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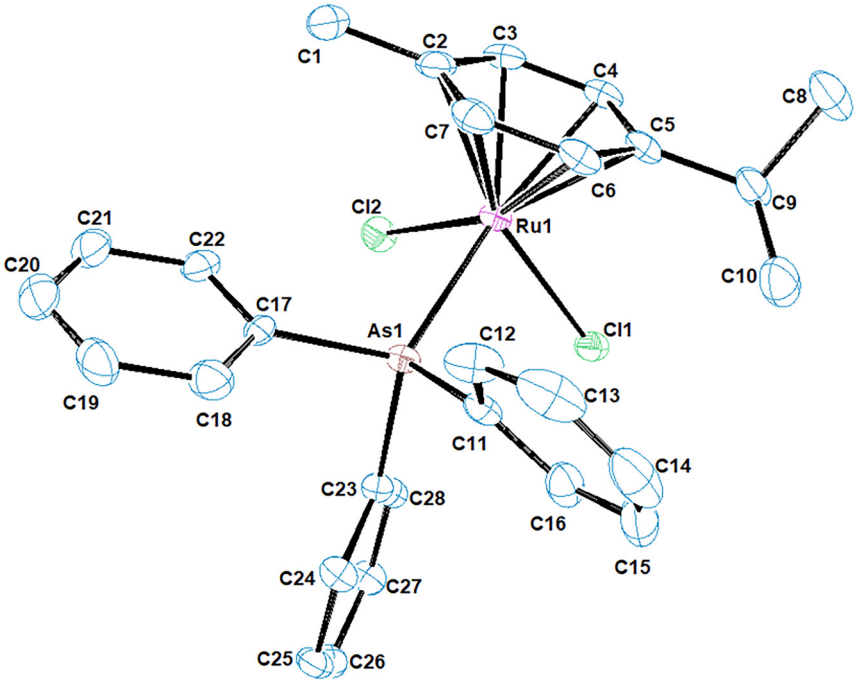
The crystal structure of dichlorido(η^6-*p*-cymene)(triphenylarsine)ruthenium(II), $C_{28}H_{29}AsCl_2Ru$



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Abstract

$C_{28}H_{29}AsCl_2Ru$, monoclinic, $P2_1/n$ (no. 14), a = 15.4135(9) Å, b = 9.2514(5) Å, c = 35.444(2) Å, β = 97.000(3)°, V = 5016.5(5) Å^3, Z = 8, $R_{gt}(F)$ = 0.0537, $wR_{ref}(F^2)$ = 0.1127, T = 100 K.

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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:	Red hexagonal
Size:	0.20 × 0.45 × 0.62 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.16 mm^{-1}
Diffractometer, scan mode:	Bruker (D8 Quest), φ and ω scan
θ_{max}, completeness:	28.3°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	273096, 12482, 0.085
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 10,807
$N(param)_{refined}$:	583
Programs:	Bruker[1], SHELX[2], Olex2[3]

1 Source of materials

All manipulations were carried out using Schlenck techniques under an inert atmosphere of argon. A solution of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ (0.254 g, 0.106 mmol) and $AsPh_3$ (0.320 g, 0.001 mmol) in CH_2Cl_2 (20 ml) were refluxed for 15 h. The solvent was removed under reduced pressure. The residue was washed with hexane (3 × 10 ml) to afford an orange-red solid. The ruthenium complex was crystallized

