molbank

MDPI

Short Note

Bromo(5-cyclohexyl-1-methyl-1*H*-1,2,4-triazol-4-ium-3-yl)bis(triphenylphosphane)palladium Tetrafluoroborate

Andrey Y. Chernenko [1], Igor V. Lavrentev [1], Maxim A. Shevchenko [1], Mikhail E. Minyaev [2], Konstantin E. Shepelenko [1,*] and Victor M. Chernyshev [1,*]

[1] Platov South Russian State Polytechnic University (NPI), 346428 Novocherkassk, Russia; chernenko.andrew@mail.ru (A.Y.C.); lavr19981112@gmail.com (I.V.L.); maxshevch@yandex.ru (M.A.S.)
[2] Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, 119991 Moscow, Russia; mminyaev@ioc.ac.ru
* Correspondence: kon1990@bk.ru (K.E.S.); chern13@yandex.ru (V.M.C.)

Abstract

Transition metal complexes bearing protic N-heterocyclic carbene (pNHC) ligands are promising precatalysts for organic reactions due to their capacity for unique hydrogen-bonding interactions. Herein, we report the synthesis and structural characterization of the first Pd(II) complex featuring a pNHC derived from 1,2,4-triazole—a heterocyclic system previously unexplored for the preparation of metal/pNHC complexes. The complex was synthesized via oxidative addition of 3-bromo-5-cyclohexyl-1-methyl-1*H*-1,2,4-triazole to $Pd(PPh_3)_4$ in the presence of NH_4BF_4. Its molecular structure was characterized by NMR spectroscopy and X-ray diffraction analysis.

Keywords: protic N-heterocyclic carbenes; 1,2,4-triazoles; palladium(II) complex; phosphines

check for updates

Academic Editor: Kristof Van Hecke

Received: 22 October 2025
Revised: 4 November 2025
Accepted: 5 November 2025
Published: 10 November 2025

Citation: Chernenko, A.Y.; Lavrentev, I.V.; Shevchenko, M.A.; Minyaev, M.E.; Shepelenko, K.E.; Chernyshev, V.M. Bromo(5-cyclohexyl-1-methyl-1*H*-1,2,4-triazol-4-ium-3-yl)bis(triphenylphosphane)palladium Tetrafluoroborate. *Molbank* **2025**, *2025*, M2086. https://doi.org/10.3390/M2086

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

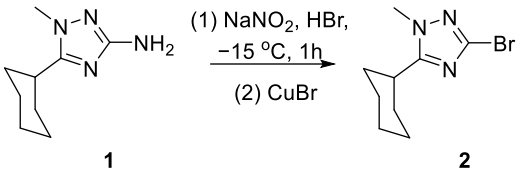
1. Introduction

Protic N-heterocyclic carbenes (pNHCs) are a distinct class of ligands characterized by a H substituent on a nitrogen atom of the NHC ring, setting them apart from classical NHCs [1,2]. This Brønsted-acidic NH moiety is pivotal, as it facilitates unique reactivity—such as hydrogen bonding—and enables a wide array of post-complexation modifications [3]. Palladium complexes with this class of ligands represent promising platforms for catalysis and materials science [4]. Although protic Pd/NHC complexes with ligands derived from pyridine [5–7], (benz)imidazole [8–10], theophylline [11], adenine [11,12], and indole [13] have been reported, complexes featuring protic 1,2,4-triazol-3(5)-ylidene ligands remain unexplored. In this work, we report the first example of a palladium complex with a protic 1,2,4-triazole-derived N-heterocyclic carbene, obtained by selective palladation of 3-bromo-5-cyclohexyl-1-methyl-1H-1,2,4-triazole with $Pd(PPh_3)_4$, and its structural characterization by NMR spectroscopy and single-crystal X-ray analysis.

2. Results and Discussion

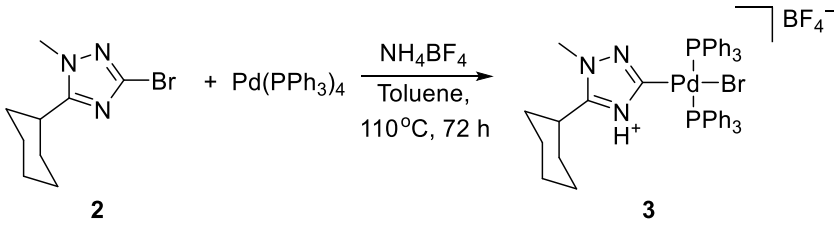
Synthesis

The pNHC ligand precursor, 3-bromo-1-methyl-5-cyclohexyl-1,2,4-triazole (**2**), was obtained by a Sandmeyer reaction of aminotriazole **1** [14,15] in 47% yield (Scheme 1).



