Crystal structure of dichlorido(*N*-(biphenyl-2-ylmethyl)-*N*-(2-ethoxyethyl)]-imidazolidin-2-ylidene(η^6 -hexamethylbenzene)ruthenium, $\text{Ru}(\text{C}_{12}\text{H}_{18})(\text{C}_{20}\text{H}_{24}\text{N}_2\text{O})\text{Cl}_2$

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Abstract

$\text{C}_{32}\text{H}_{42}\text{Cl}_2\text{N}_2\text{ORu}$, monoclinic, $P2_1/c1$ (no. 14), $a = 12.930(4)$ Å, $b = 18.094(6)$ Å, $c = 13.655(4)$ Å, $\beta = 114.00(2)^\circ$, $V = 2918.4$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.046$, $wR_{\text{ref}}(F^2) = 0.133$, $T = 193$ K.

Source of material

All reactions were performed using Schlenk-type flask under argon and standard high vacuum-line techniques. Solvents were analytical grade and distilled under Ar. A solution of tetraaminoethene (1.1 mmol) and $[\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)]_2$ (1.0 mmol) in toluene (15 mL) was heated in a water bath (95–100 °C) for 3 h; after cooling to 25 °C, hexane (10 mL) was added and the solution cooled to –15 °C. Precipitated orange solid was filtered off and recrystallised from dichloromethane/hexane (15 mL, 30 mL) and title compound was isolated in 85 % yield.

Experimental details

During structure refinement, the positional parameters of the H atoms were calculated using coupled or rotating rigid-body models. The H atom U_{iso} values were refined independently from the C atoms, but restrained to equal values within each individual moiety. The result suggested disorder correction negligible, but supported structure model consistency.

Discussion

We have recently embarked on a study of metal complexes of *N*-heterocyclic carbenes. As part of this program we have synthesized some arene–ruthenium complexes. *N*-heterocyclic carbenes have recently emerged as an important family of ligands with electronic characteristics similar to those of phosphines [1,2]. The use of imidazol-2-ylidene, imidazolidin-2-ylidene metal complexes rapidly showed an increased interest since it was demonstrated that they are efficient catalysts in important chemical transformations, such as carbon–carbon coupling reactions, CO–ethylene copolymerization, Ru-catalysed olefins metathesis, furan synthesis, Rh-catalysed hydrosilylations [3–7].

Complexes containing imidazolin-2-ylidenes, which are neutral two-electron-donor ligands with negligible π -back-bonding, are thermally rather stable. This feature represents an essential prerequisite for the synthesis of highly efficient catalysts. Employment of sterically demanding *N*-heterocyclic carbenes, which resemble bulky phosphines with respect to their bonding, has led to the synthesis of new robust ruthenium, rhodium and palladium catalysts, which are less oxygen sensitive in comparison to the phosphine analogues [5,6,8–11]. In this study, we have synthesised and crystallized the $[\text{RuCl}_2\{\text{[N-(biphenyl-2-ylmethyl)-N-(2-ethoxyethyl)]-imidazolidin-2-ylidene}\}(\text{C}_6\text{Me}_6)]$ and its structural analysis has been undertaken.

The complex is best thought of as containing an octahedrally coordinated ruthenium centre with the arene ligand occupying three sites. There are three coordination bonds of ruthenium atom with the electrons of the C_6Me_6 ring, two symmetrical Ru–Cl bonds and one Ru–C3 bond involving the imidazole ring, the coordination around the Ru atom is six-fold, which is in this case distorted octahedrally. The small steric demand of the imidazole ligand is reflected in the $90.02(10)^\circ$ and $89.02(10)^\circ$ C3–Ru–Cl angles. These are significantly bigger than the comparable angles in the pyridine substituted complexes $[\text{RuCl}_2(\text{py})(\eta^6\text{-arene})]$ [12]. On the other side of the coordination sphere, the Ru–Cl1 (2.424(1) Å) and Ru–Cl2 (2.410(1) Å) bond lengths are somewhat different from each other. The Cl1–Ru–Cl2 bond angle is $85.3(1)^\circ$.

