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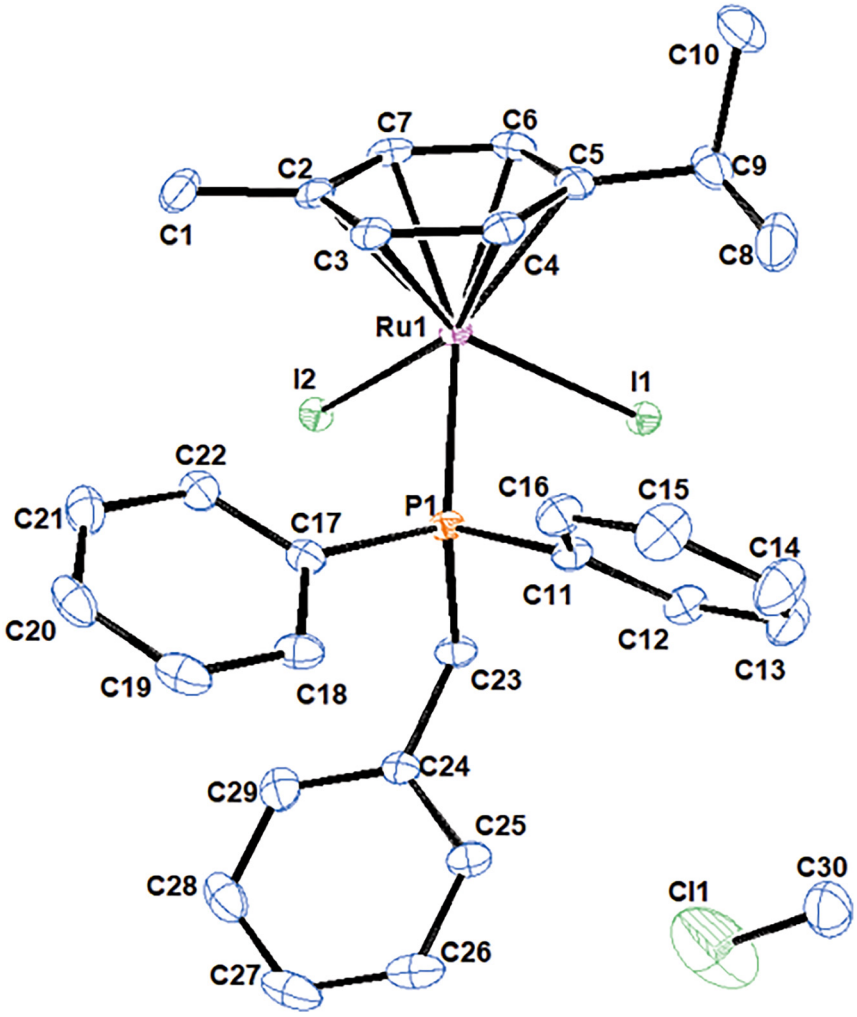
# The crystal structure of ($\eta^6$-*p*-cymene) benzyldiphenylphosphine-diiodido-ruthenium(II) dichloromethane solvate

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**Abstract**

$C_{59}H_{64}Cl_2I_4P_2Ru_2$, triclinic, $P\bar{1}$ (no. 2), $a$ = 7.5074(2) Å, $b$ = 10.8867(3) Å, $c$ = 18.7012(6)) Å, $\alpha$ = 96.696(1)°, $\beta$ = 99.956(1)°, $\gamma$ = 104.730(1)°, $V$ = 1435.14(7) Å$^3$, $Z$ = 1, $R_{gt}(F)$ = 0.0190, $wR_{ref}(F^2)$ = 0.0443, $T$ = 100 K.

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

**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Red block |
| Size: | 0.35 × 0.18 × 0.12 mm |
| Wavelength: | Mo *K*α radiation (0.71073 Å) |
| $\mu$: | 2.86 $mm^{-1}$ |
| Diffractometer, scan mode: | Bruker D8, $\varphi$ and $\omega$ scans |
| $\theta_{max}$, completeness: | 27.5°, 100 % |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 86775, 6555, 0.038 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 6,281 |
| $N(param)_{refined}$: | 319 |
| Programs: | Bruker,[1] SHELX,[2] Olex2[3,4] |

parameters can be found in the cif-file attached to this article.

