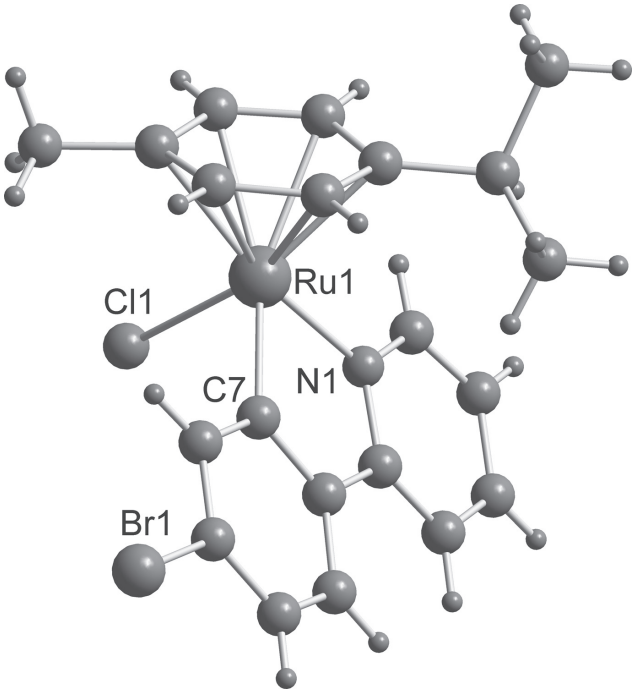
Chen Xu* and Xin-Hua Lou

Crystal structure of (η^6-1-methyl-4-isopropylbenzene)-[5-bromo-2-(2-pyridyl)phenyl-κ^2 *C*,*N*]-chloro-ruthenium(II), $C_{21}H_{21}BrClNRu$



https://doi.org/10.1515/ncrs-2020-0058
Received January 30, 2020; accepted February 29, 2020; available online March 25, 2020

Abstract

$C_{21}H_{21}BrClNRu$, triclinic, $P\bar{1}$ (no. 2), $a = 8.2185(4)$ Å, $b = 10.1626(5)$ Å, $c = 11.9356(6)$ Å, $\alpha = 100.399(4)°$, $\beta = 90.005(4)°$, $\gamma = 93.434(4)°$, $V = 978.68(9)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0353$, $wR_{ref}(F^2) = 0.0676$, $T = 291(2)$ K.

CCDC no.: 1980576

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	$0.20 \times 0.18 \times 0.17$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	2.98 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω
θ_{max}, completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8149, 3997, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3292
$N(param)_{refined}$:	229
Programs:	CrysAlis^{PRO} [1], SHELX [2]

Source of material

The title compound was obtained from the reaction of 2-(4-bromophenyl)pyridine and $[RuCl_2(p\text{-cymene})]_2$ according to literature procedures [3] and recrystallized from a dichloromethane/petroleum ether solution at room temperature to give the desired crystals suitable for single-crystal X-ray diffraction.

Experimental details

A suitable crystal was selected and measured on a Xcalibur, Eos, Gemini diffractometer. The diffraction data was collected using the CrysAlis^{Pro} program [1]. The structure was solved with the ShelXS structure solution program using Patterson Method and refined with the ShelXL [2] refinement package using least-squares minimisation. H atoms were added using the riding models implemented in the SHELX system.

Comment

Cyclometalated complexes have attracted considerable attention due to their wide applications [4–7]. Various methods for the preparation of these complexes have been developed, among which C—H activation is the simplest and most direct process [8–10]. In addition, C—H activation to form a cyclometalated complex has become an integral part of many catalytic cycles [11–13]. In recent years

