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Dichloride[1-(2,4,6-trimethylbenzyl)-3-(biphenyl-2-ylmethyl)-imidazolidin-2-ylidene (η^6 -hexamethylbenzene)]ruthenium

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The single crystal X-ray structure of the imidazolidin ruthenium complex, $C_{38}H_{46}N_2Cl_2Ru$, was determined. The complex is an orthorhombic space group $Pbca$ with $a = 17.3586(32)$ Å, $b = 14.4447(27)$ Å, $c = 27.4325(52)$ Å, and $V = 6878.466(4)$ Å³ with $Z = 8$ for $D_{calc} = 1.357$ g/cm³. It exhibits the expected 3-legged piano stool geometry. There is one coordination bond of the ruthenium atom with the electrons of the η^6 -hexamethylbenzene, 2 symmetrical Ru-Cl bonds, and one Ru-C bond involving the imidazole ring. The coordination around the ruthenium atom is 4-fold, which in this case is pseudo-tetrahedral.

Key Words: Arenes, carbenes, imidazole, ruthenium complex, X-ray structure

Introduction

The conversion of metal carbenes into useful organic functionalities is an important area of research in synthetic applications. Nonetheless, the reaction of a metal carbene complex with a halogen to provide the corresponding organic halide has been rarely reported.¹⁻³ In the last decade, *N*-heterocyclic carbenes have been the subject of intense research in the field of organometallic chemistry. These derivatives have been shown to behave as phosphine mimics.⁴⁻⁶ In addition, *N*-heterocyclic carbenes of 1,3-imidazolylidene and 1,3-imidazolinylidene have been used as ancillary ligands in transition metal chemistry.^{6,7} Significant improvements in catalytic performance have recently brought benefits to fine chemistry via the simple substitution of a phosphine ligand by a nucleophilic heterocyclic diaminocarbene, such as an imidazolylidene

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ligand. Illustrative examples are found in various catalytic reactions with palladium catalysts, in cross-coupling, and ruthenium catalysts for the formation of furans and cyclopropanation.^{8–12}

In our previous works,^{5,7,9–15} we have reported syntheses, characterizations, catalytic activities, and crystal structures of some imidazolidin-2-ylidene derivatives and their metal complexes. In the present work, we report the structural properties of dichlorido(1-(2,4,6-trimethylbenzyl)-3-(biphenyl-2-ylmethyl)-imidazolidin-2-ylidene (η^6 -hexamethyl benzene))ruthenium, (I).

Experimental

Instrumentation and crystal structure determination

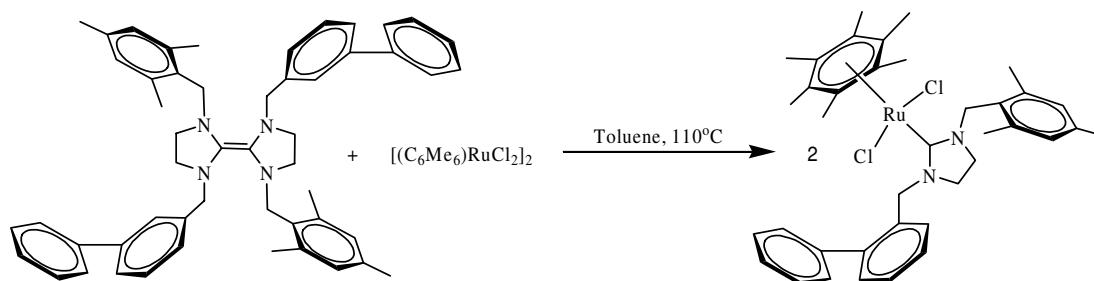
Single crystal X-ray data were collected with a Rigaku Mercury AFC8S CCD diffractometer using monochromatic MoK α ($\lambda = 0.71073 \text{ \AA}$) radiation. The structure was solved by direct and conventional Fourier methods. Full-matrix least-squares refinements were based on F². SHELXTL was the program used for calculations.¹⁶ Further details concerning data collection and refinements are given in Table 1.