Scheme 1. Synthesis of compound **2**.

The target complex **3** was synthesized in 64% yield by reaction of bromotriazole **2** with $Pd(PPh_3)_4$ in toluene at 110 °C for 72 h in the presence of NH_4BF_4 (Scheme 2). Complex **3** was isolated as a pale yellow, crystalline solid, which is stable under ambient conditions. It is almost insoluble in non-polar organic solvents (e.g., hexane or Et_2O) but soluble in polar solvents such as DMF, DMSO, MeCN, $CHCl_3$, and EtOH. Notably, complex **3** undergoes rapid decomposition with the formation of palladium black upon heating with strong bases such as KOH or KOtBu in DMSO or EtOH, which is typical for many classical Pd/NHC complexes [16]. The molecular structure of complex **3** was confirmed by NMR spectroscopy (See Figures S3 and S4 in the Supplementary Materials) and single-crystal X-ray analysis (Figure 1, Tables 1–3).



Scheme 2. Synthesis of palladium complex **3**.

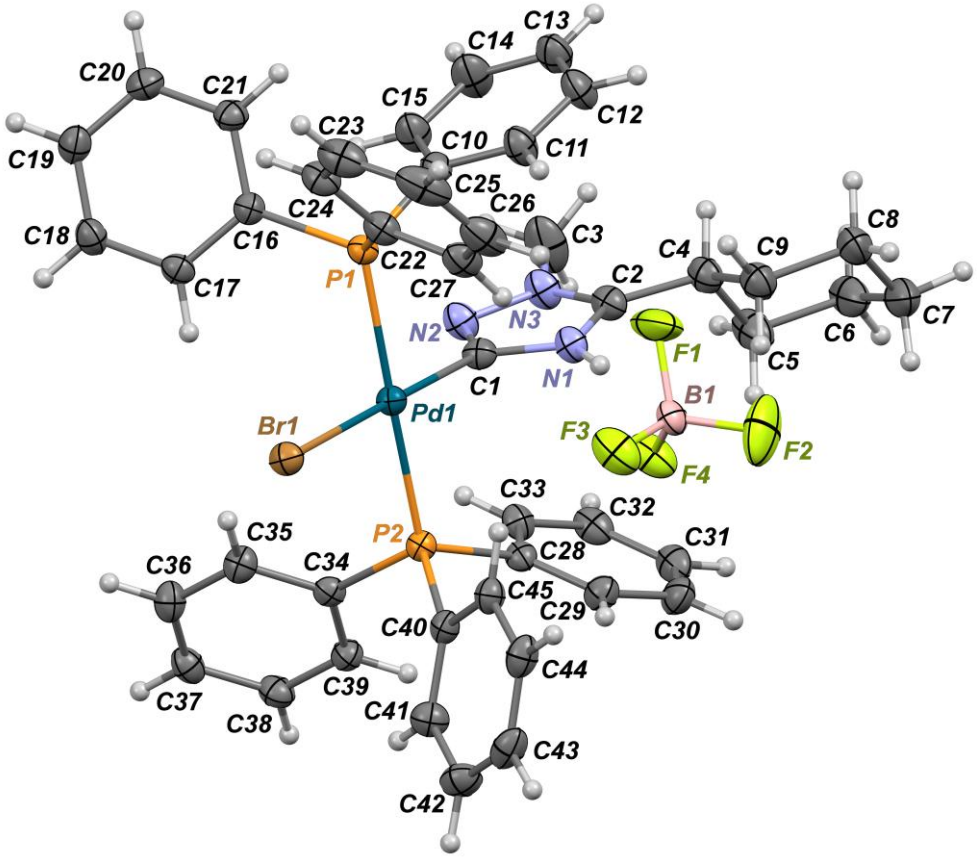


Figure 1. The ORTEP diagram of **3** with the thermal ellipsoids drawn at the 50% probability level.

Table 1. Selected bond lengths (Å) and angles (°) for complex **3**.