***Corresponding author: Chen Xu,** School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212003, China, e-mail: xubohan@163.com. https://orcid.org/0000-0003-4128-2035
Xin-Hua Lou: College of Food and Pharmacy, Luoyang Normal University, Luoyang 471022, China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ru1	0.63592(3)	0.70553(2)	0.69809(2)	0.03091(9)
Br1	1.11799(6)	1.16030(5)	0.85882(4)	0.08564(19)
Cl1	0.73219(10)	0.68533(8)	0.50393(7)	0.0435(2)
N1	0.4420(3)	0.8009(3)	0.6408(2)	0.0356(6)
C1	0.3018(4)	0.7367(4)	0.5951(3)	0.0466(9)
H1	0.2895	0.6441	0.5885	0.056*
C2	0.1777(5)	0.8024(5)	0.5582(3)	0.0647(12)
H2	0.0804	0.7561	0.5310	0.078*
C3	0.1999(5)	0.9381(5)	0.5623(3)	0.0724(13)
H3	0.1187	0.9846	0.5353	0.087*
C4	0.3419(5)	1.0051(4)	0.6062(3)	0.0581(10)
H4	0.3581	1.0968	0.6084	0.070*
C5	0.4611(4)	0.9352(3)	0.6473(3)	0.0397(8)
C6	0.6166(4)	0.9935(3)	0.6981(3)	0.0374(8)
C7	0.7236(4)	0.9023(3)	0.7257(2)	0.0344(7)
C8	0.8765(4)	0.9536(3)	0.7712(3)	0.0431(8)
H8	0.9528	0.8960	0.7883	0.052*
C9	0.9133(5)	1.0904(4)	0.7904(3)	0.0490(10)
C10	0.8064(6)	1.1796(4)	0.7648(3)	0.0580(11)
H10	0.8342	1.2712	0.7793	0.070*
C11	0.6578(5)	1.1312(3)	0.7176(3)	0.0540(10)
H11	0.5844	1.1899	0.6984	0.065*
C12	0.4925(4)	0.6368(3)	0.8335(3)	0.0396(8)
C13	0.6460(4)	0.6958(3)	0.8764(3)	0.0447(9)
H13	0.6499	0.7666	0.9380	0.054*
C14	0.7918(4)	0.6494(3)	0.8280(3)	0.0466(9)
H14	0.8907	0.6879	0.8597	0.056*
C15	0.7917(4)	0.5456(3)	0.7321(3)	0.0445(9)
C16	0.6369(4)	0.4816(3)	0.6925(3)	0.0410(8)
H16	0.6332	0.4098	0.6319	0.049*
C17	0.4935(4)	0.5240(3)	0.7422(3)	0.0402(8)
H17	0.3954	0.4786	0.7160	0.048*
C18	0.9463(5)	0.5050(4)	0.6734(4)	0.0696(12)
H18A	0.9272	0.4837	0.5927	0.104*
H18B	0.9830	0.4278	0.6997	0.104*
H18C	1.0281	0.5775	0.6903	0.104*
C19	0.3329(5)	0.6842(4)	0.8830(3)	0.0526(10)
H19	0.2551	0.6747	0.8194	0.063*
C20	0.2683(5)	0.5886(4)	0.9621(4)	0.0746(13)
H20A	0.3437	0.5924	1.0242	0.112*
H20B	0.2567	0.4987	0.9199	0.112*
H20C	0.1642	0.6154	0.9914	0.112*
C21	0.3385(6)	0.8302(4)	0.9421(4)	0.0801(14)
H21A	0.4059	0.8418	1.0092	0.120*
H21B	0.2302	0.8549	0.9630	0.120*
H21C	0.3829	0.8860	0.8913	0.120*

ruthenium complexes as highly active catalysts have successfully been applied to organic synthesis such as arylation, dehydrogenation and other coupling reactions [13–15]. As a continuation of our interest in the synthesis and application of cyclometalated complexes, we report the crystal structure of the title cyclometalated ruthenium complex.