Table 1. Summary of crystallographic data and parameters of (I).

| CCDC deposit no. | CCDC-613013 |
|---|--|
| Empirical formula | C ₃₈ H ₄₆ N ₂ Cl ₂ Ru |
| Formula weight | 702.74 |
| Temperature, K | 173(2) |
| Wavelength, \AA | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | Pbca |
| Unit cell dimensions | |
| <i>a</i> , \AA | 17.3586(32) |
| <i>b</i> , \AA | 14.4447(27) |
| <i>c</i> , \AA | 27.4325(52) |
| Volume, \AA^3 | 6878.466(4) |
| <i>Z</i> | 8 |
| Density (calculated), Mg/m ³ | 1.357 |
| Absorption coefficient, mm ⁻¹ | 0.640 |
| F(000) | 2928 |
| Crystal size, mm | 0.80 x 0.24 x 0.12 |
| θ range for data collection, deg | 1.89 to 25.00 |
| Index ranges | -20 \leq h \leq 20 -15 \leq k \leq 16 -25 \leq l \leq 32 |
| Reflections collected | 34,134 |
| Independent reflections | 5897 [R(int) = 0.0357] |
| Absorption correction | REQAB (multi-scan) ¹⁷ |
| Refinement method | Full-matrix least-squares on F ² |
| Data/restraints/parameters | 5897/0/385 |
| Goodness-of-fit on F ² | 1.152 |
| Final R indices [I > 2 σ (I)] | R1 = 0.0451, wR2 = 0.0906 |
| R indices (all data) | R1 = 0.0544, wR2 = 0.0943 |
| Largest diff. peak and hole, e. \AA^{-3} | 0.742 and -0.461 |

Synthesis

All reactions were performed using Schlenk-type flasks under Ar and standard high vacuum-line techniques. Analytical grade solvents were distilled under Ar. The synthesis of tetra aminoethane was accomplished employing a 3-step procedure as described in the literature.¹⁰ The title compound was prepared from functional tetra aminoethane in toluene at 95-100 °C (Scheme). A solution of tetra aminoethane (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. An orange precipitate was filtered off and re-crystallized from dichloromethane:hexane (15:30 mL). The complex was obtained with an 85% yield.¹⁸ Dichlorido(1-(2,4,6-trimethylbenzyl)-3-(biphenyl-2-ylmethyl)-imidazolidin-2-ylidene(η^6 -hexamethylbenzene))ruthenium: M.p. 249 °C; Analysis (% Calc/found): for $\text{C}_{38}\text{H}_{46}\text{N}_2\text{RuCl}_2$: C: 64.94/64.98, H: 6.60/ 6.66, N: 3.99/3.96. FAB (m/z): 702.78.



Scheme

Results and Discussion

We herein report the crystal structure of (I). All of the characterization data are in agreement with the molecular structure of (I) and data in the literature.¹⁸ The molecular structure of (I) is shown in the Figure, with the atom-numbering scheme. Selected bond lengths and angles are given in Table 2. Table 3 lists the non-hydrogen atomic coordinates for the title compound.

Table 2. Selected bond distances (Å) and angles (°) for (I).

| Bond distances | | | | |
|----------------|-----------|----------|------------|--|
| Ru1-C3 | 2.073(3) | N1-C2 | 1.473(4) | |
| Ru1-Cl1 | 2.4263(9) | Ru···C17 | 2.2047(14) | |
| Ru1-Cl2 | 2.4115(9) | Ru···C18 | 2.2026(12) | |
| C3-N1 | 1.345(4) | Ru···C19 | 2.2021(13) | |
| C3-N2 | 1.359(4) | Ru···C20 | 2.2764(16) | |
| N1-C29 | 1.464(4) | Ru···C21 | 2.2893(15) | |
| N2-C4 | 1.445(4) | Ru···C22 | 2.2121(14) | |
| N1-C1 | 1.474(4) | | | |
| Bond angles | | | | |
| Cl1-Ru1-Cl2 | 83.99(3) | C3-N1-C1 | 113.7(3) | |
| C3-Ru1-Cl1 | 92.53(9) | C3-N2-C4 | 128.5(3) | |
| C3-Ru1-Cl2 | 88.80(9) | N1-C1-C2 | 102.6(3) | |
| Ru1-C3-N1 | 127.4(2) | N2-C2-C1 | 102.9(3) | |
| Ru1-C3-N2 | 125.5(2) | | | |

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (I).