## 1 Source of materials

All reagents are commercially available and were used without further purification. All manipulations were carried out using standard Schlenk techniques under an inert atmosphere of argon. A solution of benzyldiphenylphosphine ($PPh_2Bn$), (0.068 g, 0.246 mmol) in $CH_2Cl_2$ (5 mL) was slowly added to a solution of [($\eta^6$-*p*–cymene)$RuI_2$]$_2$(0.115 g, 0.117 mmol) in $CH_2Cl_2$ (5 mL). The resulting dark brown solution was stirred at room temperature for 16 h. After filtration, the solvent was removed *in vacuo*. The residue was suspended in hexane (15 mL). After filtration, the resulting brown solid was washed with hexane and dried under vacuum. Yield (0.164 g, 91 %). Crystals were obtained from a $CH_2Cl_2$ solution of the titled compound layered with $Et_2O$ at room temperature.

## 2 Experimental details

Intensity data was determined on a Bruker D8 Quest Microfocus with a Photon III detector diffractometer. 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 $U_{iso}(H) = 1.2\ U_{eq}(C)$ or $U_{iso}(H) = 1.5\ U_{eq}(C)$.[2] The structure was solved in the Olex2–1.5 suite of programs and refined with SHELXL-2019/3 refinement package.[3,4] Diagrams and publication material were generated using ORTEP-3.[5]

## 3 Discussion

The chemistry of half sandwich ($\eta^6$–arene)ruthenium(II) complexes has been widely studied due to the potential of these complexes as diagnostic and therapeutic agents which have significantly impacted anticancer drug development.[6] The ruthenium complexes have unique biochemical properties, such as potential ability to form a labile complex, to have different oxidation states under physiological conditions and to mimic iron ions, all these properties could influence the thermodynamic and kinetic properties of a metallodrug.[7–10]

Phosphine ligands are well known for their electron donor properties and are extensively used in coordination chemistry as spectator ligands to stabilize both low and high transition metals valence states.[11] The triphenylphosphine ligand has been shown to play a crucial role in facilitating the binding of the ruthenium (Ru) complex to DNA, which can lead to the distortion of its secondary and tertiary structures. This interaction is significant in the study of metal-based drugs and their potential applications in medicine, particularly in cancer treatment.[12] However, Ru(II) arene complexes bearing derivative triphenylphosphine ligands have been less widely studied.

The title compound is of interest as it contains a lipophilic benzyldiphenylphosphine ligand as well as two labile iodido ligands in a mutually *cis*-configuration which could be key structural features for anticancer activity.[13] As steric effects are known to be crucial in the reactivity of transition metal complexes bearing tertiary phosphine ligands, our findings reported here will extend the knowledge of the solid-state molecular structure of this class of complex.[14]

The ruthenium coordination sphere in the title structure is constructed with a hexahaptic cymene group, benzyldiphenylphosphine ($PPh_2Bn$) and two iodido ligands forming a pseudo-octahedral structure. The crystal structure includes one half of a $CH_2Cl_2$ solvent molecule that resides around an inversion center. The cymene ring is planar, with the $\pi$-bonds within the ring having unequal bond lengths ranging from 1.392 Å to 1.436 Å. The $\eta^6$-*p*-cymene ligand is asymmetrically bonded to ruthenium, with Ru – $C_{Arene}$ bond lengths in the range 2.209–2.256 Å. The distance between the centroid of the $\eta^6$-*p*-cymene ring and the Ru is 1.725 Å. The bond distances of Ru to the two iodido ligands are 2.7214 (2) Å and 2.7360 (2) Å for I1 and I2, respectively. The I–Ru–I angle measures 90.226(7)° while the P–Ru–I2 angle measures 89.010(14)° and the P–Ru–I1 angle measures 85.422(14)° which supports the pseudo-octahedral geomtery assigned to the molecule. The Ru–P bond length is 2.3566(6) Å. The effective cone angle of the PPh2Bn

ligand was measured at 142° using the Tolman cone angle model, this value correlates with the value reported by Muller and Davis for this ligand in the [$RuCl_2(\eta^6$-benzene){ $PPh_2(CH_2C_6H_5)$-$\kappa$P }] complex.[15,16]