Atom	Length/Å	Atom	Angle/°
Pd(1)-Br(1)	2.4721(3)	P(1)-Pd(1)-Br(1)	91.532(16)
Pd(1)-P(1)	2.3558(6)	P(2)-Pd(1)-Br(1)	92.031(15)
Pd(1)-P(2)	2.3308(6)	P(2)-Pd(1)-P(1)	175.81(2)
Pd(1)-C(1)	1.977(2)	C(1)-Pd(1)-Br(1)	177.40(7)
		C(1)-Pd(1)-P(1)	88.20(7)
		C(1)-Pd(1)-P(2)	88.34(7)

Table 2. Hydrogen bonds for **3**.

***D*-H...A**	**d(*D*-H), Å**	**d(H...A), Å**	**d(*D*...A), Å**	**<(*D*HA)/°**
N(1)-H(1)...F(4)	0.88(3)	2.03(3)	2.872(3)	159(3)
N(1)-H(1)...F(4A)	0.88(3)	1.79(3)	2.622(11)	158(3)
N(1)-H(1)...F(1B)	0.88(3)	1.92(4)	2.72(3)	150(3)

Table 3. Crystal data and structure refinement for **3**.

Parameter	Value
Empirical formula	$C_{45}H_{45}BBrF_4N_3P_2Pd$
Formula weight	962.90
Temperature	100.0(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 12.75750(10) Å
	b = 24.1966(3) Å
	c = 13.2159(2) Å
	β = 93.4020(10)°
Volume	4072.40(9) $Å^3$
Z	4
Density (calculated)	1.571 g/cm^3
Absorption coefficient	1.571 mm^{-1}
F(000)	1952
Crystal size	0.74 × 0.41 × 0.14 mm^3
θ range for data collection	2.156 to 27.998°
Index ranges	$-16 \leq h \leq 16$, $-31 \leq k \leq 31$, $-17 \leq l \leq 17$
Reflections collected	58,724
Independent reflections	9841 [R(int) = 0.0381]
Observed reflections	9111
Completeness to $\theta_{max}/\theta_{full}$	1.000/1.000
Max./min. transmission	1.00000/0.51526
Data/restraints/parameters	9841/166/551
Goodness-of-fit on F^2	1.033
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0327, wR_2 = 0.0887
R indices (all data)	R_1 = 0.0353, wR_2 = 0.0903
Largest diff. peak/hole	1.900/−0.603 e·$Å^{-3}$
CCDC deposition number	2497031

The ^{1}H NMR spectrum of **3** displays a number of multiplets between 0.8 and 1.75 ppm corresponding to the cyclohexyl group, a singlet for the NMe group at 3.34 ppm, aromatic proton resonances for the PPh_3 ligands at 7.39–7.63 ppm, and a broadened NH resonance at

13.04 ppm. The observed broadening of the NH signal is consistent with proton exchange and tautomerism, as the acidic proton may be located on either the N4 or N1 atom of the triazole ring; therefore, a prototropic equilibrium, characteristic of 1,2,4-triazoles, is anticipated [17–19]. Presumably due to these prototropic equilibria, some signals in the ^{13}C NMR spectrum are broadened and merge into the baseline; for example, the signal for the carbenic carbon is not distinctly observed.

A crystal suitable for X-ray crystallography was obtained by slow crystallization from a 1:1 CH_2Cl_2/Et_2O mixture. Selected bond lengths and angles for **3** are presented in Table 1 (crystallographic atom numbering is used). The crystal structure of **3** (Figure 1, Table 3) belongs to the monoclinic system, space group $P2_1/n$, and reveals a distorted square-planar coordination geometry around the metal center with bond angles P(1)-Pd(1)-Br(1) = 91.532(16)° and C(1)-Pd(1)-Br(1) = 177.40(7)° (Table 1). In the crystalline state, the "mobile" proton is located on the N1 atom. This tautomer could be stabilized by NH···F hydrogen bonds with the BF_4^- anion (Table 2). Significant orientational disorder of the BF_4^- anion was also observed. Despite this disorder, a hydrogen bond is formed with each of the anion's orientational isomers (Table 2). This type of disorder is not unprecedented and has been previously reported in analogous systems, such as simple tetramethylammonium salts with the BF_4^- anion [20]. The bond lengths Pd(1)-C(1) = 1.977(2) Å and Pd(1)-P(1) = 2.3558(6) Å are similar to those found in analogous palladium complexes with benzimidazole-type ligands (Table 1) [9].