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq}^* |
|-------|-----------|-----------|----------|------------|
| Ru(1) | 6665(1) | 9840(1) | 10,40(1) | 22(1) |
| Cl(2) | 7647(1) | 8664(1) | 10,96(1) | 34(1) |
| Cl(1) | 6334(1) | 9063(1) | 284(1) | 32(1) |
| N(2) | 8175(2) | 10,893(2) | 864(1) | 27(1) |
| N(1) | 340(2) | 11,226(2) | 301(1) | 26(1) |
| C(1) | 7990(2) | 11849(3) | 190(1) | 34(1) |
| C(2) | 8524(2) | 11693(3) | 615(1) | 30(1) |
| C(3) | 7457(2) | 10694(2) | 697(1) | 24(1) |
| C(4) | 8550(2) | 10,559(3) | 1300(1) | 29(1) |
| C(5) | 9301(2) | 10,048(2) | 1202(1) | 31(1) |
| C(6) | 9458(2) | 9668(3) | 749(1) | 39(1) |
| C(7) | 10,138(2) | 9184(3) | 667(2) | 47(1) |
| C(8) | 0658(2) | 9056(3) | 1036(2) | 51(1) |
| C(9) | 10512(2) | 9433(3) | 1488(2) | 54(1) |
| C(10) | 9839(2) | 9933(3) | 1578(1) | 39(1) |
| C(11) | 9718(1) | 10,350(2) | 2079(1) | 50(1) |
| C(12) | 10,032(1) | 11,200(2) | 2210(1) | 61(1) |
| C(13) | 9858(1) | 11,589(2) | 2660(1) | 83(2) |
| C(14) | 9369(1) | 11,128(2) | 2980(1) | 96(2) |
| C(15) | 9054(1) | 10,278(2) | 2849(1) | 97(2) |
| C(16) | 9229(1) | 9889(1) | 2399(1) | 76(2) |
| C(17) | 5922(1) | 11,000(1) | 1268(1) | 28(1) |
| C(18) | 6493(1) | 10,842(1) | 1635(1) | 27(1) |
| C(19) | 6577(1) | 9951(1) | 1839(1) | 29(1) |
| C(20) | 6061(1) | 9224(1) | 1701(1) | 32(1) |
| C(21) | 5500(1) | 9371(1) | 1343(1) | 32(1) |
| C(22) | 5449(1) | 10,282(1) | 11,08(1) | 29(1) |
| C(23) | 5800(1) | 11,994(1) | 1096(1) | 35(1) |
| C(24) | 6986(2) | 11,658(3) | 1796(1) | 36(1) |
| C(25) | 7176(2) | 9756(3) | 2230(1) | 42(1) |
| C(26) | 6170(3) | 8284(3) | 1936(2) | 47(1) |
| C(27) | 4978(2) | 8607(3) | 1174(2) | 48(1) |
| C(28) | 4865(2) | 10,403(3) | 711(1) | 43(1) |
| C(29) | 6633(2) | 11,284(2) | 13(1) | 26(1) |
| C(30) | 6782(2) | 11,636(2) | -500(1) | 25(1) |
| C(31) | 6552(2) | 12,530(2) | -637(1) | 29(1) |
| C(32) | 6687(2) | 12,829(3) | -1109(1) | 34(1) |
| C(33) | 7052(2) | 12,281(3) | -1451(1) | 37(1) |
| C(34) | 7275(2) | 11,401(3) | -1311(1) | 35(1) |
| C(35) | 7150(2) | 11,064(2) | -842(1) | 28(1) |
| C(36) | 6150(3) | 13,176(3) | -288(1) | 46(1) |
| C(37) | 7202(3) | 12,623(4) | -1965(2) | 63(1) |
| C(38) | 7407(2) | 10,100(3) | -714(1) | 40(1) |

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The complex has a similar arrangement to dichlorido(*N*-(biphenyl-2-ylmethyl)-*N*-(2-ethoxyethyl)]-imidazolidin-2-ylidene(η^6 -hexamethylbenzene)ruthenium¹³ and dichloride (1-(2,4,6-trimethylbenzyl)-3-(2-methoxyethyl)-imidazolidin-2-ylidene(η^6 -hexamethyl benzene))ruthenium¹⁹, as recently described. The title compound adopts the typical piano-stool geometry with a pseudo-tetrahedral arrangement of the η^6 -

hexamethyl benzene ring, the 2 chloride ligands, and the C atom of the imidazole ligand around the ruthenium metal center (Figure).