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A striking feature is the C—C bond alternation around the ring with an average C—C (short) of 1.416(5) Å and C—C (long) of 1.446(6) Å. The bond lengths Ru—M1 (M1 is the midpoint between C20 and C21 atoms), Ru—M2 (M2 is midpoint between C17 and C22) and Ru—M3 (M3 is midpoint between C18 and C19) are 2.143(1), 2.092(1) Å and 2.089(1) Å, respectively. The Ru- η bond angles are 61.0(2)° (M1—Ru—M2), 61.6(1)° (M2—Ru—M3) and 61.2(1)° (M1—Ru—M3). The arene ring is planar with Ru—C distance between 2.199(4) Å and 2.260(4) Å. All the other bond lengths fall within the expected range.

Table 1. Data collection and handling.

Crystal:	orange prismatic, size 0.07 × 0.17 × 0.75 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	7.49 cm ⁻¹
Diffraction, scan mode:	Bruker SMART CCD, ω
$2\theta_{\max}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	13486, 5093
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4139
$N(\text{param})_{\text{refined}}$:	373
Program:	SHELXTL 5.1 [13]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	-0.0877	0.1193	0.4235	0.025(7)
H(1B)	4e	-0.0612	0.0842	0.5359	0.025
H(2A)	4e	0.1172	0.0766	0.5543	0.017(7)
H(2B)	4e	0.0949	0.1307	0.4583	0.017
H(4A)	4e	0.2564	0.2529	0.6600	0.016(7)
H(4B)	4e	0.2586	0.2072	0.5650	0.016
H(6)	4e	0.2149	0.0953	0.7478	0.03(1)
H(7)	4e	0.3455	0.0152	0.8714	0.04(1)
H(8)	4e	0.5384	0.0231	0.9047	0.03(1)
H(9)	4e	0.5992	0.1146	0.8188	0.03(1)
H(12)	4e	0.5908	0.2631	0.8246	0.03(1)
H(13)	4e	0.6579	0.3608	0.7542	0.04(1)
H(14)	4e	0.5939	0.3751	0.5690	0.04(1)
H(15)	4e	0.4645	0.2906	0.4525	0.06(2)
H(16)	4e	0.4019	0.1903	0.5222	0.03(1)
H(23A)	4e	-0.1738	0.3642	0.3902	0.055(9)
H(23B)	4e	-0.0781	0.3139	0.3837	0.055
H(23C)	4e	-0.0924	0.3953	0.3408	0.055
H(24A)	4e	0.1262	0.3797	0.3938	0.049(8)
H(24B)	4e	0.0960	0.3019	0.4254	0.049
H(24C)	4e	0.2180	0.3344	0.4863	0.049

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(25A)	4e	0.3216	0.3769	0.6119	0.054(9)
H(25B)	4e	0.3393	0.3772	0.7325	0.054
H(25C)	4e	0.3400	0.4518	0.6744	0.054
H(26A)	4e	0.1888	0.5089	0.8397	0.09(1)
H(26B)	4e	0.2813	0.5077	0.7929	0.09
H(26C)	4e	0.2638	0.4383	0.8532	0.09
H(27A)	4e	0.0265	0.4711	0.8252	0.12(2)
H(27B)	4e	-0.0960	0.4754	0.7342	0.12
H(27C)	4e	-0.0119	0.5416	0.7526	0.12
H(28A)	4e	-0.2013	0.4823	0.5415	0.062(9)
H(28B)	4e	-0.1958	0.4114	0.6095	0.062
H(28C)	4e	-0.2238	0.4042	0.4869	0.062
H(29A)	4e	-0.2069	0.2286	0.4370	0.028(8)
H(29B)	4e	-0.1628	0.2735	0.5427	0.028
H(30A)	4e	-0.1922	0.1651	0.6266	0.032(9)
H(30B)	4e	-0.3054	0.2071	0.5496	0.032
H(31A)	4e	-0.4423	0.1276	0.4386	0.038(9)
H(31B)	4e	-0.3890	0.0831	0.5451	0.038
H(32A)	4e	-0.4115	0.0283	0.3457	0.07(1)
H(32B)	4e	-0.4879	0.0037	0.4042	0.07
H(32C)	4e	-0.3589	-0.0165	0.4529	0.07