The single-crystal X-ray analyses shows that the title complex adopts a typical "piano-stool" configuration with one chlorido ligand and one *C*,*N*-bidentate ligand as the three legs [16]. The pyridyl and benzyl ring are approximately coplanar as found in related cyclometalated complexes containing the same 2-(4-bromophenyl)pyridine ligand [17, 18]. Upon binding of the cyclometalated ligand to ruthenium a planar five-menbered chelate ring is formed. The chlorido ligand is almost perpendicular to the above planar chelate ring [N_1–Ru_1–$Cl_1 = 85.04(8)°$ and C_7–Ru_1–$Cl_1 = 88.17(8)°$]. The Ru—C(arene) distances vary considerably from 2.151(3) Å to 2.267(3) Å. The Ru—N and Ru—C bond lengths of the title complex are similar to those of the related cyclometalated ruthenium complexes [3, 9, 14]. In the crystal there exist C—H···Cl hydrogen bonds, where the coordinated chlorido ligand forms hydrogen bonds with the adjacent C—H group of pyridyl ring (Cl···H = 2.913, and 2.919 Å) [19–21]. In addition, the bromine atom in benzyl ring also forms C—H···Br hydrogen bonds with the adjacent C—H group of arene ring (Br···H = 3.042 Å), thereby contributing to the formation of a 2D architecture that extends along the (0 1 0) plane 2D architecture.

Acknowledgements: This work was supported by the high-level introduction of talent research start-up foundation of Jiangsu University of Science and Technology.

References

1. Agilent Technologies: CrysAlis^{PRO} Software system, version 1.171.38.41r. Agilent Technologies UK Ltd, Oxford, UK (2011).
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
3. Zhang, L. L.; Li, L. H.; Wang, Y. Q.; Yang, Y. F.; Liu, X. Y.; Liang, Y. M.: Ruthenium-catalyzed direct C—H amidation of arenes: a mechanistic study. Organometallics **33** (2014) 1905–1908.
4. Niu, J. L.; Hao, X. Q.; Gong, J. F.; Song, M. P.: Symmetrical and unsymmetrical pincer complexes with group 10 metals: synthesis *via* aryl C—H activation and some catalytic applications. Dalton Trans. **40** (2011) 5135–5150.
5. Xu, C.; Dong, X. M.; Wang, Z. Q.; Hao, X. Q.; Li, Z.; Duan, L. M.; Ji, B. M.; Song, M. P.: Triphenylphosphine-cyclometallated iridium(III) pyrimidine complexes: synthesis, crystal structures and application in α-alkylation of ketones with alcohols. J. Organomet. Chem. **700** (2012) 214–218.
6. Ackermann, L.: Carboxylate-assisted ruthenium-catalyzed alkyne annulations by C-H/Het-H bond functionalizations. Acc. Chem. Res. **47** (2014) 281–295.
7. Han, X.; Li, H. M.; Xu, C.; Xiao, Z. Q.; Wang, Z. Q.; Fu, W. J.; Hao, X. Q.; Song, M. P.: Water-soluble palladacycles containing hydroxymethyl groups: synthesis, crystal structures and use as catalysts for amination and Suzuki coupling of reactions. Transition Met. Chem. **41** (2016) 403–411.
8. Boutadla, Y.; Al-Duaij, O.; Davies, D. L.; Griffith, G. A.; Singh, K.: Mechanistic study of acetate-assisted C—H activation