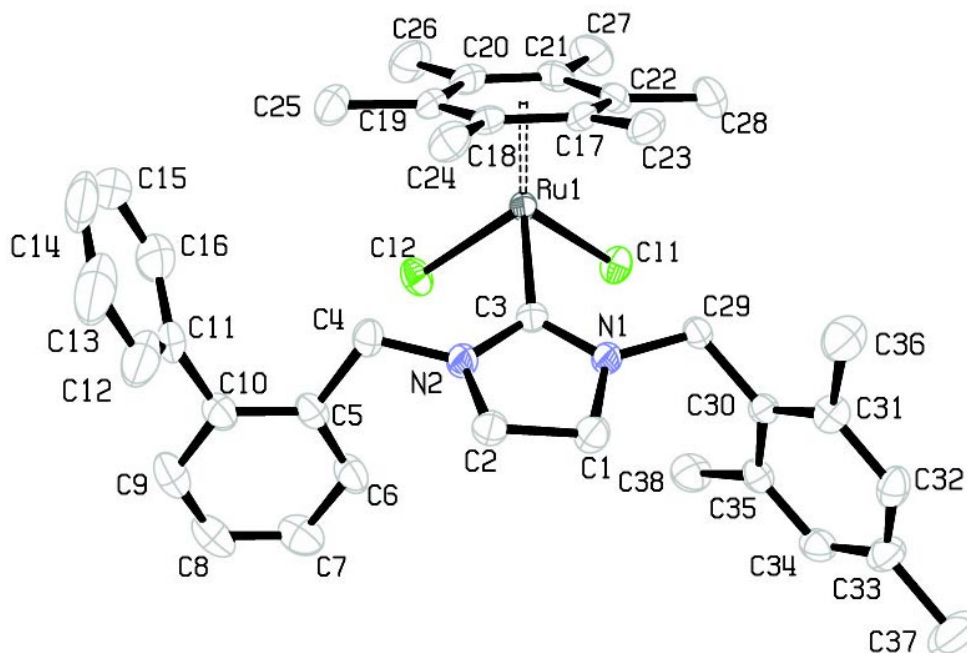


Figure. A drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The 6-membered ring of the 2,4,6-trimethylbenzyl is planar, with a maximum deviation from the plane of 0.033(3) Å. The C-C bond lengths within the 2,4,6-trimethylbenzyl ring are equal within experimental error.^{13,19} The Ru-C distances that belong to the 2,4,6-trimethylbenzyl ring are almost equal, with an average Ru-C_{ring}: 2.2312(14) Å [range 2.2021(13) - 2.2893(15) Å]. These Ru-C distances are very close to those reported for other ruthenium complexes [average Ru-C = 2.227(4) Å¹⁹ and average Ru-C = 2.225(4) Å¹³].

The average Ru-Cl bond length [2.4263(9) Å and 2.4115(9) Å] is almost equal to the average bond length of 2.420 Å in the other Ru(II) complexes.^{13,15,19,20} The small steric demand of the imidazole ligand is reflected in the Cl-Ru-C3 angles. The C3-Ru-Cl1 and C3-Ru-Cl2 angles are 92.53(9)° and 88.80(9)°, respectively. They are almost equal to the corresponding values 90.99(10)° and 89.79(10)° in another Ru(II) complex,¹⁹ but significantly larger than the angles in the pyridine-substituted complex (dichloro(η^6 -hexamethylbenzene)(pyridine-*N*)ruthenium)²¹ where these angles are 86.16(10)° and 86.12(10)°. In addition, the dihedral angle of C_t-Ru-C3-N (C_t: centroid of C17, C18, C19, C20, C21 and C22) is 86.65° in the title compound. This angle is in agreement with the small steric demand of the imidazole ligand. The corresponding angle is 23.7° in RuCl₂[*N*-(2,4,6-trimethylbenzyl)-*N*-(2,4,6-trimethylbenzyl)]-imidazolidin-2-ylidene],¹⁹ which has a strong distortion of the carbene ligand due to the coordination of one N substituent.

The Ru-C3 [2.073(3) Å] distance is equal within the experimental error for dichlorido(*N*-(biphenyl-2-ylmethyl)-*N*-(2-ethoxyethyl)]-imidazolidin-2-ylidene(η^6 -hexamethylbenzene)ruthenium [2.069(5) Å].¹³

Supplementary material

Crystallographic data (excluding structural factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data [CCDC-613013] can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44 (1223) 336-033, E-mail: deposit@ccdc.cam.ac.uk].

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