Crystal structure of dichloro-*N*-(3,4,5-trimethoxy-benzyl)-*N*-(*n*-butyl)]-imidazolidin-2-ylideneruthenium(II), $RuCl_2(C_{17}H_{26}N_2O_3)$

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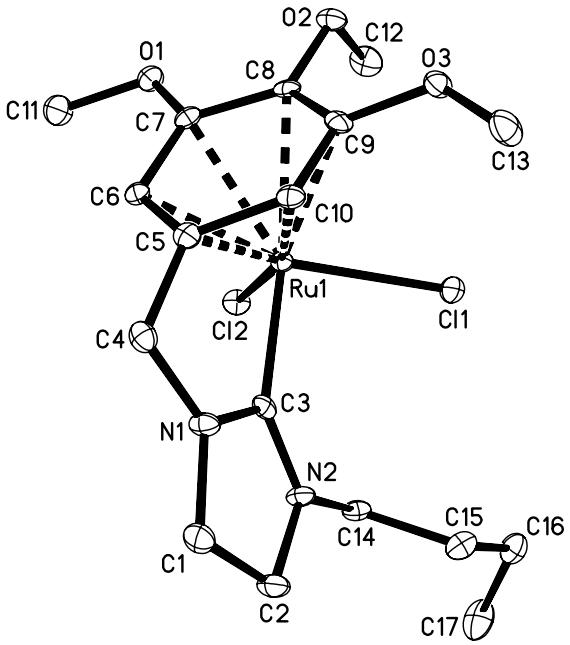

Abstract

$C_{17}H_{26}Cl_2N_2O_3Ru$, monoclinic, $P12_1/n1$ (no. 14), a = 10.180(1) Å, b = 11.985(1) Å, c = 16.017(2) Å, β = 106.419(2)°, V = 1874.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.109, 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 $[RuCl_2(p\text{-cymene})]_2$ (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 red solid was filtered off and recrystallized from dichloromethane/hexane (15 mL:30 mL, yield 85 %).

Experimental details

While positions of the H atoms were calculated, their U_{iso} restrained to equal values of each moiety were refined.

Discussion

In the last decade *N*-heterocyclic carbenes have been the subject of intense research in the field of organometallic chemistry [1,2]. Because of the extraordinary properties they have found utility in a great variety of catalytic processes which include C-C coupling reactions [3], formation of furans [4-6], cyclopropanation [7], hydroformylation [8] and polymerization reactions [9]. Our contribution to this field has started with syntheses of imidazolidin-2-ylidenes complexes of Rh(I) and Ru(II) which are capable of catalyzing the cyclopropanation of styrene with ethyl diazoacetate and intramolecular cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran in good yields [5-7]. We have now considered the possibility of generating heterocyclic carbenes that have a pendent arene group to evaluate their ability to chelate the ruthenium atom, stabilize the complex or create catalytic activity [10-12].

The title complex is best thought of as containing an octahedrally coordinated ruthenium centre with the arene occupying three sites. Two Ru—Cl bonds and the Ru—C3 bond complete the distorted octahedra. If one calculates the mid-points (M_n) of three alternating C—C bonds in each complex, they occupy three vertices of the octahedron. Unlike some similar complexes, the arene ring does not have three definite short C—C bonds corresponding to the three coordination sites (d(Ru1—C3) = 2.030(3) Å, d(Ru1—C5) = 2.087(3) Å, d(Ru1—C6) = 2.167(3) Å, d(Ru1—C7) = 2.313(3) Å, d(Ru1—C8) = 2.300(3) Å, d(Ru1—C9) = 2.286(3) Å and d(Ru1—C10) = 2.195(3)) Å [12]. However, two of the bonds are slightly shorter than the other four and they are site bonds. The complete coordination sphere for each complex using *M*1-*M*3 as the arene sites shows angles (*M*–Ru–*M*) which vary from 60.00(1)° to 62.18(1)°. The small steric demand of the imidazole ligand is reflected in the Cl–Ru–C3 angles which vary from 92.2(1)° to 93.0(1)°. These are significantly larger than the angles in the pyridine substituted complexes $[RuCl_2(py)(\eta^6\text{arene})]$ [13]. The Ru—Cl distances differ somewhat, from a minimum of 2.4191(8) Å to a maximum of 2.4268(8) Å. The Cl–Ru–Cl angle is 90.1(1)°.

Table 1. Data collection and handling.

Crystal:	red, prismatic, size 0.12 × 0.27 × 0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.40 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8241, 3202
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2920
$N(param)_{refined}$:	243
Program:	SHELXTL [14]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	4*e*	1.1556	0.1660	0.1976	0.033(7)
H(1B)	4*e*	1.0626	0.1259	0.2547	0.033
H(2A)	4*e*	1.1746	0.2356	0.3631	0.033(7)
H(2B)	4*e*	1.2745	0.2685	0.3088	0.033
H(4A)	4*e*	0.8424	0.1675	0.1140	0.026(6)
H(4B)	4*e*	0.9256	0.2278	0.0592	0.026
H(6)	4*e*	0.8507	0.4104	–0.0079	0.017(8)
H(10)	4*e*	0.6841	0.2803	0.1797	0.03(1)
H(11A)	4*e*	0.8842	0.5867	–0.0539	0.036(6)
H(11B)	4*e*	0.7793	0.6600	–0.1225	0.036
H(11C)	4*e*	0.7647	0.5298	–0.1250	0.036
H(12A)	4*e*	0.6599	0.7032	0.1822	0.044(7)
H(12B)	4*e*	0.5636	0.7812	0.1127	0.044
H(12C)	4*e*	0.6977	0.7335	0.0966	0.044
H(13A)	4*e*	0.5033	0.3065	0.2261	0.037(6)
H(13B)	4*e*	0.4714	0.3994	0.2865	0.037
H(13C)	4*e*	0.6236	0.3684	0.2931	0.037
H(14A)	4*e*	1.1149	0.5351	0.3139	0.022(6)
H(14B)	4*e*	1.2593	0.4812	0.3413	0.022
H(15A)	4*e*	1.0660	0.4442	0.4334	0.036(8)
H(15B)	4*e*	1.2161	0.4020	0.4625	0.036
H(16A)	4*e*	1.1487	0.6295	0.4542	0.048(9)
H(16B)	4*e*	1.1802	0.5620	0.5401	0.048
H(17A)	4*e*	1.4050	0.5388	0.5386	0.039(6)
H(17B)	4*e*	1.3694	0.6662	0.5348	0.039
H(17C)	4*e*	1.3740	0.6031	0.4499	0.039

