **2**.—A perspective view of the complex cation of **1** is shown in Fig. 1. The hydride was not located but its existence is inferred from the spectroscopic results described above and the assumption of a Ru$^{II}$ oxidation state. The Ru–N(1) distance of 2.308(4) Å is significantly longer than Ru–N(2) and Ru–N(3) [2.208(3) and 2.222(3) Å respectively]. Presumably this is due to the stronger *trans* influence of the hydride over the olefinic groups. The cod ligand is in the usual tub form.[15] The Ru–C distances are longer than the corresponding ones in [Ru(NH$_2$NMe$_2$)$_3$(cod)H]$^+$.[9b] In the latter, the C=C distances are 1.41(2) and 1.40(2) Å, whereas in **1**, these are 1.398(5) and 1.384(6) Å.

Fig. 2 shows a perspective view of the cation of **2**. The metal-bonded part of the η$^5$-C$_8$H$_{11}$ ring does not deviate from planarity and is characterized by C–C bond lengths not significantly different from each other. These structural features are characteristic of the co-ordination of an η$^5$-cyclooctadienyl ligand. Similar observations on other η$^5$-cyclooctadienylmetal complexes have been previously reported.[16]

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