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	4e	0.06325(2)	0.33482(2)	0.66238(2)	0.0184(2)	0.0158(2)	0.0176(2)	-0.0006(1)	0.0049(2)	0.0007(1)
Cl(1)	4e	-0.05844(8)	0.30003(6)	0.75078(8)	0.0301(5)	0.0271(6)	0.0286(5)	-0.0011(4)	0.0151(4)	0.0033(5)
Cl(2)	4e	0.21560(8)	0.29075(6)	0.82284(7)	0.0254(5)	0.0309(6)	0.0220(5)	0.0011(4)	0.0022(4)	0.0065(4)
O(1)	4e	-0.2783(2)	0.1141(2)	0.4890(3)	0.032(2)	0.032(2)	0.059(2)	-0.015(1)	0.024(2)	-0.017(2)
N(1)	4e	-0.0556(2)	0.1963(2)	0.5402(3)	0.019(2)	0.017(2)	0.027(2)	-0.002(1)	0.006(1)	-0.004(2)
N(2)	4e	0.1266(3)	0.1844(2)	0.5979(3)	0.018(2)	0.020(2)	0.026(2)	-0.001(1)	0.007(1)	-0.001(2)
C(1)	4e	-0.0420(3)	0.1234(2)	0.4990(3)	0.029(2)	0.020(2)	0.022(2)	-0.004(2)	0.008(2)	-0.002(2)
C(2)	4e	0.0827(3)	0.1225(2)	0.5222(3)	0.030(2)	0.018(2)	0.029(2)	-0.000(2)	0.012(2)	-0.006(2)
C(3)	4e	0.0432(3)	0.2298(2)	0.5972(3)	0.020(2)	0.021(2)	0.015(2)	0.003(2)	0.005(2)	0.008(2)
C(4)	4e	0.2441(3)	0.2045(2)	0.6284(3)	0.022(2)	0.023(2)	0.027(2)	0.001(2)	0.010(2)	0.006(2)
C(5)	4e	0.3276(3)	0.1516(2)	0.7064(3)	0.022(2)	0.020(2)	0.021(2)	0.002(2)	0.008(2)	-0.002(2)
C(6)	4e	0.2936(3)	0.0990(2)	0.7611(3)	0.028(2)	0.029(2)	0.033(2)	0.001(2)	0.016(2)	0.002(2)
C(7)	4e	0.3710(4)	0.0515(2)	0.8347(3)	0.038(2)	0.025(2)	0.033(2)	0.004(2)	0.016(2)	0.007(2)
C(8)	4e	0.4846(4)	0.0564(2)	0.8552(3)	0.036(2)	0.026(2)	0.028(2)	0.012(2)	0.009(2)	0.004(2)
C(9)	4e	0.5200(3)	0.1102(2)	0.8030(3)	0.024(2)	0.027(2)	0.031(2)	0.007(2)	0.008(2)	-0.000(2)
C(10)	4e	0.4442(3)	0.1575(2)	0.7288(3)	0.022(2)	0.022(2)	0.020(2)	0.001(2)	0.007(2)	-0.003(2)
C(11)	4e	0.4878(3)	0.2176(2)	0.6810(3)	0.018(2)	0.024(2)	0.029(2)	0.002(2)	0.010(2)	-0.000(2)
C(12)	4e	0.5648(3)	0.2683(2)	0.7483(3)	0.029(2)	0.034(3)	0.025(2)	-0.003(2)	0.005(2)	-0.001(2)
C(13)	4e	0.6044(4)	0.3263(3)	0.7068(4)	0.027(2)	0.038(3)	0.039(3)	-0.008(2)	0.006(2)	-0.006(2)
C(14)	4e	0.5670(4)	0.3345(2)	0.5976(4)	0.031(2)	0.035(3)	0.044(3)	-0.004(2)	0.016(2)	0.006(2)
C(15)	4e	0.4908(3)	0.2845(3)	0.5286(3)	0.031(2)	0.037(3)	0.028(2)	0.002(2)	0.012(2)	0.002(2)
C(16)	4e	0.4528(3)	0.2258(2)	0.5700(3)	0.022(2)	0.030(2)	0.027(2)	0.001(2)	0.008(2)	-0.002(2)
C(17)	4e	-0.0178(3)	0.3899(2)	0.5038(3)	0.029(2)	0.017(2)	0.020(2)	0.001(2)	0.007(2)	0.003(2)
C(18)	4e	0.1019(3)	0.3823(2)	0.5324(3)	0.029(2)	0.016(2)	0.023(2)	-0.000(2)	0.010(2)	0.004(2)

