

Crystal structure of dichlorido(*N*-(biphenyl-2-ylmethyl)-*N*-(2-ethoxyethyl)]-imidazolidin-2-ylidene(η^6 -hexamethylbenzene)ruthenium, Ru(C₁₂H₁₈)(C₂₀H₂₄N₂O)Cl₂

H. Arslan^{*I,II}, D. Vanderveer^I, I. Özdemir^{III}, B. Cetinkaya^{IV} and S. Yasar^{III}

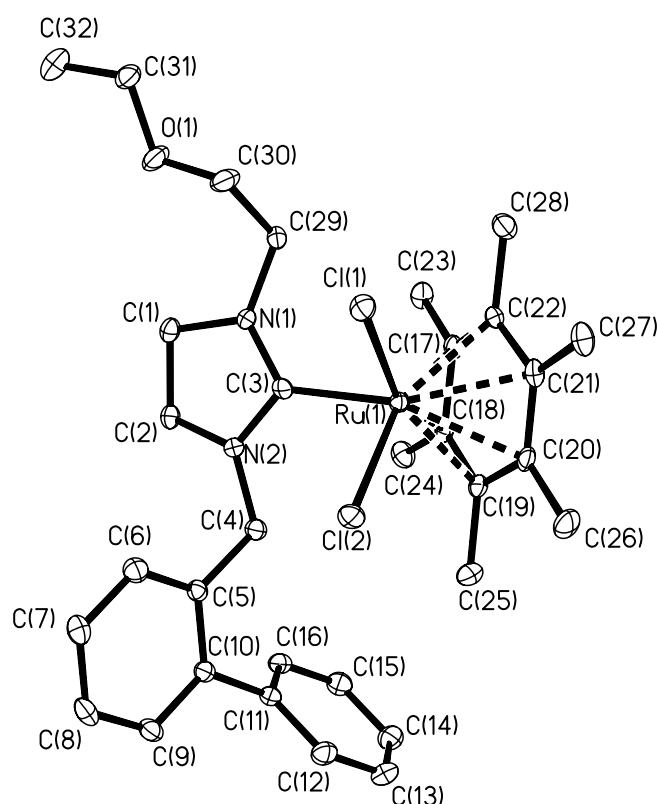
^I Georgia Institute of Technology, School of Chemistry and Biochemistry, 770 State Street, Atlanta, Georgia 30332-0400, USA

^{II} Mersin University, Faculty of Arts and Sciences, Department of Chemistry, 33343 Mersin, Turkey

^{III} İnönü University, Faculty of Science and Arts, Chemistry Department, 44069 Malatya, Turkey

^{IV} Ege University, Department of Chemistry, 35100 Bornova Izmir, Turkey

Received December 22, 2003, accepted and available on-line January 17, 2004; CCDC no. 1267/1195



Abstract

C₃₂H₄₂Cl₂N₂ORu, monoclinic, *P*12₁/*c*1 (no. 14), *a* = 12.930(4) Å, *b* = 18.094(6) Å, *c* = 13.655(4) Å, β = 114.00(2)°, *V* = 2918.4 Å³, *Z* = 4, *R*_{gt}(*F*) = 0.046, *wR*_{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 [RuCl₂(η^6 -C₆Me₆)]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 [RuCl₂{[*N*-(biphenyl-2-ylmethyl)-*N*-(2-ethoxyethyl)]-imidazolidin-2-ylidene}{C₆Me₆}] 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 C₆Me₆ 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)° and 89.02(10)° C3—Ru—C1 angles. These are significantly bigger than the comparable angles in the pyridine substituted complexes [RuCl₂(py)(η^6 -arene)] [12]. On the other side of the coordination sphere, the Ru—C11 (2.424(1) Å) and Ru—C12 (2.410(1) Å) bond lengths are somewhat different from each other. The C11—Ru—C12 bond angle is 85.3(1)°.

* Correspondence author (e-mail: arslanh@mersin.edu.tr)

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
Diffractometer, scan mode:	Bruker SMART CCD, ω
$2\theta_{\max}$:	50°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	13486, 5093
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 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	-0.1982	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	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> 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)

References

- Lappert, M. F.: The coordination chemistry of electron-rich alkenes (enetetramines). *J. Organomet. Chem.* **358** (1988) 185-214.
- Bourissou, D.; Guerriet, O.; Gabbai, P. F.; Bertrand, G.: Stable Carbenes. *Chem. Rev.* **100** (2000) 39-91.
- Herrmann, W. A.; Reisinger, C. P.; Spiegler, M.: Chelating *N*-heterocyclic carbene ligands in palladium-catalyzed heck-type reactions. *J. Organomet. Chem.* **557** (1998) 93-96.
- Zhang, C. M.; Huang, J. K.; Trudell, M. L.; Nolan, S. P.: Palladium-imidazol-2-ylidene complexes as catalysts for facile and efficient suzuki cross-coupling reactions of aryl chlorides with arylboronic acids. *J. Org. Chem.* **64** (1999) 3804-3805.
- Cetinkaya, B.; Özdemir, I.; Bruneau, C.; Dixneuf, P. H.: Ruthenium-carbene catalysts for the synthesis of 2,3-dimethylfuran. *J. Mol. Catal. A* **118** (1997) L1-L4.
- Özdemir, I.; Yigit, B.; Cetinkaya, B.; Ulku, D.; Tahir, M. N.; Arici, C.: Synthesis of a water-soluble carbene complex and its use as catalyst for the synthesis of 2,3-dimethylfuran. *J. Organomet. Chem.* **633** (2001) 27-32.
- Cetinkaya, B.; Özdemir, I.; Dixneuf, P. H.: Synthesis and catalytic properties of *N*-functionalist carbene complexes of rhodium(I) and ruthenium(II). *J. Organomet. Chem.* **534** (1997) 153-158.
- Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H.: Efficient and recyclable monomeric and dendritic Ru-based metathesis catalysts. *J. Am. Chem. Soc.* **122** (2000) 8168-8179.
- Gessler, S.; Randl, S.; Blechert, S.: Synthesis and metathesis reactions of a phosphine-free dihydroimidazole carbene ruthenium complex. *Tetrahedron Lett.* **41** (2000) 9973-9976.
- Cetinkaya, B.; Demir, S.; Özdemir, I.; Toupet, L.; Semeril, D.; Bruneau, C.; Dixneuf, P. H.: First ruthenium complexes with a chelating arene carbene ligand as catalytic precursors for alkene metathesis and cycloisomerisation. *New J. Chem.* **25** (2001) 519-521.
- Cetinkaya, B.; Demir, S.; Özdemir, I.; Toupet, L.; Semeril, D.; Bruneau, C.; Dixneuf, P. H.: η^6 -Mesityl,1-Imidazolinylidene-Carbene-Ru(II) Complexes: catalytic activity of their allenylidene derivatives in alkene metathesis and cycloisomerisation reactions. *Chem. Eur. J.* **9** (2003) 2323-2330.
- Steedman, A. J.; Burrell, A. K.: Dichloro(η^6 -hexamethylbenzene)-(pyridine-*N*)ruthenium. *Acta Crystallogr. C* **53** (1997) 864-866.
- Sheldrick, G. M.: SHELXTL v. 5.1. Structure determination software suite. Bruker AXS, Madison, Wisconsin, USA 1998.