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4307 (4)	0.9230 (6)	0.70430 (16)	0.0354 (13)
H1A	0.494189	0.922206	0.711286	0.053*
H1B	0.403079	0.976654	0.723490	0.053*
H1C	0.416717	0.969654	0.679484	0.053*
C2	0.3971 (3)	0.7706 (6)	0.70224 (14)	0.0255 (10)
C3	0.4232 (3)	0.6699 (6)	0.73213 (13)	0.0232 (10)
H3	0.462326	0.700278	0.753451	0.028*
C4	0.3922 (3)	0.5272 (5)	0.73059 (12)	0.0213 (9)
H4	0.409672	0.463234	0.751082	0.026*
C5	0.3347 (3)	0.4768 (6)	0.69863 (13)	0.0217 (9)
C6	0.3077 (3)	0.5759 (6)	0.66936 (13)	0.0238 (10)
H6	0.267683	0.545901	0.648306	0.029*
C7	0.3395 (3)	0.7197 (6)	0.67094 (14)	0.0250 (10)
H7	0.321726	0.783537	0.650461	0.030*
C8	0.2275 (4)	0.3145 (7)	0.72268 (17)	0.0409 (14)
H8A	0.247831	0.346449	0.748610	0.061*
H8B	0.206771	0.214438	0.723255	0.061*
H8C	0.179512	0.376924	0.711736	0.061*
C9	0.3032 (3)	0.3234 (6)	0.69827 (14)	0.0275 (11)
H9	0.352044	0.262438	0.710762	0.033*
C10	0.2754 (4)	0.2605 (7)	0.65864 (16)	0.0410 (15)
H10A	0.226086	0.316188	0.646019	0.061*
H10B	0.257773	0.159411	0.661003	0.061*
H10C	0.324528	0.265606	0.643562	0.061*
C11	0.3700 (3)	0.5365 (5)	0.57964 (12)	0.0199 (9)
C12	0.2939 (3)	0.6151 (7)	0.56979 (14)	0.0322 (12)
H12	0.292474	0.715114	0.575757	0.039*
C13	0.2200 (4)	0.5485 (9)	0.55126 (15)	0.0422 (16)
H13	0.167908	0.602775	0.544955	0.051*
C14	0.2218 (4)	0.4037 (8)	0.54195 (16)	0.0451 (17)
H14	0.171576	0.358633	0.528760	0.054*
C15	0.2969 (4)	0.3250 (7)	0.55196 (16)	0.0384 (14)
H15	0.298354	0.225320	0.545663	0.046*
C16	0.3705 (3)	0.3899 (6)	0.57109 (14)	0.0279 (11)
H16	0.421467	0.333947	0.578406	0.033*
C17	0.4810 (3)	0.8107 (5)	0.59428 (13)	0.0205 (9)
C18	0.4470 (4)	0.8569 (6)	0.55764 (14)	0.0304 (11)
H18	0.413324	0.792822	0.540802	0.037*
C19	0.4632 (4)	0.9972 (6)	0.54625 (16)	0.0350 (13)
H19	0.439648	1.029364	0.521670	0.042*
C20	0.5133 (4)	1.0902 (6)	0.57039 (18)	0.0369 (13)
H20	0.525621	1.184597	0.561918	0.044*
C21	0.5459 (4)	1.0472 (6)	0.60689 (17)	0.0323 (12)
H21	0.579263	1.111986	0.623646	0.039*
C22	0.5285 (3)	0.9061 (5)	0.61865 (14)	0.0260 (10)
H22	0.549767	0.875907	0.643699	0.031*
C23	0.5661 (3)	0.5256 (5)	0.58785 (13)	0.0188 (9)
C24	0.5621 (3)	0.5325 (5)	0.54825 (13)	0.0223 (9)
H24	0.512470	0.573603	0.533638	0.027*
C25	0.6308 (3)	0.4791 (5)	0.53023 (13)	0.0223 (9)
H25	0.628239	0.484284	0.503347	0.027*
C26	0.7028 (3)	0.4184 (5)	0.55155 (14)	0.0234 (10)
H26	0.749857	0.382344	0.539283	0.028*
C27	0.7066 (3)	0.4101 (5)	0.59090 (13)	0.0230 (10)
H27	0.755980	0.367583	0.605381	0.028*