of 2-substituted pyridines with $[MCl_2Cp^*]_2$ (M = Rh, Ir) and $[RuCl_2(p\text{-cymene})]_2$. Organometallics **28** (2009) 433–440.
9. Flegeau, E. F.; Bruneau, C.; Dixneuf, P. H.; Jutand, A.: Autocatalysis for C—H bond activation by ruthenium(II) complexes in catalytic arylation of functional arenes. J. Am. Chem. Soc. **133** (2011) 10161–10170.
10. Xiao, Z. Q.; Xu, C.; Li, H. M.; Han, X.; Wang, Z. Q.; Fu, W. J.; Hao, X. Q.; Song, M. P.: Two fluorescent cyclopalladated arylpyrazine complexes: synthesis, crystal structures and application in the double Suzuki coupling of *N*-heteroaryl halides with 1,4-benzenediboronic acid. Transition Met. Chem. **40** (2015) 501–508.
11. Lakshman, M. K.; Deb, A. C.; Chamala, R. R.; Pradhan, P.; Pratap, R.: Direct arylation of 6-phenylpurine and 6-arylpurine nucleosides by ruthenium-catalyzed C—H bond activation. Angew. Chem. Int. Ed. **50** (2011) 11400–11404.
12. Xu, C.; Wang, Z. Q.; Zhang, Y. P.; Dong, X. M.; Hao, X. Q.; Fu, W. J.; Ji, B. M.; Song, M. P.: Synthesis and structural characterization of palladacycles with polydentate ligands by a stepwise coupling route-palladacycles containing halides as efficient catalysts and substrates. Eur. J. Inorg. Chem. **31** (2011) 4878–4888.
13. Li, H. M.; Tu, T. Y.; Han, X.; Wang, Z. Q.; Fu, W. J.; Hao, X. Q.; Song, M. P.; Xu, C.: C—H Monoarylation of naphthylpyrimidines with aryl chlorides catalyzed by a water-soluble ruthenium complex. Synlett **29** (2018) 1729–1734.
14. Taketoshi, A.; Koizumi, T.; Kanbara, T.: Aerobic oxidative dehydrogenation of benzylamines catalyzed by a cyclometalated ruthenium complex. Tetrahedron Lett. **51** (2010) 6457–6459.
15. Li, H. M.; Xu, C.; Wang, Z. Q.; Fu, W. J.: A half sandwich ruthenium(II) complex with *N*-4,6-dimethyl-2pyrimidinylimidazole: synthesis, crystal structure and application in *N*-alkylation of amines with alcohols. Bull. Korean. Chem. Soc. **36** (2015) 2557–2560.
16. Ivanovic, I.; Jovanovic, K. K.; Gligorijevic, N.; Radulovic, S.; Arion, V. B.; Sheweshein, K. S. A. M.; Tesic, Z.; Sipka, S.: Ruthenium(II)-arene complexes with substituted picolinato ligands: synthesis, structure, spectroscopic properties and antiproliferative activity. J. Organomet. Chem. **749** (2014) 343–349.
17. Xu, C.; Li, H. M.; Xiao, Z. Q.; Wang, Z. Q.; Tang, S. F.; Ji, B. M.; Hao, X. Q.; Song, M. P.: Cyclometalated Pd(II) and Ir(III) 2-(4-bromophenyl)pyridine complexes with *N*-heterocyclic carbenes (NHCs) and acetylacetonate (acac): synthesis, structures, luminescent properties and application in one-pot oxidation/Suzuki coupling of aryl chlorides containing hydroxymethyl. Dalton Trans. **43** (2014) 10235–10247.
18. Xu, C.; Song, Y. L.; Wang, Z. Q.: Crystal structure of [2-(4-bromophenyl)pyridine-k^2C^2,N^1)bromo[1,3-bis(4-methylphenyl)imidazol-2-ylidene-kC^{12})] palladium(II), $PdBr(C_{11}H_7NBr)[(C_3H_2N_2)(C_7H_7)_2]$. Z. Kristallogr. NCS **230** (2015) 99–100.
19. Brammer, L.; Bruton, E. A.; Sherwood, P.: Understanding the behavior of halogens as hydrogen bond acceptors. Cryst. Growth Des. **1** (2001) 277–290.
20. Pastuszko, A.; Niewinna, K.; Czyz, M.; Jozwiak, A.; Malecka, M.; Budzisz, E.: Synthesis, X-ray structure, electrochemical properties and cytotoxic effects of new arene ruthenium(II) complexes. J. Organomet. Chem. **745–746** (2013) 64–70.
21. Lou, X. H.: Crystal structure of chlorido-(5-acetyl-2-(5-methylpyridin-2-yl)benzen-1-ido-k^2C^2,N^1)-pyridine*kN*-palladium(II), $C_{19}H_{17}ClN_2OPd$. Z. Kristallogr. NCS **234** (2019) 1233–1235.