Table 3. Continued.

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(19)	4e	0.1811(3)	0.4105(2)	0.6319(3)	0.024(2)	0.016(2)	0.032(2)	−0.003(2)	0.010(2)	0.005(2)
C(20)	4e	0.1410(3)	0.4487(2)	0.7025(3)	0.028(2)	0.014(2)	0.027(2)	−0.004(2)	0.005(2)	0.002(2)
C(21)	4e	0.0239(3)	0.4546(2)	0.6763(3)	0.035(2)	0.017(2)	0.025(2)	0.002(2)	0.012(2)	−0.001(2)
C(22)	4e	−0.0560(3)	0.4232(2)	0.5769(3)	0.022(2)	0.015(2)	0.028(2)	0.003(2)	0.007(2)	0.005(2)
C(23)	4e	−0.0978(3)	0.3635(2)	0.3948(3)	0.036(2)	0.026(2)	0.018(2)	−0.001(2)	0.004(2)	−0.001(2)
C(24)	4e	0.1389(4)	0.3463(2)	0.4522(4)	0.039(2)	0.030(3)	0.033(3)	0.005(2)	0.018(2)	0.005(2)
C(25)	4e	0.3069(3)	0.4034(3)	0.6657(4)	0.025(2)	0.033(3)	0.046(3)	−0.006(2)	0.011(2)	0.001(2)
C(26)	4e	0.2264(4)	0.4786(3)	0.8064(4)	0.039(2)	0.031(3)	0.031(2)	−0.007(2)	−0.003(2)	−0.007(2)
C(27)	4e	−0.0182(4)	0.4888(2)	0.7541(4)	0.048(3)	0.024(2)	0.036(2)	0.005(2)	0.020(2)	−0.005(2)
C(28)	4e	−0.1806(3)	0.4310(2)	0.5514(3)	0.030(2)	0.029(2)	0.033(2)	0.006(2)	0.012(2)	−0.001(2)
C(29)	4e	−0.1689(3)	0.2246(2)	0.5136(3)	0.024(2)	0.017(2)	0.033(2)	0.001(2)	0.006(2)	0.000(2)
C(30)	4e	−0.2411(4)	0.1788(3)	0.5532(4)	0.024(2)	0.039(3)	0.048(3)	−0.010(2)	0.018(2)	−0.016(2)
C(31)	4e	−0.3872(3)	0.0907(2)	0.4762(4)	0.026(2)	0.032(3)	0.035(2)	−0.006(2)	0.009(2)	0.008(2)
C(32)	4e	−0.4137(4)	0.0203(3)	0.4143(4)	0.048(3)	0.040(3)	0.041(3)	−0.018(2)	0.018(2)	−0.005(2)

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