C28	0.6381 (3)	0.4639 (5)	0.60922 (13)	0.0208 (9)
H28	0.640823	0.458269	0.636100	0.025*
C29	0.9346 (4)	0.4444 (6)	0.70343 (15)	0.0334 (12)
H29A	0.919499	0.400617	0.678305	0.050*
H29B	0.907027	0.389262	0.722375	0.050*
H29C	0.998164	0.443182	0.710084	0.050*
C30	0.9023 (3)	0.5979 (5)	0.70270 (13)	0.0239 (10)
C31	0.9299 (3)	0.6959 (5)	0.73296 (13)	0.0222 (9)
H31	0.969439	0.663320	0.753878	0.027*
C32	0.9001 (3)	0.8385 (5)	0.73253 (12)	0.0205 (9)
H32	0.919500	0.901062	0.753081	0.025*
C33	0.8404 (3)	0.8914 (5)	0.70137 (13)	0.0213 (9)
C34	0.8125 (3)	0.7961 (6)	0.67152 (13)	0.0248 (10)
H34	0.772602	0.828562	0.650693	0.030*
C35	0.8432 (3)	0.6524 (6)	0.67221 (13)	0.0265 (11)
H35	0.823757	0.590099	0.651597	0.032*
C36	0.7320 (4)	1.0455 (7)	0.72675 (17)	0.0380 (13)
H36A	0.685373	0.982954	0.714637	0.057*
H36B	0.709749	1.144171	0.728467	0.057*
H36C	0.751857	1.009258	0.752337	0.057*
C37	0.8091 (3)	1.0455 (6)	0.70291 (14)	0.0258 (10)
H37	0.857327	1.104123	0.716768	0.031*
C38	0.7828 (4)	1.1161 (7)	0.66429 (15)	0.0391 (14)
H38A	0.832641	1.114829	0.649565	0.059*
H38B	0.764972	1.216295	0.667981	0.059*
H38C	0.733964	1.062572	0.650540	0.059*
C39	0.8681 (3)	0.8490 (5)	0.58198 (12)	0.0193 (9)
C40	0.8693 (3)	0.9987 (5)	0.57829 (13)	0.0221 (9)
H40	0.920043	1.051568	0.587952	0.027*
C41	0.7968 (4)	1.0709 (6)	0.56058 (14)	0.0301 (11)
H41	0.798523	1.172933	0.557751	0.036*
C42	0.7218 (4)	0.9957 (7)	0.54697 (15)	0.0346 (13)
H42	0.672265	1.045707	0.534849	0.041*
C43	0.7196 (4)	0.8479 (7)	0.55112 (16)	0.0375 (13)
H43	0.668048	0.796025	0.542036	0.045*
C44	0.7927 (3)	0.7733 (6)	0.56861 (14)	0.0291 (11)
H44	0.790732	0.671245	0.571327	0.035*
C45	0.9779 (3)	0.5701 (5)	0.59173 (13)	0.0198 (9)
C46	0.9485 (3)	0.5336 (5)	0.55429 (13)	0.0235 (10)
H46	0.918296	0.603272	0.537948	0.028*
C47	0.9628 (4)	0.3963 (6)	0.54060 (14)	0.0288 (11)
H47	0.942400	0.372135	0.515008	0.035*
C48	1.0069 (3)	0.2947 (5)	0.56437 (15)	0.0273 (11)
H48	1.017525	0.201028	0.554959	0.033*
C49	1.0357 (3)	0.3293 (5)	0.60189 (15)	0.0272 (10)
H49	1.064601	0.258375	0.618245	0.033*
C50	1.0225 (3)	0.4666 (5)	0.61565 (13)	0.0233 (10)
H50	1.043623	0.490535	0.641187	0.028*
C51	1.0612 (3)	0.8582 (5)	0.58628 (12)	0.0189 (9)
C52	1.0477 (3)	0.8685 (5)	0.54684 (13)	0.0220 (9)
H52	0.994276	0.836105	0.533268	0.026*
C53	1.1124 (3)	0.9262 (5)	0.52743 (14)	0.0254 (10)
H53	1.103465	0.933335	0.500493	0.030*
C54	1.1901 (3)	0.9735 (5)	0.54731 (14)	0.0281 (11)
H54	1.235116	1.010530	0.533956	0.034*
C55	1.2024 (3)	0.9669 (5)	0.58674 (15)	0.0270 (11)