3. Materials and Methods

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance Neo 300 spectrometer (Rheinstetten, Germany) operating at 300 MHz and 75 MHz, respectively. Chemical shifts are reported relative to the residual proton signals of $CDCl_3$ (δ 7.26 ppm) or DMSO-d_6 (δ 2.50 ppm) for ^1H NMR, and the carbon signals of $CDCl_3$ (δ 77.16 ppm) or DMSO-d_6 (δ 39.52 ppm) for ^{13}C NMR. Compound **2** was analyzed in $CDCl_3$, whereas complex **3** was analyzed in a CD_2Cl_2/DMSO-d_6 mixture. Coupling constants (*J*) are reported in Hertz (Hz). Copies of the ^1H and ^{13}C NMR spectra for compounds **2** and **3** are provided in Figures S1–S4 (Supplementary Materials).

*3.1. Synthesis of 3-Bromo-5-cyclohexyl-1-methyl-1H-1,2,4-triazole (**2**)*

3-Amino-5-cyclohexyl-1*H*-1,2,4-triazole (**1**) (0.361 g, 2.0 mmol) was dissolved in 48% aqueous HBr (10 mL) and cooled to −15 °C. Sodium nitrite (0.152 g, 2.2 mmol) was added in small portions over 30 min with vigorous stirring. The reaction mixture was stirred for an additional 30 min at this temperature. Copper(I) bromide (0.717 g, 5.0 mmol) and potassium bromide (0.476 g, 4.0 mmol) were then added sequentially. The mixture was stirred for 1 h while allowing it to warm to room temperature. The reaction mixture was carefully neutralized to pH 7–8 by the slow addition of a saturated aqueous sodium carbonate solution. The aqueous layer was extracted with dichloromethane (5 × 7 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to a volume of approximately 3 mL. The crude product was purified by flash column chromatography on silica gel, eluting with dichloromethane to afford the title compound as a white solid. Yield 0.229 g (47%). ^1H NMR ($CDCl_3$, 300 MHz) 1.18–1.42 (m, 4H), 1.57–1.78 (m, 3H), 1.80–1.92 (m, 4H), 2.67 (tt, *J* = 11.8, 3.3 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): 25.6, 26.0, 31.0, 35.3, 35.4, 138.4, 161.8.

*3.2. Synthesis of Bromo(5-cyclohexyl-1-methyl-1H-1,2,4-triazol-4-ium-3-yl)bis(triphenylphosphane)palladium Tetrafluoroborate (**3**)*

A 7 mL screw-capped tube equipped with a magnetic stir bar was charged with 3-bromo-1-methyl-5-cyclohexyl-1*H*-1,2,4-triazole (**2**) (0.293 g, 1.2 mmol), $Pd(PPh_3)_4$ (1.156 g, 1.0 mmol), NH_4BF_4 (0.734 g, 7.0 mmol), and dry toluene (3 mL) under an argon atmosphere. The tube was sealed, and the reaction mixture was heated at 110 °C with stirring for 72 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (7 mL) and filtered through a short pad of Celite. The filtrate was concentrated under reduced pressure to a volume of approximately 1 mL and diluted with Et_2O (5 mL). The resulting precipitate was collected by filtration and recrystallized from a dichloromethane/diethyl ether mixture. The product was obtained as a pale yellow crystalline solid after drying under vacuum at 50 °C overnight. Yield: 0.616 g (64%). ^{1}H NMR (DMSO-d_6/CD_2Cl_2 (1/1, *v*/*v*), 300 MHz): δ 0.77–0.97 (m, 2H), 1.03–1.32 (m, 5H), 1.74 (d, *J* = 13.1 Hz, 3H), 2.30 (t, *J* = 12.5 Hz, 1H), 3.32 (s, 3H), 7.35–7.44 (m, 12H), 7.45–7.53 (m, 6H), 7.55–7.67 (m, 12H), 13.04 (s, 1H). ^{13}C NMR (DMSO-d_6/CD_2Cl_2 (1/1, *v*/*v*), 75 MHz): δ 24.4, 24.5, 29.3, 32.7, 35.3, 127.6, 127.7, 127.8, 129.2, 129.5, 129.9, 130.4, 131.3, 133.8, 133.9, 134.0, 154.5.