## References


1. Bruker *APEX-5, SAINT-Plus* (Version 8.8.4.0, Including XPREP) and *SADABS (Version 2016)*; Bruker AXS Inc.: Madison, Wisconsin. USA, 2019.
2. Sheldrick, G. M. Crystal Structure Refinement with *SHELX*. *Acta Crystallogr.* **2015**, *C71*, 3–8.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
4. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A.; Puschmann, H. The Anatomy of a Comprehensive Constrained, Restrained Refinement Program for the Modern Computing Environment – Olex2 Dissected. *Acta Crystallogr. A: Found. Adv.* **2015**, *A71*, 59–75.
5. Farrugia, L. J. *ORTEP-3 for Windows* (Version 2020.1). *J. Appl. Cryst.* **2012**, *45*, 849–854.
6. Yan, Y. K.; Melchart, M.; Habtemaria, A.; Sadler, P. J. Organometallic Chemistry, Biology and Medicine: Ruthenium Arene Anticancer Complexes. *ChemComm* **2005**, *38*, 4764–4776.
7. Bruijnincx, P. C.; Sadler, P. J. Controlling Platinum, Ruthenium, and Osmium Reactivity for Anticancer Drug Design. *Adv. Inorg. Chem.* **2009**, *61*, 1–62.
8. Yousuf, I.; Bashir, M.; Arjmand, F.; Tabassum, S. Advancement of Metal Compounds as Therapeutic and Diagnostic Metallodrugs: Current Frontiers and Future Perspectives. *Coord. Chem. Rev.* **2021**, *445*, 214104.
9. Sonkar, C.; Sarkar, S.; Mukhopadhyay, S. Ruthenium(II)–arene Complexes as Anti-metastatic Agents, and Related Techniques. *RSC Med. Chem.* **2022**, *13*, 22–38.
10. Jabłońska-Wawrzycka, A.; Rogala, P.; Michałkiewicz, S.; Hodorowicz, M.; Barszcz, B. Ruthenium Complexes in Different Oxidation States: Synthesis, Crystal Structure, Spectra and Redox Properties. *Dalton Trans.* **2013**, *42*, 6092–6101.
11. Power, P. P. Stable Two-Coordinate, Open-Shell ($d^1$–$d^9$) Transition Metal Complexes. *Chem. Rev.* **2012**, *112*, 3482–3507.
12. Sáez, R.; Lorenzo, J.; Prieto, M. J.; Font–Bardia, M.; Calvet, T.; Omeñaca, N.; Moreno, V. Influence of $PPh_3$ Moiety in the Anticancer Activity of New Organometallic Ruthenium Complexes. *J. Inorg. Biochem.* **2014**, *136*, 1–12.
13. Monareng, J. M.; Clayton, H. S. Crystal Structure of dibromo-dicarbonyl-bis(tricyclohexylphosphine)-Osmium(II) Dichloromethane Solvate. *Z. Kristallogr. – New Cryst. Struct.* **2023**, *238*, 689–692.
14. Hierso, J. C.; Amardeil, R.; Bentabet, E.; Broussier, R.; Gautheron, B.; Meunier, P.; Kalck, P. Structural Diversity in Coordination Chemistry of Tridentate and Tetradentate Polyphosphines of Group 6 to 10 Transition Metal Complexes. *Coord. Chem. Rev.* **2003**, *236*, 143–206.
15. Tolman, C. A. Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis. *Chem. Rev.* **1977**, *77*, 313–348.
16. Muller, A.; Davis, W. ($\eta^6$-benzene)(benzyldiphenylphosphane) dichloro-Ruthenium(II) Dichloromethane. *Acta Crystallogr.* **2012**, *A64*, 112–122.