Table 2: (continued)

	x	y	z	U_{iso}^*/U_{eq}
H55	1.254858	1.003032	0.600287	0.032*
C56	1.1382 (3)	0.9076 (5)	0.60658 (13)	0.0220 (9)
H56	1.147038	0.901059	0.633524	0.026*
As1	0.47082 (3)	0.61244 (5)	0.61142 (2)	0.01673 (10)
As2	0.96982 (3)	0.76514 (5)	0.61146 (2)	0.01582 (10)
Cl1	0.50618 (7)	0.33441 (12)	0.67030 (3)	0.0221 (2)
Cl2	0.60144 (7)	0.65452 (13)	0.69402 (3)	0.0231 (2)
Cl3	1.10543 (7)	0.71071 (13)	0.69237 (3)	0.0232 (2)
Cl4	1.01233 (7)	1.03494 (12)	0.67217 (3)	0.0211 (2)
Ru1	0.45179 (2)	0.57596 (4)	0.67819 (2)	0.01608 (8)
Ru2	0.95617 (2)	0.79378 (4)	0.67898 (2)	0.01528 (8)

by slow diffusion of petroleum ether 40–60 °C into a concentrated dichloromethane solution at ambient temperature. Red hexagonal crystals were obtained overnight. Yield (0.276 g, 86 %).

2 Experimental details

Intensity data was determined on a Bruker D8 Quest Microfocus with a Photon III detector diffractometer at 173 K. Data reduction was carried out using the SAINT-Plus version 6.02.6 software program, and SADABS was used to process empirical absorption correction.[1] The aromatic H atoms were placed in geometrically idealised positions and constrained to maintain fixed distances relative to their parent carbon atoms, with a specified C–H bond length of 0.93 Å for aromatic C–H bonds with $U_{iso}(H) = 1.2U_{eq}(C)$ or $U_{iso}(H) = 1.5U_{eq}(C)$.[2] The structure was solved in the Olex2-1.5 suite of programs, using charge flipping and refined with SHELXL-2019/3 refinement package.[3,4] Diagrams and publication material were generated using ORTEP-3.[5]

3 Discussion

Drug resistance to cancer and malaria poses a significant challenge concerning therapeutic interventions. Recent investigations into the anticancer and antimalarial properties of half-sandwich ruthenium(II)-arene complexes have highlighted the efficacy of this class of complexes against various cancers and malaria.[6,7] Notably, *p*-cymene ruthenium(II) complexes exhibit potential as therapeutic agents due to their unique properties and mechanisms of action.[8,9] In this paper, we report the crystal structure of the ruthenium complex, [$RuCl_2(\eta^6$-*p*-cymene)($AsPh_3$)].

The asymmetric unit contains two molecules (Ru1 and Ru2) which both exhibit a pseudo-octahedral structure. In this arrangement, the ruthenium centre is coordinated with two chloride ions, a triphenylarsine ligand and a hexahapto *p*-cymene ligand. The molecular structures of the two ruthenium complexes are nearly identical, with minor differences. The η^6-*p*-cymene ring is planar, while the C=C bonds within the ring have slightly unequal bond lengths, ranging from 1.403 Å to 1.431 Å and 1.404 Å to 1.435 Å for complexes Ru1 and Ru2 respectively. The *p*-cymene ligand is asymmetrically bonded to ruthenium, with Ru1–$C_{(Arene)}$ bond lengths in the range 2.173–2.223 Å, to accommodate the sterically demanding $AsPh_3$ ligand. The Ru–Arene(centroid) distance was also measured as 1.686 Å and 1.688 Å for Ru1 and Ru2 complexes, respectively, which is within the range of similar reported structures in literature.[8] These measurements indicate favourable proximity that allows for adequate overlap between the metal d-orbital and the π-system of the cymene ligand, which is crucial for stabilizing the overall structure.[10] The Ru–As bond lengths are measured at 2.4430(5) Å and 2.4424(5) Å for Ru1 and Ru2 complexes, respectively. The average Ru–Cl bond length is 2.417 Å for both complexes, and falls within the range of 2.2971–2.4357 Å for previously reported complexes of this type.[11,12] Furthermore, the Cl–Ru–Cl angles measured at 88.29(4)° and 88.23(4)° for Ru1 and Ru2, respectively, supports the pseudo-octahedral geometry assigned to the molecule and is comparable to values reported for similar complexes.[13,14]

Weak intramolecular non-covalent interactions were identified in the structure, including hydrogen bonds and T-type intermolecular π–π stacking. The structural analysis reveals that the coordination environment around the ruthenium centre is influenced by both steric and electronic factors, contributing to the overall stability of the complex. The bond distances and angles are in agreement with previously reported data for ruthenium(II)–arene complexes.

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