3.3. X-Ray Crystallography

X-ray diffraction data were collected at 100K on a four-circle Rigaku XtaLAB Synergy-S diffractometer (Rigaku Corporation, Tokyo, Japan), equipped with a HyPix-6000HE area-(Rigaku Corporation, Japan) (kappa geometry, shutterless ω-scan technique), using monochromatized Mo K_α-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program version 1.171.44 (Rigaku Oxford Diffraction: Abingdon, UK) [21]. The structure was solved by direct methods using SHELXT [22] and refined on F^2 using SHELXL-2018 [23] in the OLEX2 program [24]. All non-hydrogen atoms were refined with individual anisotropic displacement parameters. A location of atom H1 at N1 was found from the electron density-difference map. All other hydrogen atoms were positioned geometrically and refined as riding atoms with relative isotropic displacement parameters.

4. Conclusions

The applicability of 1-alkyl-3-brominated-1,2,4-triazoles as precursors for previously unexplored triazole-derived pNHCs has been demonstrated. The first Pd(II) complex featuring a 1,2,4-triazole-derived pNHC ligand was prepared via palladation of 3-bromo-5-cyclohexyl-1-methyl-1*H*-1,2,4-triazole with $Pd(PPh_3)_4$ in the presence of NH_4BF_4. NMR spectroscopy and single-crystal X-ray diffraction studies revealed a significant propensity for prototropic tautomerism in complexes with 1,2,4-triazole-derived pNHCs, making them particularly interesting targets for future research in coordination chemistry, catalysis, and materials science.

Supplementary Materials: The following supporting information are available online. Figures S1–S4: ^{1}H and ^{13}C NMR spectra of compounds **2** and **3**.

Author Contributions: A.Y.C. experiments, data curation, and formal analysis, I.V.L., M.A.S. experiments, K.E.S. formal analysis and writing—original draft preparation, M.E.M. SC-XRD analysis, V.M.C. writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: The work has been supported by the Ministry of Science and Higher Education of the Russian Federation (project No 075-03-2024-152/1, FENN 2024-0003) at the Laboratory "Novel

composite and functional materials with specific properties" within the framework of National Project "Science and Universities".

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Crystallographic data for the structure of complex 3 was deposited in the Cambridge Crystallographic Data Centre as supplementary publication CCDC 2497031. Further inquiries can be directed to the corresponding author(s).