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	4*e*	0.84511(2)	0.47458(2)	0.16202(2)	0.0134(2)	0.0131(2)	0.0154(2)	0.00023(8)	0.0025(1)	–0.00083(8)
Cl(1)	4*e*	0.84209(8)	0.55296(7)	0.30064(5)	0.0244(4)	0.0262(4)	0.0184(4)	0.0028(3)	0.0043(3)	–0.0045(3)
Cl(2)	4*e*	0.99967(8)	0.62115(6)	0.14452(5)	0.0209(4)	0.0186(4)	0.0261(5)	–0.0034(3)	0.0057(3)	0.0007(3)
O(1)	4*e*	0.7043(2)	0.6002(2)	–0.0304(1)	0.025(1)	0.027(1)	0.019(1)	0.004(1)	0.006(1)	0.0065(9)
O(2)	4*e*	0.5493(2)	0.6225(2)	0.0788(1)	0.018(1)	0.021(1)	0.028(1)	0.0044(9)	0.002(1)	–0.0001(9)
O(3)	4*e*	0.5348(2)	0.4594(2)	0.1897(2)	0.019(1)	0.024(1)	0.025(1)	0.0015(9)	0.009(1)	0.0038(9)
N(1)	4*e*	0.9910(3)	0.2650(2)	0.1859(2)	0.019(1)	0.014(1)	0.024(2)	0.003(1)	–0.001(1)	–0.003(1)
N(2)	4*e*	1.1116(3)	0.3729(2)	0.2884(2)	0.019(1)	0.017(1)	0.020(2)	0.005(1)	–0.001(1)	0.003(1)
C(1)	4*e*	1.0995(4)	0.1901(3)	0.2334(2)	0.033(2)	0.019(2)	0.030(2)	0.009(1)	0.010(2)	0.002(1)
C(2)	4*e*	1.1800(3)	0.2636(3)	0.3080(2)	0.021(2)	0.025(2)	0.028(2)	0.007(1)	0.002(1)	0.003(1)
C(3)	4*e*	1.0009(3)	0.3695(2)	0.2192(2)	0.014(2)	0.017(2)	0.021(2)	–0.001(1)	0.009(1)	0.002(1)
C(4)	4*e*	0.8860(3)	0.2363(2)	0.1066(2)	0.023(2)	0.019(2)	0.026(2)	–0.001(1)	0.009(2)	–0.005(1)
C(5)	4*e*	0.7831(3)	0.3306(2)	0.0881(2)	0.016(2)	0.017(2)	0.021(2)	–0.005(1)	0.002(1)	–0.006(1)
C(6)	4*e*	0.7905(3)	0.4170(2)	0.0284(2)	0.014(2)	0.023(2)	0.016(2)	–0.002(1)	0.001(1)	–0.003(1)
C(7)	4*e*	0.7065(3)	0.5133(3)	0.0237(2)	0.016(2)	0.021(2)	0.016(2)	–0.004(1)	–0.001(1)	–0.004(1)
C(8)	4*e*	0.6291(3)	0.5287(2)	0.0827(2)	0.012(2)	0.014(2)	0.018(2)	0.000(1)	–0.004(1)	–0.003(1)
C(9)	4*e*	0.6169(3)	0.4392(3)	0.1385(2)	0.009(2)	0.022(2)	0.024(2)	–0.004(1)	0.003(1)	–0.005(1)
C(10)	4*e*	0.6928(3)	0.3403(3)	0.1419(2)	0.015(2)	0.018(2)	0.020(2)	–0.002(1)	0.001(1)	–0.002(1)
C(11)	4*e*	0.7903(4)	0.5936(3)	–0.0877(2)	0.033(2)	0.040(2)	0.027(2)	0.004(2)	0.013(2)	0.010(2)
C(12)	4*e*	0.6238(4)	0.7180(3)	0.1210(3)	0.033(2)	0.019(2)	0.039(2)	0.003(2)	0.010(2)	–0.001(2)
C(13)	4*e*	0.5332(4)	0.3765(3)	0.2542(3)	0.033(2)	0.037(2)	0.040(2)	0.010(2)	0.021(2)	0.015(2)
C(14)	4*e*	1.1655(3)	0.4706(3)	0.3407(2)	0.014(2)	0.021(2)	0.022(2)	–0.001(1)	–0.000(2)	0.003(1)
C(15)	4*e*	1.1582(4)	0.4620(3)	0.4339(2)	0.025(2)	0.023(2)	0.024(2)	–0.006(1)	0.002(2)	0.002(1)
C(16)	4*e*	1.2016(4)	0.5687(3)	0.4856(2)	0.035(2)	0.033(2)	0.022(2)	–0.002(2)	0.006(2)	–0.004(2)
C(17)	4*e*	1.3510(4)	0.5967(3)	0.5039(3)	0.046(2)	0.050(2)	0.029(2)	–0.023(2)	0.008(2)	–0.013(2)

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