Acknowledgments: The authors acknowledge the Shared Research Center 'Nanotechnologies' of the Platov South-Russian State Polytechnic University for NMR services and the Shared Research Center of Zelinsky Institute of Organic Chemistry for X-ray analysis.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Jahnke, M.C.; Hahn, F.E. Complexes Bearing Protic N-Heterocyclic Carbenes: Synthesis and Applications. *Chem. Lett.* **2015**, *44*, 226–237. [CrossRef]
2. Kuwata, S.; Hahn, F.E. Complexes Bearing Protic N-Heterocyclic Carbene Ligands. *Chem. Rev.* **2018**, *118*, 9642–9677. [CrossRef] [PubMed]
3. Leow, M.Y.; Ho, C.C.; Gardiner, M.G.; Bissember, A.C. Non-Classical Anionic Naked N-Heterocyclic Carbenes: Fundamental Properties and Emerging Applications in Synthesis and Catalysis. *Catalysts* **2018**, *8*, 620. [CrossRef]
4. Zhu, J.; Lindsay, V.N.G. Benzimidazolyl Palladium Complexes as Highly Active and General Bifunctional Catalysts in Sustainable Cross-Coupling Reactions. *ACS Catal.* **2019**, *9*, 6993–6998. [CrossRef]
5. Crociani, B.; di Bianca, F.; Giovenco, A.; Scrivanti, A. Protonation and methylation reactions of 2-pyridyl-palladium(II) and -platinum(II) complexes. *J. Organomet. Chem.* **1983**, *251*, 393–411. [CrossRef]
6. Poulain, A.; Neels, A.; Albrecht, M. Palladium Complexes Containing Potentially Chelating Pyridylidene-Type Carbene Ligands. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1871–1881. [CrossRef]
7. Jahnke, M.C.; Pichl, R.M.C.; Hahn, F.E. Oxidative Addition of 2-Halogenopyridines and 2-Chloroquinoline to Zero-Valent Group 10 Metals. *Z. Anorg. Allg. Chem.* **2021**, *647*, 448–455. [CrossRef]
8. Hervé, A.; Jahnke, M.C.; Pape, T.; Hahn, F.E. Synthesis of Palladium and Platinum Complexes with an NH, NEt-substituted Benzimidazolin-2-ylidene Ligand. *Z. Anorg. Allg. Chem.* **2013**, *639*, 2450–2454. [CrossRef]
9. Das, R.; Hepp, A.; Daniliuc, C.G.; Hahn, F.E. Synthesis of Complexes with Protic NH,NH-NHC Ligands via Oxidative Addition of 2-Halogenoazoles to Zero-Valent Transition Metals. *Organometallics* **2014**, *33*, 6975–6987. [CrossRef]
10. Jahnke, M.C.; Hervé, A.; Kampert, F.; Hahn, F.E. Synthesis of palladium complexes with anionic N,NR- or neutral NH,NR-theophylline-derived NHC ligands. *Inorganica Chim. Acta* **2021**, *515*, 120055. [CrossRef]
11. Blumenberg, J.; Wilm, L.F.B.; Hahn, F.E. Synthesis of PdII Complexes Bearing pNHC Ligands by Oxidative Addition of 8-Halogenotheophyllines and 8-Bromoadenine to Pd0. *Organometallics* **2020**, *39*, 1281–1287. [CrossRef]
12. Jahnke, M.C.; Mandal, S.; Kampert, F.; Tan, T.T.Y.; Müller, J.; Hahn, F.E. Oxidative addition of 8-bromo-9-ethyl-1,N6-ethenoadenine to d10 metals. *Inorganica Chim. Acta* **2023**, *546*, 121291. [CrossRef]
13. Termühlen, S.; Blumenberg, J.; Hepp, A.; Daniliuc, C.G.; Hahn, F.E. Preparation of Complexes Bearing N-Alkylated, Anionic or Protic CAACs Through Oxidative Addition of 2-Halogenoindole Derivatives. *Angew. Chem. Int. Ed.* **2021**, *60*, 2599–2602. [CrossRef] [PubMed]
14. Teng, M.; Lonergan, D.; Perez, C.; Nammalwar, B.; Fan, J.; Martin, D.P.; Puerta, D.T. Substituted Piperidines and Substituted Tetrahydropyridines as Immune-Modulating Compounds. WO2023205173A1, 18 April 2023.
15. Teng, M.; Puerta, D.T.; Lonergan, D.; Perez, C.; Nammalwar, B.; Martin, D.P. Glutaminyl-Peptide Cyclotransferase like (qpctl) Protein Inhibitors and Uses Thereof. WO2022086920A1, 19 October 2021.
16. Chernyshev, V.M.; Khazipov, O.V.; Shevchenko, M.A.; Chernenko, A.Y.; Astakhov, A.V.; Eremin, D.B.; Pasyukov, D.V.; Kashin, A.S.; Ananikov, V.P. Revealing the unusual role of bases in activation/deactivation of catalytic systems: O-NHC coupling in M/NHC catalysis. *Chem. Sci.* **2018**, *9*, 5564–5577. [CrossRef] [PubMed]
17. Elguero, J.; Katritzky, A.R.; Denisko, O.V. Prototropic Tautomerism of Heterocycles: Heteroaromatic Tautomerism—General Overview and Methodology. In *Advances in Heterocyclic Chemistry*; Katritzky, A.R., Ed.; Academic Press: Amsterdam, The Netherlands, 2000; Volume 76, pp. 1–84.
18. Ozimiński, W.P.; Dobrowolski, J.C.; Mazurek, A.P. DFT studies on tautomerism of C5-substituted 1,2,4-triazoles. *J. Mol. Struct. Theochem* **2004**, *680*, 107–115. [CrossRef]
19. Pylypenko, O.O.; Okovytyy, S.I.; Sviatenko, L.K.; Voronkov, E.O.; Shabelnyk, K.P.; Kovalenko, S.I. Tautomeric behavior of 1,2,4-triazole derivatives: Combined spectroscopic and theoretical study. *Struct. Chem.* **2023**, *34*, 181–192. [CrossRef]

20. Yamamuro, O.; Onoda-Yamamuro, N.; Matsuo, T.; Suga, H.; Kamiyama, T.; Ishigaki, T.-R.; Asano, H. X-ray and neutron diffraction studies of methylammonium tetrafluoroborate: Highly disordered orientations of $CH_3NH_3^+$ and BF_4^- ions. *J. Phys. Chem. Sol.* **1995**, *56*, 183. [CrossRef]
21. *CrysAlisPro*, Version 1.171.44; Rigaku Oxford Diffraction: Abingdon, UK, 2025.
22. Sheldrick, G.M. SHELXT-Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3–8. [CrossRef] [PubMed]
23. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8. [CrossRef]
24. 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. Cryst.* **2009**, *42*, 339–341. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.